Stereochemistry of Sulfur Compounds. I. Stereochemical Reaction Cycles Involving an Open Chain Sulfoxide, Sulfimide, and Sulfoximide[1,2]

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Abstract: Treatment of (+)-(*R*)-methyl *p*-tolyl sulfoxide ((+)-(*R*)-I) of maximum rotation with either *N*-sulfinyl-*p*-toluenesulfonamide or *N,N'*-bis(*p*-toluenesulfonyl)sulfur diimide in pyridine at 0° gave (80 and 95%) (−)-(*S*)-*N*-(*p*-tosyl)methyl-*p*-tolylsulfimide ((−)-(*S*)-II), which in base at 25° gave (94%) (+)-(*R*)-I of 94% optical purity. Imidation of (+)-(*R*)-I of maximum rotation with tosyl azide gave (70%) (−)-(*R*)-*N*-tosylmethyl-*p*-tolylsulfoximide ((−)-(*R*)-III) of 99% maximum rotation. Oxidation of (−)-(*S*)-II of maximum rotation with *m*-chloroperbenzoic acid gave (65%) (−)-(*R*)-III of 98% maximum rotation. Hydrolysis of (−)-(*R*)-III of maximum rotation with concentrated sulfuric acid at 25° gave (99%) (−)-(*R*)-methyl-*p*-tolylsulfoximide ((−)-(*R*)-IV) of 99% maximum rotation. Conversion of (−)-(*R*)-IV of maximum rotation to (−)-(*R*)-III was accomplished either with pyridine and tosyl chloride (86% yield, 99% maximum rotation) or by treatment of (−)-(*R*)-IV with first sodium and benzene followed by tosyl chloride (62, 97% of maximum rotation). Sulfoximide, (−)-(*R*)-IV, of 98% maximum rotation, when treated with a mixture of nitromethane and solid nitrosyl hexafluorophosphate at 0°, gave (75%) (+)-(*R*)-I of 97% maximum rotation. Sulfoximide (−)-(*R*)-IV, when treated with cold sodium hypochlorite, gave (−)-(*R*)-*N*-chloromethyl-*p*-tolylsulfoximide ((−)-(*R*)-V). The absolute configuration of (+)-(*R*)-I is already known, and those of (−)-(*R*)-III and (−)-(*R*)-IV were determined by X-ray methods. The absolute configuration of (−)-(*S*)-II was established by comparison of the melting point composition diagram of (−)-II and (−)-III, and of (+)-II and (−)-III. Clearly the nucleophilic substitution reactions at sulfur, (+)-I ⇄ (−)-II, proceed with inversion, and the electrophilic, (+)-I → (−)-III and (−)-II → (−)-III, proceed with retention of configuration, as does (−)-IV → (+)-I. Optical rotatory dispersion curves of (+)-I, (−)-II, (−)-III, and (−)-IV exhibit well-defined Cotton effects, and these are correlated with their configurations. In the conversion of (+)-I to (−)-II the same reagent appears to donate an imide group and accept an oxygen atom, and thus it is concluded that the sulfur, oxygen, and nitrogen must be included in a ring system that is part of the same transition state and possibly the same intermediate. Kinetic studies of the reaction indicate it to be second order in concentration of the sulfur diimide reagent. Thus, the ring system cannot be any more than six-membered, which is much too small to accommodate a linear arrangement of incoming and leaving groups. An intermediate is proposed that accommodates all data in which the incoming and leaving groups occupy the equatorial positions of a trigonal-bipyramid intermediate rather than the classical axial positions. Maps are developed that identify the stereochemical courses of associative substitution reactions on tetrahedra that form trigonal bipyramids and square pyramids capable of undergoing pyramidal reorganization.

In recent years the mechanisms and especially the stereochemical course of nucleophilic substitution reactions at second-row element centers have elicited considerable attention. Substitution at silicon has been observed to occur with both retention[4a] and inversion,[4b] and these reactions have been interpreted as involving trigonal-bipyramidal transition states in which the entering and leaving groups occupy apiequatorial and apiaxial[5] (retention)[4a] or both apiaxial positions (inversion).[4b]

Nucleophilic substitution reactions at phosphorus have also been found to occur with both retention and inversion mechanisms. For example, the Wittig reaction[6a] and alkaline hydrolysis of phosphetanium,[6b] phospholanium,[6c] and alkoxyphosphetanium[6d] salts all occur with retention. Acyclic phosphonium[6a] and acyclic alkoxyphosphonium[6e] salts cleave with inversion upon alkaline hydrolysis. Another typical inversion reaction is the Grignard synthesis of optically active phosphine oxides.[7] Hydrolyses of phosphorus esters have been demonstrated to proceed through trigonal-

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(2) Preliminary accounts of portions of this work have appeared: (a) J. Day and D. J. Cram, *J. Amer. Chem. Soc.*, **87**, 4398 (1965); (b) D. R. Rayner, D. M. von Schriltz, J. Day, and D. J. Cram, *ibid.*, **90**, 2721 (1968).

(3) (a) National Institutes of Health Postdoctoral Fellow, 1966–1967; (b) National Institutes of Health Special Research Fellow, 1969–1970.

(4) (a) L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *J. Amer. Chem. Soc.*, **89**, 857 (1967); (b) L. H. Sommer, W. D. Korte, and P. G. Rodewald, *ibid.*, **89**, 862 (1967).

(5) The two types of apexes of a trigonal bipyramid have been variously termed axial, apical, or polar and equatorial, radial, or basal. The terms axial and equatorial are the most familiar to organic chemists, and their conversion to apiaxial and apiequatorial allows them to be applied to the apexes of bipyramids. Use of the api prefix only once or twice in a paper fixes the context of the terms. The prefix can be dropped from then on unless the positions on a six-membered ring also need to be differentiated. This *suggested* nomenclature is exemplified here.

(6) (a) W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. Vander Werf, *J. Amer. Chem. Soc.*, **86**, 2378 (1964); (b) R. J. Corfield, J. R. Shutt, and S. Trippett, *Chem. Commun.*, 789 (1969); (c) K. L. Marsi, *J. Amer. Chem. Soc.*, **91**, 4724 (1969); (d) K. E. DeBruin, G. Zon, K. Naumann, and K. Mislow, *ibid.*, **91**, 7027 (1969); (e) G. Zon, K. E. DeBruin, K. Naumann, and K. Mislow, *ibid.*, **91**, 7023 (1969).

(7) O. Korpium, R. A. Lewis, J. Chickos, and K. Mislow, *ibid.*, **90**, 4842 (1968), and references cited therein.

bipyramidal intermediates,[8a] which undergo pseudorotation[8b,c] in certain cases before they decompose.

Fewer studies of the stereochemistry of substitution at sulfur have been reported. Nucleophilic substitutions at sulfur for the most part have been observed to proceed with inversion.[9] Thus, sulfinate esters react with Grignard reagents stereospecifically[9a] to give sulfoxides,[9b] alkoxysulfonium salts with hydroxide to give sulfoxides,[9c] sulfinic esters with lithium amide[9d] or magnesium amide[9e] reagents to give sulfinamides,[9d,e] sulfinamides with Grignard reagents to give sulfoxides,[9e,f] sulfonate esters with Grignard reagents to give sulfones,[9g] and ethoxy-3-methylthietanium salts with hydroxide,[9j] all with inversion. The first example of nucleophilic substitution of sulfoxides that occurs with retention of configuration to be reported[10a] involved ^{18}O exchange of (+)-methyl *p*-tolyl sulfoxide with ^{18}O-dimethyl sulfoxide at elevated temperatures. More recently, *N*-phthaloylmethionine sulfoxide has been reported to react with *N*-sulfinyl-*p*-toluenesulfonamide to yield the corresponding sulfimide with retained configuration at sulfur.[10b]

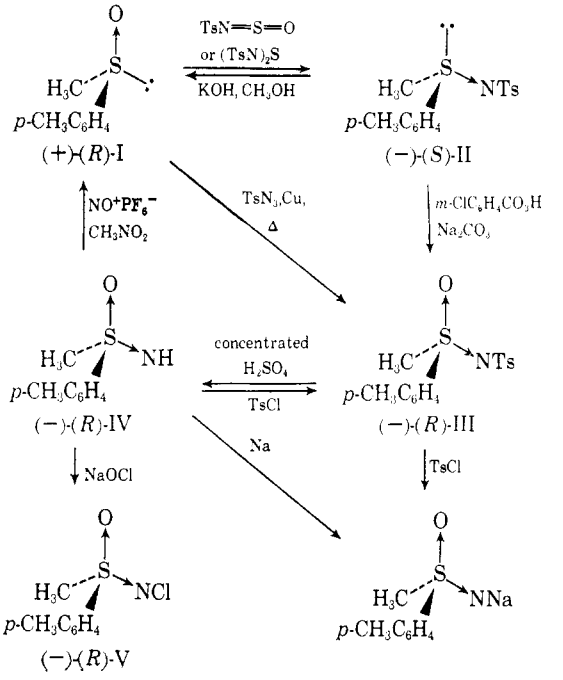
The research reported in this series of papers was initiated for a number of purposes. (1) The stereochemical course of a relatively small number of substitution reactions at sulfur had been examined, and we wished to survey a large number of both nucleophilic and electrophilic reactions and extract from the results correlations between stereochemical course and electrical character of the entering and leaving groups. Since knowledge of the stereochemical course of a reaction depends on a determination of maximum rotation and relative configurations of starting materials and products, we concentrated our attention on those reaction sequences that provided cycles of reactions, *e.g.*, A → B → A or A → B → C → A. (2) Some of the reactions studied involve a twofold ligand exchange reaction between two substituted sulfur atoms, and examination of the starting material and products suggested that the entering and leaving groups were part of the same ring system at some point along the reaction coordinate of structural change. This feature places certain structural restrictions on the transition states and intermediates in the reaction and provides clues as to mechanism. (3) Since a variety of stable compounds of sulfur are known in which sulfur carries three or four ligands of widely differing types, study of the mechanism of substitution at this element allows a high degree of flexibility in choice of substrate structure. For example, rates and stereochemistry of substitution of both open-chain and cyclic sulfoxides can be compared. (4) The stability and polarity of many compounds with sulfur as their chiral center make polymers containing such chiral centers attractive optically active adsorbants for possible resolution of racemates by chromatography.

In this paper we report the results of a study of the stereochemistry of the interconversions of sulfoxides, sulfimides, and sulfoximides.[11] In all but one case we used reactions already reported in the literature, but whose stereochemical course had not been examined, or if one had been examined, it had been reported to go with no or low stereospecificity. In all cases we searched for conditions that maximized stereospecificity, and in most reactions studied, the degree of stereospecificity varied considerably with the reaction conditions. This initial study centered around optically pure (+)-(*R*)-methyl *p*-tolyl sulfoxide ((+)-(*R*)-I) as starting material, partly because it is easily prepared and because its absolute configuration is established.[9b,9h]

Results

Reactions. The stereochemical courses of the reactions formulated in Chart I have been examined, and

Chart I



have been found to go under the proper conditions with a minimum of 96% stereospecificity as measured before the products were fractionally crystallized. In the conversion of sulfoxide I to sulfimide II with either *N*-sulfinyl-*p*-toluenesulfonamide[12a,b] or *N*,*N*′-bis-(*p*-tosyl)sulfur diimide[12c] (yields of 51 and 95%) the reactions were only highly stereospecific when run at 0° in dry pyridine as solvent. The reaction rate in pyridine was much faster than in other solvents tried, and in general, the lower the temperature the more stereospecific the reaction.

Use of *p*-tosylamide and phosphorus pentoxide in the conversion of sulfoxide (+)-(*R*)-I to sulfimide II[13]

(8) (a) P. C. Haake and F. H. Westheimer, *J. Amer. Chem. Soc.*, **83**, 1102 (1961); (b) E. A. Dennis and F. H. Westheimer, *ibid.*, **88**, 3432 (1966); (c) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

(9) (a) K. K. Andersen, *Tetrahedron Lett.*, 93 (1962); (b) M. Axelrod, P. Bickart, J. Jacobus, M. M. Green, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4835 (1968), and references cited therein; (c) C. R. Johnson and D. McCants, Jr., *ibid.*, **87**, 5404 (1965); (d) A. Nudelman and D. J. Cram, *ibid.*, **90**, 3869 (1968); (e) S. Colonna, R. Giovini, and F. Montanari, *Chem. Commun.*, 865 (1968); (f) J. Jacobus and K. Mislow, *ibid.*, 253 (1968); (g) M. A. Sabol and K. K. Andersen, *J. Amer. Chem. Soc.*, **91**, 3603 (1969); (h) H. Hope, U. de la Camp, G. D. Homer, A. W. Messing, and L. H. Sommer, *Angew. Chem., Int. Ed. Engl.*, **8**, 612 (1969); (i) K. Mislow, M. M. Green, P. Lauer, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **87**, 1958 (1965); (j) R. Tang and K. Mislow, *ibid.*, **91**, 5644 (1969).

(10) (a) S. Oae, M. Yokoyama, M. Kise, and N. Furukawa, *Tetrahedron Lett.*, 4131 (1968); (b) B. W. Christensen and A. Kjaer, *Chem. Commun.*, 934 (1969).

(11) IUPAC 1965 Rules: P. E. Verkade, *Pure Appl. Chem.*, **11**, 158 (1965). The terms sulfilimine and sulfoximine are used in *Chemical Abstracts*.

(12) (a) G. Schultz and G. Kresze, *Angew. Chem.*, **75**, 1022 (1963); (b) G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzschke, H. Smalla, and A. Trede, *ibid.*, **74**, 135 (1962); (c) W. Wucherpfennig and G. Kresze, *Tetrahedron Lett.*, 1671 (1966).

in chloroform gave racemic II and largely racemized recovered I. Employment of a mixture of 3 mol of triethylamine and 1 mol of phosphorus pentoxide in dichloromethane at 25° gave 70% optically pure (−)-(*S*)-II (66% yield) and 26% racemized recovered I. Under the conditions of the experiment, the product was shown to be optically stable. In polyphosphoric acid, (+)-(*R*)-I was found to undergo complete and rapid racemization.

Stereospecific hydrolysis of sulfimide (−)-(*S*)-II to give (+)-(*R*)-I was accomplished in 94% yield in methanol saturated with potassium hydroxide at 16°.[14] Acidic hydrolysis of (−)-(*S*)-II in 12 *N* sulfuric acid at 100° or 12 *N* hydrochloric acid at 25° gave racemic I. Others[15] reported that optically active *S*-methyl-*S*-(3-carboxyphenyl)-*N*-*p*-toluenesulfonylsulfimide[16] underwent hydrolysis stereospecifically with 12 *N* hydrochloric acid at 100°. We have no explanation for the stereospecificity reported in this latter reaction, particularly in view of the report[17] that hydrochloric acid racemizes sulfoxides under a variety of conditions.

Imidation (no mechanism implied) with tosyl azide–copper[18] of (+)-(*R*)-I of maximum rotation gave 70% of sulfoximide (−)-(*R*)-III of essentially maximum rotation (99%). Oxidation of sulfimide (−)-(*S*)-II of maximum rotation with *m*-chloroperbenzoic acid in acetone in the presence of anhydrous sodium carbonate also gave (−)-(*R*)-III (65%) of essentially maximum rotation (98%).[19,20] These conversions completed a three-reaction cycle in which the configurations of I, II, and III were interrelated, and which is superimposed on the two-reaction cycle involving only I and II.

A third cycle involving two reactions was completed as follows. The *N*-tosylsulfoximide (−)-(*R*)-III of maximum rotation was hydrolyzed with concentrated sulfuric acid at 25° to give (99%) (−)-(*R*)-IV of essentially maximum rotation (99%).[21] Treatment of (−)-(*R*)-IV of maximum rotation with sodium in refluxing benzene followed by tosyl chloride gave 62% (−)-(*R*)-III of 97% maximum rotation.[22] A better method involved pyridine and tosyl chloride at 25° and gave (−)-(*R*)-III in 86% yield and 99% maximum rotation.

A fourth cycle was completed through use of a new reaction. When (−)-(*R*)-IV of 98% maximum rotation in nitromethane was treated at 0° with excess nitrosyl hexafluorophosphate, an exothermic, gas-producing reaction occurred to give a 75% yield of (+)-(*R*)-I of 97% maximum rotation. Thus, this reaction proceeded with 99% stereospecificity. Although the gas produced was not identified, it was probably nitrous oxide.[23] This last cycle involves (+)-(*R*)-I → (−)-(*R*)-III ⇄ (−)-(*R*)-IV → (+)-(*R*)-I. The discovery of the reaction (−)-(*R*)-IV → (+)-(*R*)-I provides a convenient route for the preparation of optically active sulfoxides not available through the usual Grignard synthesis or the platinum complex reaction.[24] Racemic sulfoxides can be converted readily in good yields by treatment with hydrazoic acid[25] into sulfoximides which in turn are basic enough to be resolvable as salts of optically active sulfonic acids.[26] Finally, optically active sulfoximides can be converted stereospecifically to optically active sulfoxides.

Another reaction broadens the use of optically active sulfoximides as interesting reaction intermediates. Treatment of sulfoximide (−)-(*R*)-IV of maximum rotation with cold sodium hypochlorite gave (60%) the *N*-chloro derivative, (−)-(*R*)-V of maximum rotation.[27] The stability of the sulfoximide coupled with the fact that both *N*-metallo and *N*-chloro derivatives are readily prepared, suggests that these substances can be used to prepare a large variety of compounds by electrophilic or nucleophilic substitution on nitrogen. Such possibilities are being actively explored. These transformations are summarized in Chart I.

All of the reactions of Chart I proceeded in good yields with 96–100% stereospecificity. Fractional crystallization of the products in these stereochemical reaction cycles produced in each case sharp melting compounds whose rotations were slightly higher than the values of material obtained without fractional crystallization. The rotations taken before and after optical purification of each compound correlated with each other compound of a given cycle, and the internal consistency of the data establishes that the samples of maximum rotation were optically pure. Thus, the stereospecificity of each individual reaction can be calculated with considerable certainty.

Reagents. A polarimetric study was made of the rate of conversion of sulfoxide (+)-(*R*)-I to sulfimide (−)-(*S*)-II with either *N*-sulfinyl-*p*-toluenesulfonamide (VI), or *N*,*N*′-bis(*p*-tosyl)sulfur diimide (VII) in pyri-

(13) (a) D. S. Tarbell and C. Weaver, *J. Amer. Chem. Soc.*, **63**, 2939 (1941); (b) N. Newman, Ph.D. Dissertation, University of Minnesota, 1964.

(14) R. Appel and W. Buchner [*Chem. Ber.*, **95**, 855 (1962)] reported that simple sulfimides quickly undergo hydrolysis in the presence of base.

(15) G. Kresze and B. Wustrow, *ibid.*, **95**, 2652 (1962).

(16) S. G. Clarke, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 188 (1927).

(17) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **86**, 1452 (1964).

(18) H. Kwart and A. A. Kahn, *ibid.*, **89**, 1950 (1967).

(19) Optically active sulfimides previously have been oxidized to optically active sulfoximides with potassium permanganate.[13] Aromatic methyl groups were oxidized at the same time with this reagent.

(20) After our communication[2b] on the imidation and oxidation had been submitted, a communication by M. A. Sabol, R. W. Davenport, and K. K. Andersen [*Tetrahedron Lett.*, 2159 (1968)] appeared, which reported that imidation of (+)-(*R*)-I gave (−)-(*R*)-III and oxidation of (−)-*S*-II gave (−)-(*R*)-III. The degree of stereospecificity of their reactions could not be determined from their results, particularly since optically impure materials can be fractionally crystallized to optical purity in these series, and no yield data were reported. C. R. Johnson and J. J. Rigau (*J. Org. Chem.*, **33**, 4340 (1968)) have carried out somewhat similar reactions to those discussed here in the cyclic 4-*tert*-butylthiane 1-oxide sytem. Our results and those of Johnson and Rigau are in agreement as to the predominant stereochemical courses of the sulfoxide → sulfimide, sulfoxide → sulfoximide, and sulfimide → sulfoximide reactions.

(21) H. R. Bentley and J. K. Whitehead [*J. Chem. Soc.*, 2081 (1950)] first reported hydrolysis of *N*-arenesulfonylsulfoximides to give sulfoximides.

(22) J. K. Whitehead and H. R. Bentley [*ibid.*, 1572 (1952)] first used this procedure for conversion of *S*,*S*-dimethylsulfoximide into *S*,*S*-dimethyl-*N*-*p*-toluenesulfonylsulfoximide.

(23) Nitrous oxide has been postulated as leaving group in the thermal decomposition of *N*-nitrosoaziridines; see W. Rundel and E. Müller, *Chem. Ber.*, **96**, 2528 (1963), and R. D. Clarke and G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964).

(24) A. C. Cope and E. A. Caress, *J. Amer. Chem. Soc.*, **88**, 1711 (1966).

(25) (a) J. K. Whitehead and H. R. Bentley, *J. Chem. Soc.*, 1572 (1952); (b) F. Misani, T. W. Fair, and L. Reiner, *J. Amer. Chem. Soc.*, **73**, 459 (1951).

(26) R. Fusco and F. Tenconi, *Chim. Ind. (Milan)*, **47**, 61 (1965); *Chem. Abstr.*, **62**, 10357*h* (1965).

(27) The authors have not found any examples of *N*-chlorosulfoximide in the literature, but note that *N*-bromo-*S*,*S*-dimethylsulfoximide has been prepared by direct bromination [see R. Appel, H. W. Fehlhaber, D. Hänssgen, and R. Schöllhorn, *Chem. Ber.*, **99**, 3108 (1966)].

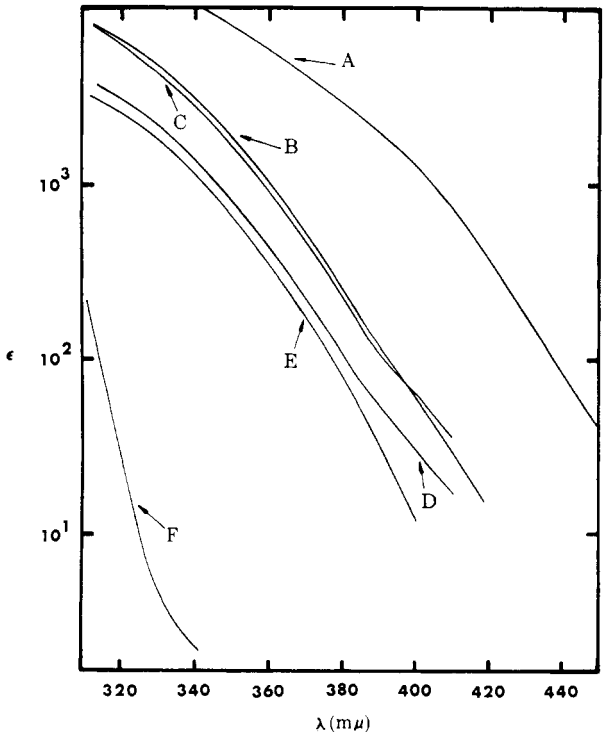


Figure 1. Ultraviolet absorption spectra (Cary Model 14M recording spectrophotometer with 0.0105-cm sample and reference cells): curve A, TsN=S=NTs in dry benzene; curve B, TsN=S=NTs in dry pyridine; curve C, TsN=S=O in dry pyridine calculated assuming disproportionation to TsN=S=NTs; curve D, TsN=S=O in dry pyridine calculated assuming no disproportionation; curve E, TsN=S=O in dry benzene; curve F, sulfur dioxide in dry pyridine.

dine. This study was complicated by the fact that VI disproportionates in pyridine to give VII and sulfur dioxide,[12c] and that VI is probably the initial product

$$2p\text{-}CH_3C_6H_4SO_2N{=}S{=}O \xrightarrow[25^\circ]{\text{pyridine}} p\text{-}CH_3C_6H_4SO_2N{=}S{=}NSO_2C_6H_4CH_3\text{-}p + SO_2$$

VI VII

of reaction of VII with sulfoxide I. A number of experiments were performed for orientation before the kinetics were examined. (1) Sulfoxide (+)-(*R*)-I was not perceptibly racemized when dissolved in either liquid SO_2 (25° for 6 days) or pyridine–sulfur dioxide (2:1 by volume, 25° for 24 hr). (2) The melting point for the diimide VII (139–140°) did not agree with that reported in the literature (120°[12c] and 119–120°[28]), and the infrared spectrum of VII in chloroform solution (medium intensity doublet: 7.25 and 7.58 μ; an intense doublet: 8.55 and 8.70 μ; a medium intensity peak at 9.18 μ) was different from that reported by others[12c] (two peaks in the region of 7.38–7.47 and 8.52–8.62 μ, and two peaks in the regions of 8.81–8.85 and 9.48–9.71 μ) in the same solvent. Accordingly, our bright yellow material was characterized by elemental analysis. The compound exhibited in its nmr spectrum the anticipated aromatic A_2B_2 quartet (centered at τ 2.41) and *p*-methyl proton peak at τ 7.56. The substance formed an adduct with butadiene, mp

(28) E. S. Levchenko and A. V. Kirsanov, *Zh. Obshch. Khim.*, 32, 2256 (1962).

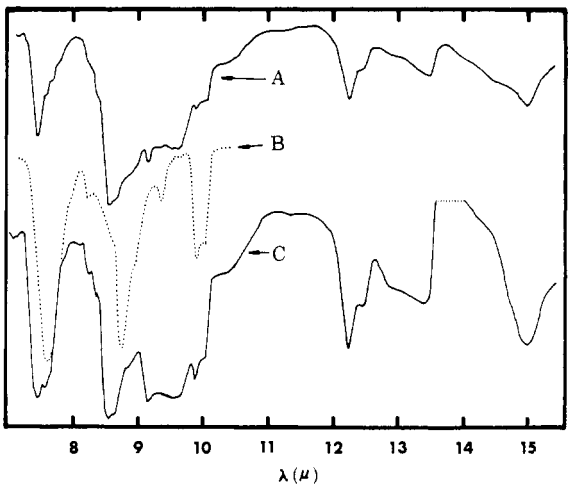


Figure 2. Infrared absorption spectra (Beckman IR-5 spectrometer) in dry pyridine with pyridine as a reference: curve A, TsN=S=NTs; curve B, sulfur dioxide; curve C, solution made by dissolving TsN=S=O in pyridine.

146–150° dec (lit. 151° dec[12c] and 175–176°[28]). When treated with water, VII gave tosylamide and sulfur dioxide as expected. (3) The *N*-sulfinyl-*p*-toluenesulfonamide (VI) gave mp 49.5–51.0° (lit.[12b] 52–53°) and exhibited a typical A_2B_2 quartet centered at τ 2.32 and a *p*-methyl proton singlet at τ 7.53 in the nmr spectrum in deuteriochloroform. The infrared spectrum of the substance in chloroform (intense peaks at 7.33, 8.03, 8.55, and 9.18 μ) is in agreement with reported infrared data for this class of compound.[12b] (4) The report that the disproportionation of VI to give VII and sulfur dioxide was catalyzed by pyridine was checked by recording ultraviolet and infrared spectral data for solutions of these substances. Figure 1 records the ultraviolet absorption spectrum for VI and VII in benzene and pyridine, and sulfur dioxide in pyridine in the region 310–450 mμ. The spectra could not be obtained at shorter wavelengths due to solvent absorption. The suggested disproportionation was assumed to occur [$2TsNSO \rightarrow (TsN)_2S + SO_2$] in pyridine, and a curve calculated (C) for the amount of sulfur diimide expected from the amount of *N*-sulfinyl compound dissolved in the pyridine. This calculated curve is the same within 10% of the curve actually obtained (B) for the sulfur diimide in pyridine, and is substantially different from the curve calculated (D) from the amount of *N*-sulfinyl compound in pyridine assuming no disproportionation. Figure 2 records the infrared spectra of sulfur diimide VII in pyridine (curve A), that of sulfur dioxide in the same solvent (curve B), and of the solution resulting from dissolving *N*-sulfinyl compound VI in pyridine. The last spectrum (C) looks like a blend of the other two (A and B). At shorter wavelengths down to 2 μ no significant bands could be discerned above the pyridine background. Solvent absorption interfered with the desired spectra in several regions. All spectra were taken immediately after mixing, and the disproportionation of VI to give VII and sulfur dioxide appeared to be instantaneous.

Kinetics. The rates of reaction were followed polarimetrically. The kinetic results are summarized in Table I. Both second-order rate constants (first order in each of (+)-(*R*)-I and VII) and third-order rate

Table I. Rate Constants for the Reaction of (+)-(*R*)-I with VII in Pyridine at 25°

Run	[(+)-(*R*)-I]$_0$, *M*	[VII]$_0$, *M*	[VII]/[(+)-(*R*)-I]$_0$	*n*[a]	% completion[b]	k^2,[c] M^{-1} min^{-1}	k^3,[c] M^{-2} min^{-1}	% stereospecificity[d]
1	0.153	0.335	2.2	21	66	0.150 ± 0.004	0.497 ± 0.001	93.5
2	0.147	0.266	1.8	14	80	0.101 ± 0.001	0.459 ± 0.003	90.2
3	0.147	0.146	1.0	18	50	0.0579 ± 0.0005	0.477 ± 0.001	90.6
4	0.147	0.0379	0.26	10	48	0.0109 ± 0.0003	0.369 ± 0.002	
5	0.103	0.0982	0.95	7	58	0.0276 ± 0.0002	0.357 ± 0.002	
6	0.366	0.0702	0.19	6	57	0.0136 ± 0.0008	0.331 ± 0.004	
7[e]	0.0652	0.0593	0.91	23	38	0.0164 ± 0.0002	0.317 ± 0.002	92.0

[a] The number of data points in the least-squares analysis is *n*. [b] Reactions were followed to 100% completion; however, only the indicated portion of the data was used to obtain rate constants due to racemization at later stages. [c] The error associated with the rate constant is the standard deviation. [d] The stereospecificity is based upon final rotations compared to the initial concentration and optical purity of (+)-(*R*)-I. [e] The reagent was 0.1186 *M* *N*-sulfinyl*p*-toluenesulfonamide.

constants (first order in (+)-(*R*)-I and second order in VII) were calculated using a least-squares treatment and data for the indicated percentage of reaction. The proportion of racemization which occurred during early stages of the reaction is small as shown by the following experiment.

A large scale reaction was carried out in parallel with run 1 with identical initial concentrations in pyridine at 25°. The preparative reaction was quenched at 50% completion of reaction by addition of water sufficient to hydrolyze unreacted VII. Unreacted I and sulfimide product II were isolated by chromatography on silica gel. The optical purities of the separated materials were determined without further purification. Recovered I was of unchanged optical purity. The product II was 97% optically pure. Final rotations indicate the optical purity of the product to be 90–94% at near 100% reaction. These results suggest that side reactions become more significant, although still small in proportion, at later stages of reaction. Thus, the per cent of stereospecificity for conversion of (+)-(*R*)-I to (−)-(*S*)-II at 25° determined from final rotations (Table I) is a lower estimate of the initial reaction's stereospecificity.

The following control experiments were conducted. (1) The rotation of a pyridine solution 0.03683 *M* in (+)-(*R*)-I and 0.01770 *M* in (−)-(*S*)-II at 25° demonstrated the rotations of these species to be additive. (2) Both (+)-(*R*)-I and (−)-(*S*)-II were shown to be optically stable in pyridine at 25°. (3) The product (−)-(*S*)-II was shown to be chemically and optically stable to the sulfur diimide reagent and to the reaction conditions. (4) A comparison of runs 6 and 7 shows that the *N*-sulfinyl compound does not give significantly different results when employed instead of the sulfur diimide reagent VII. This result is due to the rapid conversion of the former compound to VII in pyridine. (5) The reaction in pyridine at about 40° was followed by nmr, also. Peaks due to the S–CH_3 protons of I and II were observed to change in relative intensity, but no additional spectral features developed during the first 50% of reaction which could be ascribed to an intermediate in the reaction.

The rate constants listed in Table I were obtained for solutions in which initial sulfoxide concentration varied by a factor of 5 and initial sulfur diimide concentration varied by a factor of 9. The extreme values for the rate constants differ by factors of *ca.* 15 and 1.5 for second-order and third-order kinetics, respectively. The probable error for the average of the k^2's is 78%. For the average k^3, the probable error is only 16%. Thus, third-order kinetics fit the data far better than second-order kinetics.

The order of the reaction with respect to sulfur diimide (VII) can be determined by the differential method[29] from the data for runs 2, 3, and 4 in which [(+)-(*R*)-I]$_0$ is constant. A least-squares method was employed to extrapolate [VII] to zero time and to obtain the initial rate, [d[VII]/d*t*]$_0$. A plot of the initial rate against log [VII]$_0$ for the three runs gave a good straight line with a slope of 2 which corresponds to the order of the reaction with respect to the sulfur diimide reagent.

Additional support for third-order kinetics is provided by the activation parameters of the reaction. Two runs were made with solutions of identical concentrations (0.1 *M* in (+)-(*R*)-I and 0.2 *M* in VII) at 25.0 and 5.8° in pyridine. The enthalpy of activation was determined in a manner independent of the order with respect to VII.[30] Pseudo-first-order rate constants were calculated and extrapolated to zero time. The enthalpy of activation calculated from the ratio of extrapolated rate constants according to eq 1 is 3 kcal/mol. A small enthalpy of activation is consistent with results for other third-order reactions.[31] The free

$$\Delta H^{\pm} = \frac{RT_1T_2}{(T_1 - T_2)} \ln \frac{T_2 k_{T_1}}{T_1 k_{T_2}} \qquad (1)$$

energy of activation calculated according to absolute rate theory from the third-order rate constant at 25° is 20 kcal/mol. From the enthalpy and free energy, the entropy of activation is found to be −57 eu, which is a large negative value also consistent with third-order kinetics.[31]

Absolute Configurations of Compounds I–IV. The absolute configuration of sulfoxide (+)-(*R*)-I has been

(29) K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill, New York, N. Y., 1965, p 15.

(30) A pseudo-first-order rate constant is defined by

$$k^1 = -(1/[\mathrm{I}])(\mathrm{d}[\mathrm{I}]/\mathrm{d}t) = k[\mathrm{VII}]^n$$

where *k* is the *n* + 1 order rate constant for a reaction which is of order *n* in VII and first order in I. Extrapolation of k^1 to zero time gives

$$\lim_{t \to 0} k^1 = k[\mathrm{VII}]_0^n$$

where [VII]$_0$ is the initial concentration of VII. The terms in [VII]$_0$ cancel when the ratio is taken of the extrapolated pseudo-first-order rate constants for identical initial concentrations but different temperatures, *i.e.*, the ratio of actual *n* + 1 order rate constants is equal to the ratio of extrapolated pseudo-first-order rate constants.

(31) C. G. Swain, *J. Amer. Chem. Soc.*, 70, 1119 (1948).

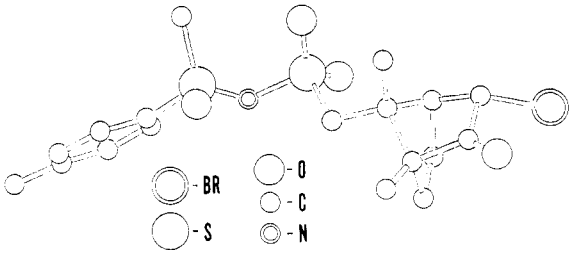


Figure 3. Machine-drawn X-ray structure showing absolute configuration of (+)-*N*-(3-*endo*-bromo-2-oxo-9-bornanesulfonyl)-methyl-*p*-tolylsulfoximide ((+)-VIII).

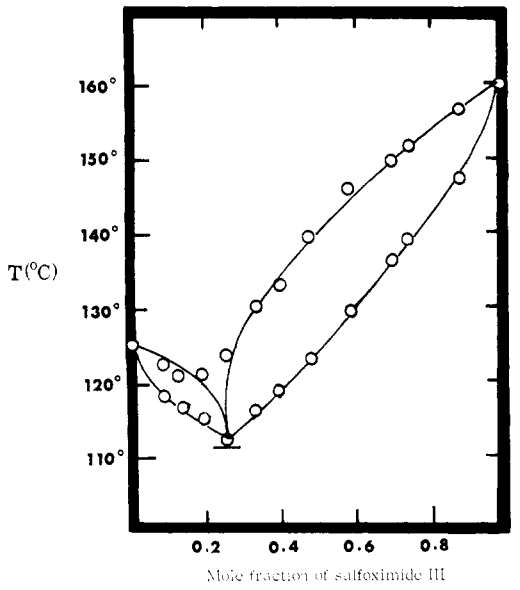
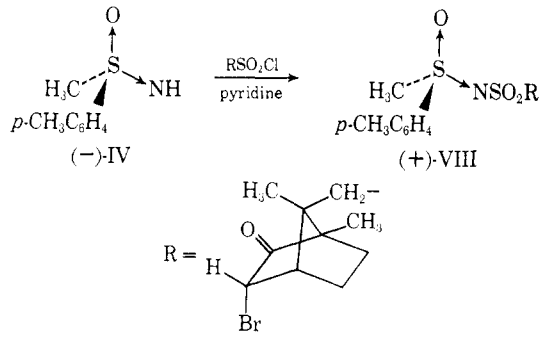


Figure 4. Melting point composition diagram for the system of (−)-*N*-(*p*-tosyl)methyl-*p*-tolylsulfimide [(−)-II] and (−)-*N*-(*p*-tosyl)-methyl-*p*-tolylsulfoximide [(−)-III].

established.[9b,h,i] The absolute configurations of chemically interrelated sulfoximides (−)-(*R*)-III and (−)-(*R*)-IV were determined as follows. Treatment of (−)-IV with (+)-3-*endo*-bromo-2-oxo-9-bornanesulfonyl chloride gave (+)-*N*-(3-*endo*-bromo-2-oxo-9-bornanesulfonyl)methyl-*p*-tolylsulfoximide ((+)-VIII) (see Chart II). The absolute configuration of this substance was determined by the X-ray anomalous dispersion technique. The compound crystallized in the orthorhombic system space group $P2_12_12_1$ with a = 7.781, b = 15.849, and c = 16.443 Å. Three-dimensional intensity data (2192 reflections) were gathered on a computer-controlled diffractometer. The crystal structure was refined by least squares to an agreement

Chart II



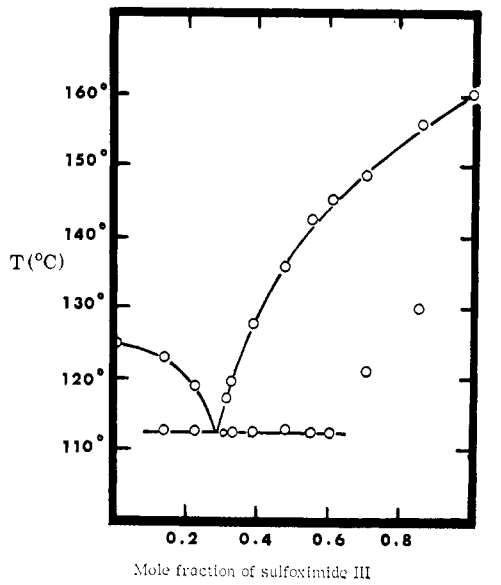


Figure 5. Melting point composition diagram for the system of (+)-*N*-(*p*-tosyl)methyl-*p*-tolylsulfimide [(+)-II] and (−)-*N*-(*p*-tosyl)-methyl-*p*-tolylsulfoximide [(−)-III].

index R of 0.074 without including anomalous dispersion. At this point, structure factors were calculated for both enantiomers including anomalous dispersion effects; the 50 reflections most affected by the anomalous dispersion gave R factors of 0.175 and 0.247 for the two possible enantiomers. Using Bijvoet's method,[32a] 14 of the 50 were checked by remeasuring $F(h, k, l)$ and $F(-h, -k, -l)$. All 14 are in agreement with the R factor indicated. The correct enantiomer is shown in Figure 3. Least-squares refinement was continued with anomalous dispersion effects included. The final R for this structure is 0.045. Details of the crystallographic investigation will be published elsewhere.[32b] The absolute configuration of the bromocamphor portion is in agreement with that found previously.[32c,d]

The absolute configuration of sulfimide (−)-II was determined by the phase-diagram method.[33] Figure 4 records the melting point composition diagram for (−)-II and (−)-III, and Figure 5 that of (+)-II and (−)-III. The shape of Figure 4 shows that (−)-II and (−)-III are isomorphous (form a series of solid solutions with no eutectic) whereas (+)-II and (−)-III form a simple eutectic (type 2 behavior[33b]). The latter diagram shows a straight initial thaw line in the neighborhood of the eutectic. This behavior shows that the solid phases of the two components (+)-II and (−)-III are immiscible. Other experiments demonstrated that (−)-II and (±)-II form a series of solid solutions as did (−)-III and (±)-III.

These experiments taken together establish the absolute configurations of all the compounds of Charts I and II.

Spectra. The ultraviolet spectra of sulfoxide I, sulfimide II, sulfoximide III, and tosylamide are re-

(32) (a) J. M. Bijvoet, *Endeavour*, **14**, 71 (1955); (b) in preparation for submittal; (c) J. A. Wunderlich, *Acta Crystallogr.*, **23**, 846 (1967); (d) F. H. Allen and D. Rogers, *Chem. Commun.*, 837 (1966).

(33) (a) A. Fredga, *Tetrahedron*, **8**, 126 (1960); (b) K. Mislow and M. Heffler [*J. Amer. Chem. Soc.*, **75**, 3668 (1952)] report similar curves for the system of 2-hydroxy-2-phenylacetamide and 2-chloro-2-phenylacetamide.

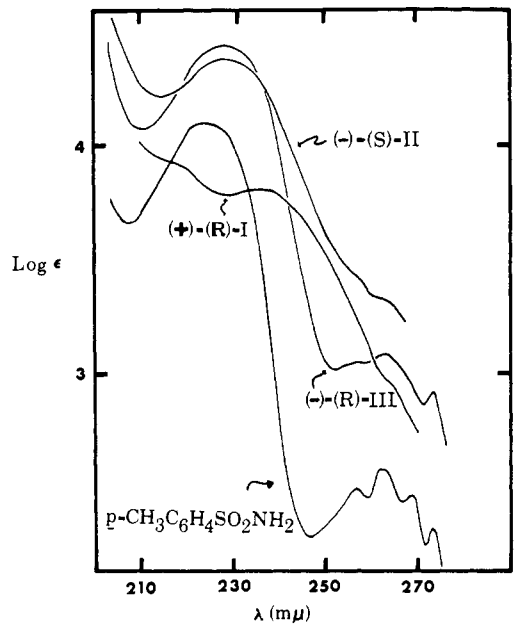


Figure 6. Ultraviolet absorption spectra of (+)-(*R*)-I, (−)-(*S*)-II, (−)-(*R*)-III, and tosylamide in absolute ethanol recorded on a Cary Model 14 M recording spectrophotometer.

corded in Figure 6, and the optical rotatory dispersion curves of (+)-(*R*)-I, (−)-(*S*)-II, and (−)-(*R*)-III are found in Figure 7. Sulfimide, sulfoximide, and tosylamide all exhibit high intensity maxima in the 220–230-mμ part of their ultraviolet spectra, and a series of bands of lower intensity in the 258–275-mμ region. The optical rotatory dispersion curves of sulfimide (−)-(*S*)-II and sulfoximide (−)-(*R*)-III are very similar. Thus (−)-(*S*)-II exhibits maxima at 243 ([φ] −45,500°) and 225 mμ ([φ] +35,500°), and [φ] is 0° at 234 and 213 mμ. Sulfoximide (−)-(*R*)-III gives maxima at 239 ([φ] −47,500°) and 226 mμ ([φ] +54,900°), and [φ] = 0 at 233 and 216 mμ. The great similarity of the ultraviolet spectra of II and III suggests that related electronic transitions dominate the spectra of the two compounds. The very close resemblance of the optical rotatory dispersion curves of (−)-(*S*)-II and (−)-(*R*)-III both in shape and signs of their Cotton effects provides additional evidence that these two compounds possess the same configurations. Thus, the formal addition of an oxygen atom to the electron pair at sulfur of (−)-II to give (−)-III (without configurational alteration) does not seriously disturb the

Table II. Chemical Shifts (τ Values) of Methyl Protons in the Nmr Spectra[a] in 20% Deuteriochloroform Solution (Ar = *p*-$CH_3C_6H_4$)

Compd	τ	Compd	τ	Compd	τ
Ar—S(=O)—CH_3	7.32	Ar—S(=O)—CH_3	6.97	Ar—S(=N—Cl)—CH_3	6.76
Ar—S(=NTs)—CH_3	7.18	Ar—S(=NH)—CH_3	6.91	Ar—S(=N—Ts)—CH_3	6.60

[a] Taken on a Varian Associates A-60 spectrometer.

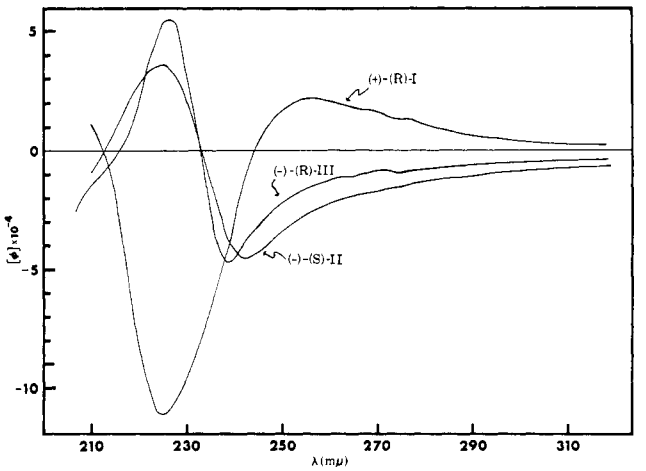


Figure 7. Optical rotatory dispersion curves for (+)-(*R*)-I, (−)-(*S*)-II, and (−)-(*R*)-III in absolute ethanol, recorded on a Cary Model 60 recording spectropolarimeter.

electronic transitions responsible for the main features of the optical rotatory dispersion curves.

Sulfoxide (+)-(*R*)-I gives maxima at 256 ([φ] +21,000°) and 226 mμ ([φ] −112,000°), and [φ] = 0 at 246 and 214 mμ. Thus, (+)-(*R*)-I and (−)-(*S*)-II have Cotton effects of opposite sign not far from one another in wavelength, a fact that correlates with their opposite configurations. Possibly the same transitions dominate the spectra of the sulfoxide and sulfimide in the region of 214–226 mμ.

Table II records the chemical shifts of the protons of the methyl group attached to sulfur of the various compounds used in this study. These data indicate that of the groups attached to sulfur NTs > NCl > NH > O >: in ability to deshield the protons of the methyl group.

Discussion

The stereochemical courses of the reactions of Chart I are discussed in the first section, followed in the second by an analysis of the symmetry properties of the reaction cycles generated by the reactions. In the third section the possible mechanisms for nucleophilic substitution at sulfur that involve trigonal bipyramids and that lead to retention or inversion of configuration are outlined. The fourth section treats the possible mechanisms which go *via* square pyramids. The fifth section involves a discussion of the mechanism of the conversion of sulfoxide I to sulfimide II, and section six the reverse reaction. The stereochemical aspects of the oxidation, imidation, and deimidation reactions are discussed in the seventh section.

The Stereochemical Courses of the Reactions. Knowledge of the absolute configurations of compounds I–IV allows the stereochemical courses of all the reactions of Chart I to be assigned. The character of the two-reaction stereochemical cycle, (+)-I ⇄ (−)-II, indicates both reactions must go with either retention or inversion. The absolute configurations of (+)-I and (−)-II demonstrate these *nucleophilic* substitution reactions at sulfur occur with inversion of configuration. The imidation (no mechanistic implication) of sulfoxide (+)-I to give sulfoximide (−)-III went with retention of configuration. These reactions, (−)-IV ⇄ (−)-III,

and (−)-IV → (−)-V must go with retention since no bonds to sulfur are made or broken. The deimidation of sulfoximide (−)-IV to (+)-I must have gone with retention, and is the formal inverse of an electrophilic substitution at sulfur. Of these reactions, the nucleophilic substitutions (I ⇄ II) are perhaps the most interesting mechanistically.

Symmetry Properties of the Three-Reaction, Diligostatic Stereochemical Cycles. The general properties of stereochemical reaction cycles recently have been delineated.[34] The stereochemical reaction cycles, (−)-III ← (+)-I → (−)-II → (−)-III and (−)-III ← (−)-II → (+)-I → (−)-III are *diligostatic* (two ligands are common to all members of the cycle). These cycles are also *podal*, since the number of *chiromers* (members) equals the number of reactions (three). When the number of chiromers exceeds the number of reactions by one, a cycle is *antipodal*, and two of the chiromers are enantiomerically related. The two cycles at hand do not contain enantiomers. The two cycles also contain a *ligand metathesis*, since in the cycles as a whole, two ligands by stepwise substitution involving a third, in effect, interchange bonding positions (the electron pair, O and NTs are the interchanging ligands). Three-reaction, diligostatic stereochemical cycles exist only when they contain a ligand metathesis.[34]

The following rules correlate the properties of stereochemical reaction cycles.

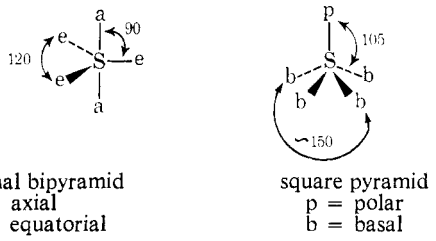
Antipodal Rule. If the cycle is antipodal, the sum of the number of reactions that go with inversion and the number of ligand metatheses found in the cycle (either zero or one) is odd.

Podal Rule. If the cycle is podal, the sum of the number of reactions that go with inversion and of ligand metatheses is even.

Application of the podal rule to the two, three-reaction stereochemical reaction cycles listed above indicates that only an odd number of reactions can occur with inversion (either three or one). Knowledge of the configurations of the three chiromers ((−)-III, (+)-I, and (−)-II) established that one reaction (the nucleophilic) occurred with inversion, the rest with retention in concert with the podal rule. The classical rule that "an odd number of inversions in a stereochemical reaction cycle involves enantiomers" clearly breaks down in these reaction cycles because of the presence of the ligand metathesis, which is the formal equivalent of an inversion.

Descriptions of Nucleophilic Substitution at Tetrahedral Sulfur That Involve Trigonal Bipyramids. Before proceeding to a discussion of the mechanism of the reactions, (+)-I ⇄ (−)-II, the possible stereochemical descriptions of nucleophilic substitution at sulfur are explored.

Nucleophilic substitution at tetrahedral sulfur increases the number of ligands bonded to sulfur in the transition state (associative path[35]). The geometry of the transition state or intermediate of increased coordination might resemble either a trigonal bipyramid, a square pyramid, or distortions of these structures.



trigonal bipyramid
a = axial
e = equatorial

square pyramid
p = polar
b = basal

The stereochemical course of an associative substitution depends on several factors: (1) which of these structures provides the lowest energy path for reaction; (2) the relative positions of the entering and leaving groups within the structure; (3) the possible polytopal rearrangements[36] that intermediates possessing these structures might undergo. Table III summarizes the possible stereochemical descriptions of mechanisms of associative substitution on tetrahedra by way of trigonal bipyramids that follow stereospecific paths. In Table III, the question of whether sulfur with five ligands (the electron pair is counted as one ligand) represents a transition state or an intermediate is not treated. However, implicit in those cases where pseudorotations[37] are envisioned, short-lived intermediates are assumed. The barriers to pseudorotations of a sulfur trigonal bipyramid have been estimated to be of the order of 6–14 kcal/mol from measurement of barriers for $CF_3N{=}SF_4$[38a] and pentacoordinate group V compounds.[38b-f]

In Table III, 1 represents the leaving and 2 the entering groups of the tetrahedron, and 3, 4, and 5 are the nonexchanging ligands. The mechanistic symbols (such as ea) refer to the positions of the leaving and entering groups on the trigonal-bipyramid intermediates or transition states, the first letter of the pair placing the leaving and the second the entering group's position. The aa process corresponds to the well-known SN2 reaction mechanism. It involves face (axial) attack on the tetrahedron, as does the ea mechanism. The ee[39] and ae mechanisms involve edge (equatorial) attack on tetrahedra.

If the entering and leaving groups (2 and 1) are identical, then the formation from and decompositions to tetrahedra of particular aa and of ee configuration are the microscopic reverse of one another. Formation and decomposition of ea and of ae trigonal bipyramids are not the microscopic reverse of one another. Thus, the principle of microscopic reversibility is satisfied only if an ae ⇄ ea stage is included in the overall scheme. If the entering and leaving groups are sufficiently different, simple ae and ea mechanisms are possible.

The aa trigonal bipyramid in uniquely defined by the configuration of the starting tetrahedron since

(34) D. C. Garwood and D. J. Cram, *J. Amer. Chem. Soc.*, **92**, 4575 (1970).

(35) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, p 8.

(36) (a) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636, 4115 (1969); (b) E. L. Muetterties, *ibid.*, **90**, 5097 (1968); (c) E. L. Muetterties, *Inorg. Chem.*, **6**, 635 (1967); (d) E. L. Muetterties and A. T. Starr, *J. Amer. Chem. Soc.*, **91**, 3098 (1969).

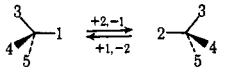
(37) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

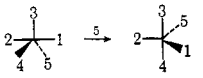
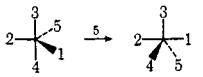
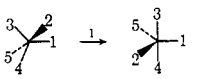
(38) (a) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964); (b) E. L. Muetterties, W. Mahler, and R. Schmutzler, *ibid.*, **2**, 613 (1963); (c) R. R. Holmes, R. M. Deiters, and J. A. Golden, *ibid.*, **8**, 2612 (1969); (d) R. R. Holmes and R. M. Deiters, *ibid.*, **7**, 2229 (1968); (e) R. R. Holmes and R. M. Deiters, *J. Amer. Chem. Soc.*, **90**, 5021 (1968); (f) R. M. Rosenberg and E. L. Muetterties, *Inorg. Chem.*, **1**, 756 (1962).

(39) To the best of our knowledge, Westheimer and coworkers[8] were the first to recognize the ee route to inversion in substitution reactions on tetrahedral species.

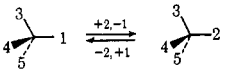
Table III. Possible Stereochemical Descriptions of Mechanisms of Associative Substitution on Tetrahedra *via* Trigonal Bipyramids That Provide Stereospecific Pathways for Reaction

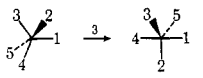
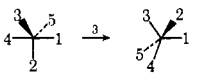
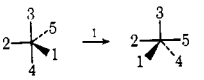
Inversion mechanisms



Mechanistic symbol	Config symbol	Trigonal bipyramid transition states or intermediates: Structures and pseudorotations
aa	12	
ee	43	
aa $\xrightarrow{5}$ ee	12 $\xrightarrow{5}$ 43	
ee $\xrightarrow{5}$ aa	43 $\xrightarrow{5}$ 12	
ea $\xrightarrow{1}$ ee	25 $\xrightarrow{1}$ 43	

Retention mechanisms



Mechanistic symbol	Config symbol	Trigonal bipyramid transition states or structures: Structure
ea	25	
ae	41	
ea $\xrightarrow{3}$ ae	25 $\xrightarrow{3}$ 41	
ae $\xrightarrow{3}$ ea	41 $\xrightarrow{3}$ 25	
ee $\xrightarrow{1}$ ea	43 $\xrightarrow{1}$ 25	

only one face is available for the mechanism. For a tetrahedron of given configuration, edge (equatorial) attack in the ee and ae mechanisms can occur on three different edges, and in the ea mechanism, face (axial) attack can occur on three different faces. When possible pseudorotations of the trigonal bipyramids are added to the possibilities, it becomes clear that some means of monitoring the configurational changes is needed.

Figure 8 provides symbols for the 20 possible trigonal bipyramids with ligands 1–5 (each different), and a map for their 30 pseudorotations.[40] Each intersection

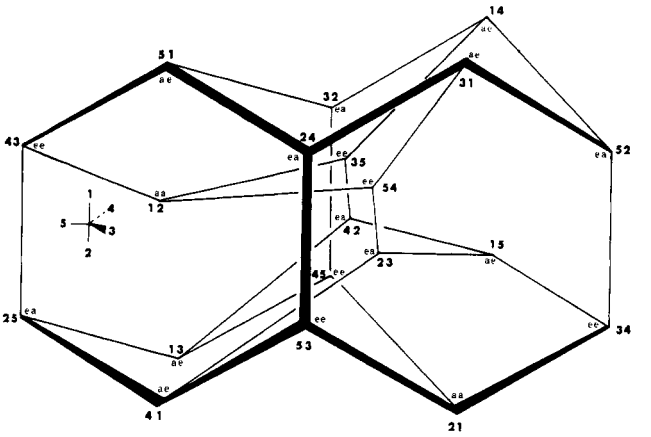


Figure 8. Map that identifies the stereochemical courses of associative substitution reactions on tetrahedra that form trigonal bipyramids capable of pseudorotating.

of lines of the map represents a configuration named by the two numbers that represent the two axial groups. The order of the numbers names the configuration. When the trigonal bipyramid is viewed along the axis from the first to the second numbered ligand, the equatorial groups are in counterclockwise order. Each line connecting two intersections represents a pseudorotation about the pivotal ligand whose number is not found in the designation of either intersection.

Figure 8 allows track to be kept of configurations when a tetrahedron with four different ligands (1, 3, 4, and 5) undergoes associative substitution *via* trigonal bipyramids to give a new tetrahedron with four different ligands (2, 3, 4, and 5). As in Table III, 1 is the leaving group and 2 the entering group. The positions of these two groups in the trigonal bipyramids are indicated in Figure 8 by a pair of letters also placed at each intersection. The first letter of the couple refers to the position of ligand 1 (a or e), and the second letter to the position of ligand 2 (a or e).

Figure 8 possesses useful symmetry properties. All of the trigonal bipyramids in the upper half of the figure when decomposed by loss of ligand 1 give tetrahedra of the same configuration. All of the trigonal bipyramids in the lower half of the figure when decomposed by loss of ligand 1 give tetrahedra of the opposite configuration. Those pseudorotations traced by lines only in the upper half or only in the lower half have no effect on the overall stereochemical course of associative substitutions on tetrahedra. However, inclusion of a pseudorotation that connects the upper to the lower half (vertical or near-vertical lines) in the overall substitution reaction has the effect of inverting the overall stereochemical course of the substitution reaction on the tetrahedron. All of the six vertical or near-vertical lines represent pseudorotations about the leaving group (1) as the pivotal ligand. These six lines define the pseudorotations of the ee $\rightleftarrows$ ea variety. The following generalization emerges: *in substitution reactions on chiral tetrahedra that involve*

(40) Other workers have proposed different maps or matrices that can be used for following pseudorotations: (a) A. T. Balaban, D. Fărcasiu, and R. Bănică, *Rev. Roum. Chim.*, **11**, 1205 (1966); (b) J. D. Dunitz and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **7**, 725 (1968); (c) P. C. Lauterbur and F. Ramirez, *J. Amer. Chem., Soc.*, **90**, 6722 (1968); (d) E. L. Muetterties, *ibid.*, **91**, 1636, 4115 (1969); (e) K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 7031 (1969). The map of Figure 8 was inspired by that of Dunitz and Prelog, and already has found use by D. Gorenstein and F. H. Westheimer, *ibid.*, **92**, 634 (1970).

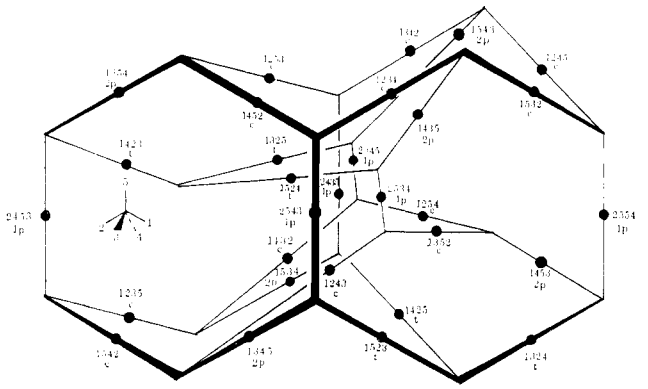


Figure 9. Map that identifies the stereochemical course of associative substitution reactions on tetrahedra that form square pyramids capable of polytopal rearrangements.

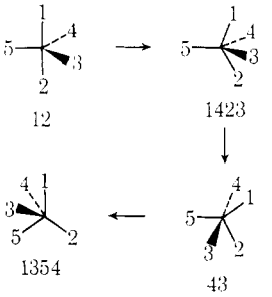
trigonal bipyramids as intermediates, only pseudorotations about the leaving group as a pivotal ligand affect the stereochemical course of the overall substitution reaction.

Examples of application of this principle are found in Table III. Inclusion of the pseudorotation aa $\rightleftarrows$ ee of the trigonal bipyramid 12 (formed by the aa mechanism) to give 43 does not affect the stereochemical course of reaction. Decomposition of either 12 or 43 by loss of ligand 1 gives the tetrahedron of the same configuration. Similarly the pseudorotations ee → aa, ae → ea, and ea → ae do not affect the stereochemical outcome of the overall substitution. However, pseudorotation of 25 (formed by an ea process) gives 43, and loss of ligand 1 from 25 gives overall retention, and from 43 gives inversion. Similarly, although the ee mechanism gives inversion, the ee → ea mechanism provides retention.[41]

Stereochemical Descriptions of Nucleophilic Substitution at Tetrahedral Sulfur That Involve Square Pyramids. Although all stable sulfur tetracoordinate species of known structure closely resemble trigonal bipyramids, the stereochemical consequences of reactions occurring through square pyramidal transition states and intermediates also will be examined. Due to the extensive structural reorganization required to move four tetrahedrally arranged ligands into basal positions of a square pyramid it is assumed that a group cannot enter directly at the polar position. The reverse process, a group leaving from the polar position of a square pyramid, is also excluded for the same reason. If a square pyramid is a transition state or an intermediate that does not undergo polytopal rearrangements, then both entering group (ligand 2) and leaving group (ligand 1) can only occupy basal positions. From a chiral tetrahedron with ligands 1–4 of a particular configuration, square pyramids of three configurations can be formed, two of which have the entering and leaving groups cis, and one trans. *Decomposition of either of the two cis-square pyramids gives product of configuration identical with that of starting material. Decomposition of the trans-square pyramid gives product of opposite configuration.* Table IV traces examples of these conversions with both structural and configurational designations (see below).

Polytopal rearrangements of square pyramids can be envisioned. Just as a pseudorotation of a trigonal bipyramid goes through a square-pyramid transition state with the polar ligand as pivotal, a polytopal rearrangement of a square pyramid goes through a trigonal bipyramid as a transition state whose two axial ligands are trans and basal in the starting and final square pyramids. These relationships are illustrated in Chart III. In Table IV and Chart III the configurations of the square pyramids are indicated by four digits, each of which stands for a ligand in the basal position. The fifth ligand not designated occupies the polar position. The convention adopted involves placing the polar ligand in back of the plane of the page, and the four basal ligands in the plane of the page. The basal ligands are then listed in clockwise order, starting with the ligand of lowest number.

Chart III. Pseudorotation of 12 to 43 about Pivotal Ligand 5, and Polytopal Rearrangement of Square Pyramid 1423 to 1354 from Polar Ligand 5 to Polar Ligand 2

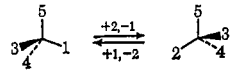
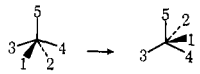
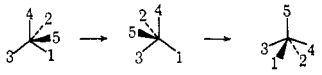
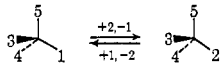
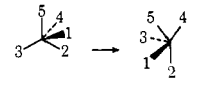
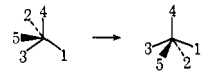
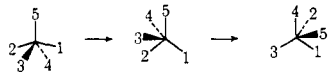


The polytopal rearrangements of square pyramids can be followed by reference to the map of Figure 9. This map resembles that for trigonal-bipyramid pseudorotations (Figure 8) except that the structures (designated by four digits) are the black dots, and points of intersection of the lines are the trigonal-bipyramid transition states for polytopal rearrangements. Unlike the usual transition state that can decompose in two directions (starting material and product), these can decompose to three, starting material and either of two products. Figure 8 charts the pseudorotations of 20 trigonal bipyramids with 30 reactions, and a minimum of five pseudorotations are needed to convert a trigonal bipyramid to its enantiomer (*e.g.*, 12 → 43 → 25 → 41 → 53 → 21). Figure 9 traces the polytopal rearrangements of 30 square pyramids through 60 reactions. A minimum of five polytopal rearrangements are required for one square pyramid to give its enantiomer (*e.g.*, 2453 → 1423 → 1524 → 1435 → 1532 → 2354).

The symmetry properties of Figure 9 allow to be traced the stereochemical course of associative substitution reactions on tetrahedra that form square pyramids. Each structural designation has an additional symbol that indicates the relative positions of the leaving group (ligand 1) and entering group (ligand 2). When both 1 and 2 are basal, they are either cis (c) or trans (t) to one another. When ligand 1 is polar, this is indicated as 1p, and when ligand 2 is polar, the structure is labeled 2p. All square pyramids except those labeled 2p can be formed directly from tetrahedra,

(41) Mislow and coworkers[4e] have developed a different "topological overview" of associative substitution on tetrahedra that involve trigonal-bipyramidal intermediates that pseudorotate. Although our treatment and that of Mislow, *et al.*, rest on the same principles, representations, the emphasis, illustrations, and applications are entirely different, and each was inspired by a different set of needs.

Table IV. Possible Stereochemical Descriptions of Mechanisms of Associative Substitution on Tetrahedra *via* Square Pyramids That Provide Stereospecific Pathways for Reaction

Mechanistic symbol	Square pyramid transition states or intermediates: Config symbol	Structures and polytopal rearrangement
	Inversion mechanisms	
12t	1423	
12t → 12t	1423 → 1524	
1p → 12t	2453 → 1423	
1p → 2p	2453 → 1354	
12c → 1p → 12t	1542 → 2453 → 1423	
	Retention mechanisms	
12c	1542	
12c → 12c	1542 → 1235	
1p → 12c	2453 → 1542	
1p → 12c	2453 → 1235	
12t → 1p → 12c	1423 → 2453 → 1542	

and all square pyramids except those labeled 1p can decompose to tetrahedra in this scheme. All of the square pyramids above the vertical (or near vertical) lines of Figure 9 when decomposed by loss of leaving group 1 give tetrahedra of one configuration, whereas those below give the opposite configuration. Therefore, to change the course of associative substitution by means of polytopal rearrangements of square pyramids, one has to pass from structures above to those below (or *vice versa*) the vertical (or near vertical) lines of Figure 9. Those structures on the vertical lines are 1p and are assumed not capable of decomposing directly to tetrahedra.

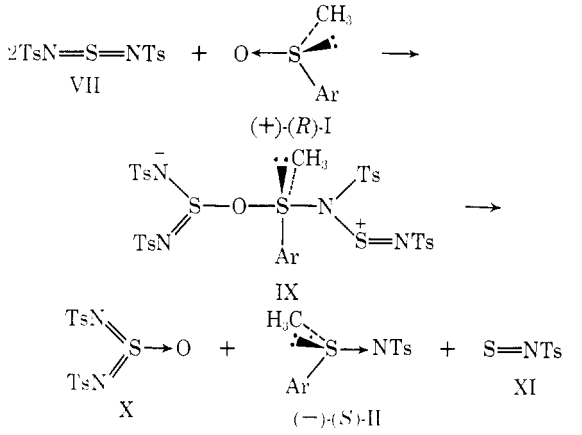
The relationships in Figure 9 provide several generalizations about the stereochemical effects of including polytopal rearrangements of square pyramids in the mechanism of associative substitution reactions on tetrahedra. (1) Rearrangements 12t → 12t or 12c → 12c have no effect on stereochemical course. (2) Rearrangements 1p → 12t or 1p → 2p lead to inversion of configuration. (3) Rearrangements 1p → 12c (there are two varieties for a given 1p structure) lead to retention of configuration. (4) The minimum number of rearrangements needed to change a reaction course is two. The sequence, 12c → 1p → 12t changes a 12c mechanism from retention to inversion, and the sequence 12t → 1p → 12c from inversion to retention. Examples of applications of these generalizations to specific structures are found in Table IV.

If the entering and leaving groups (2 and 1) are the same, then the formation from, and decompositions to tetrahedra of particular 12c (or 12t) structures are the microscopic reverse of one another, since the transition states or intermediates possess planes of symmetry. If groups 1 and 2 are ordinarily identical, they become different when placed in 1p and 2p positions. Thus associative exchange of identical groups through 1p structures can occur only through 1p → 2p, 1p → 12t, 1p → 12c, 12c → 1p → 12t, 12t → 1p → 12c or more complex routes.

Mechanism of Sulfur Diimide Conversion of Sulfoxide I to Sulfimide II. The reaction of sulfoxide (+)-(*R*)-I

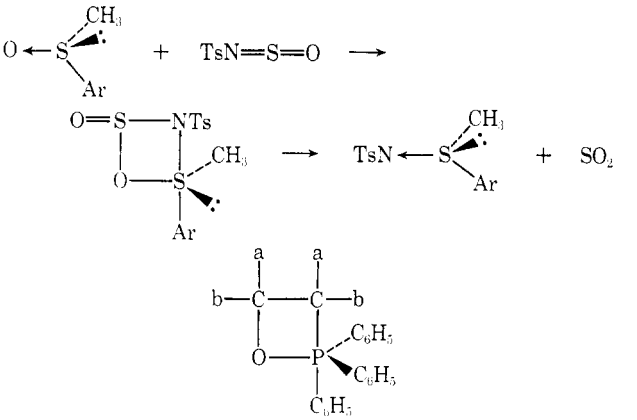
with sulfur diimide VII to produce sulfimide (−)-(*S*)-II with inversion of configuration at sulfur is second order in sulfur diimide. It is reasonable to presume that the oxygen leaving group is accepted by the diimide before the oxygen–sulfur bond is broken. Conceivably, oxygen could be removed from one axial position of a trigonal-bipyramid intermediate (IX) or transition state while the second molecule of diimide occupies the opposite axial position and donates an imide group to sulfur. Such a scheme represents the aa mechanism of Table III. Adaption of this scheme to a square bipyramid intermediate or transition state provides the 12t mechanism of Table IV. The products of such mechanisms are X and XI and are expected both to be of high energy. Structure X is a nitrogen analog of sulfur trioxide, and XI a nitrogen analog of sulfur monoxide.[42] The latter substance XI would be expected to react indiscriminately with both the former (as a pyridine complex of X) as a reducing agent, and with sulfoxide or sulfimide as an oxidizing agent.

The development of the full oxidation–reduction potential of the pair of compounds X and XI can be avoided if the leaving oxygen and entering nitrogen are part of the same ring system in a multiple ligand exchange reaction at sulfur. This mechanistic scheme does not require oxidation and reduction to occur in reverse directions during decomposition of pentacoordinate sulfur (electron pair as a ligand) on the one



hand, and subsequent reaction of the fragments formed on the other. Schultz and Kresze[12a] noted the similarity in stoichiometry between the reaction of *N*-sulfinyl compound VI with sulfoxides and the Wittig reaction, and postulated tying together the entering and leaving group in the same transition state or intermediate in the former reaction as has been demonstrated in the latter reaction. However, the Wittig reaction occurs with retention of configuration at phosphorus,[6a] and the Schultz–Kresze mechanism would predict a steric course of retention on the same ground.[8a] Such reaction paths could resemble the ae or ea mechanisms of Table III, or the 12c mechanism of Table IV. The aa mechanism of Table III in which the oxygen leaving group and nitrogen nucleophile are part of the same ring system and yet occupy the two axial positions of a trigonal-bipyramid intermediate is incompatible with the results. Such a geometry

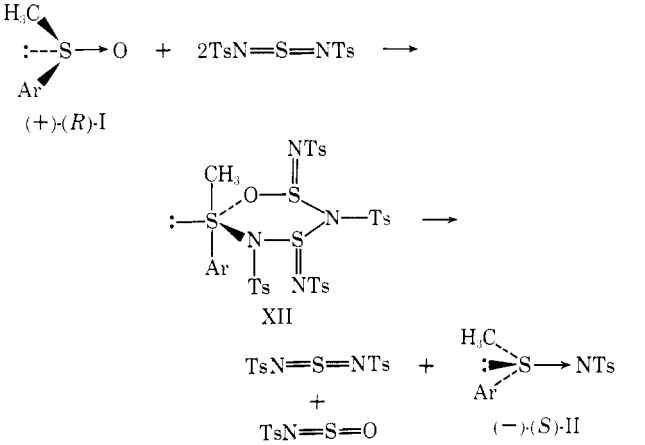
(42) P. W. Schenk and R. Steudel, *Angew. Chem., Int. Ed. Engl.*, 4, 402 (1965).



Wittig intermediate

requires a linear arrangement of the oxygen, sulfur, and nitrogen atoms. Only a ring of 10–12 atoms would be large enough to accommodate such an arrangement. Such a ring would require the reaction to be fifth or sixth order in sulfur diimide VII, rather than the observed second order. For similar reasons, the 12t mechanism of Table IV is ruled out. The ring system required to accommodate a 150° N–S–O bond angle is certainly much larger than the six-membered ring generated from one sulfoxide molecule and two sulfur diimide molecules (see below).

The simplest mechanism most consistent with the observed inversion of configuration and the termolecular character of the reaction involves the ee scheme of Table III. Intermediate or transition state XII is a trigonal bipyramid which includes both the leaving and entering groups in the same six-membered ring distributed in an ee position. Formation and decomposition of XII involve the same minimum movement of nuclei. Since one ligand is exchanged for another, XII is formed in one stereochemical sense and decomposed in another. In the overall reaction, sulfur is inverted since the electron pair is brought past the methyl and aryl groups.[8a] The unshared electron pair on sulfur is placed in an equatorial position in XII since the orbital possesses the most s character, and allows the electron pair to be closer to the nuclear charges. Formally, inversion is observed in ee mechanisms irrespective of which of the other three substituents occupy the remaining equatorial position (see Figure 8).



Some conclusions concerning possible intermediates formed prior to XII are possible. The following

scheme, in which intermediate XIII precedes formation of XII, is consistent with the kinetic results. Thus, the apparent third-order rate constant (eq 2) for the

$$k^3 = -\frac{I}{[I][VII]^2}\frac{d[I]}{dt} = \frac{k_1k_2}{k_{-1} + k_2[VII]} \quad (2)$$

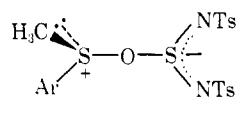
mechanism drawn will be insensitive to changes in $[VII]_0$ as required by the results, provided $k_{-1} \gg k_2 \cdot [VII]$. The validity of this condition is supported by the absence of detectable concentrations of intermediates when the reaction was followed by nmr.

$$I + VII \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} XIII$$

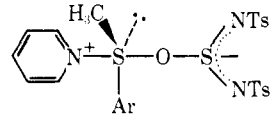
$$XIII + VII \xrightarrow{k_2} XII$$

$$XII \xrightarrow{fast} products$$

We postulate that an equilibrium is established rapidly between starting materials (that are favored) and the first formed intermediate, possibly a zwitterion of structure XIII.[43] The relative magnitudes of the three rate constants would then be $k_{-1} > k_1[VII]_0 > k_2[VII]_0$ for the range of concentrations employed in our study.



XIII



XIV

Pyridine plays some role in the high stereospecificity of the conversion of sulfoxide I to sulfimide VII. Dilution of the pyridine with dichloromethane lowers the optical purity of the product. Pyridine may solvate or bond with the positive sulfur of XIII to form XIV. An additional molecule of VII may then react with the negative end of XIV while pyridine holds configuration at sulfur.

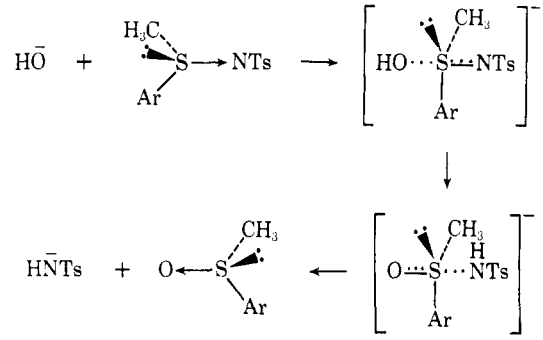
The only unattractive feature of the ee mechanism formulated above is the fact that the less electronegative groups, aryl and methyl, are forced into the axial positions, while the electronegative groups occupy the equatorial positions of XII.[44]

Tables III and IV outline further mechanistic possibilities that provide for inversion of configuration, and yet provide bond angles between the entering and leaving group that accommodate a six-membered ring. These mechanisms all involve pyramidal reorganization stages. Those that have trigonal bipyramids as intermediates (ea → ee and ee → ea of Table III) both go through ee structures. The only mechanism available that goes through a square pyramid as intermediate that gives inversion but does not involve a 12t state is the 1p → 2p mechanism of Table IV. The only negative feature of this mechanism is that no sulfur compounds are known that involve square-pyramidal structures.

(43) A protonated analog of XIII has been postulated as an intermediate in the Pfitzner–Moffatt oxidation of alcohols with dimethyl sulfoxide and *N,N'*-dicyclohexylcarbodiimide by A. F. Cooke and J. G. Moffatt, *J. Amer. Chem. Soc.*, **90**, 740 (1968) (see references cited here as well).

(44) (a) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966); (b) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1962); (c) N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *J. Amer. Chem. Soc.*, **91**, 5749 (1969).

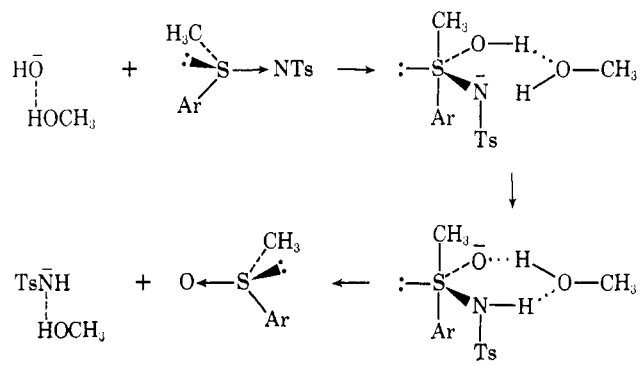
Mechanism of Base-Catalyzed Conversion of Sulfimide II to Sulfoxide I. The reaction of sulfimide (−)-(*S*)-II to sulfoxide (+)-(*R*)-I proceeds with high inversion in methanol only in the presence of a high concentration of potassium hydroxide, and has the aspect of a nucleophilic substitution. The aa mechanism of Table III places hydroxyl and tosylimide groups axial in a trigonal bipyramid, between which are distributed a negative charge. A proton transfer *via* medium provides a second intermediate which decomposes to give product.



aa mechanism

A disadvantage of this mechanism is that both axial groups, oxygen and nitrogen, carry considerable negative charge. This feature is expected to make them much less electronegative than the other three ligands, and therefore of higher energy when in axial positions.[45]

The ee mechanism of Table III provides a more attractive route. This scheme not only places the less electronegative groups in equatorial positions, but also provides an intramolecular route for the proton transfer needed for the substitution.



ee mechanism

The 12t mechanism of Table IV and the more elaborate pyramidal reorganization inversion mechanisms of Tables III and IV are less attractive possibilities.

Stereochemical Aspects of the Oxidation, Imidation, and Deimidation Mechanisms. The conversions of sulfoxide (+)-(*R*)-I and (−)-(*S*)-II to sulfoximide (−)-(*R*)-III have the aspect of electrophilic substitutions on sulfur, in which the tetrahedral structure of sulfur is undisturbed. An equivalent statement is that the electron pairs of the starting materials act as nucleophiles in displacements on oxygen or nitrogen species. These substitution reactions on sulfur are nonassociative, and are expected to proceed with retention, as is observed. The deimidation of sulfoximide (−)-(*R*)-IV

(45) (a) D. S. Frank and D. A. Usher, *ibid.*, **89**, 6360 (1967); (b) R. Kluger, F. Covitz, E. Dennis, L. D. Williams, and F. H. Westheimer, *ibid.*, **91**, 6066 (1969); (c) F. A. Cotton and P. F. Stokley, *ibid.*, **92**, 294 (1970).

to sulfoxide (+)-(*R*)-I probably involves electrophilic attack of NO^+ on S → NH to give S^+–NHNO, which decomposes to S–:, H^+, and N_2O. In such a scheme, the hydridization at sulfur is left undisturbed.[46]

Experimental Section

General. The experimentally determined melting points are reported uncorrected in degrees Celsius; corrected values would be 1% higher. Nuclear magnetic resonance spectra were obtained with ~20% solutions in deuteriochloroform–1% tetramethylsilane. Optical rotatory dispersion spectra were obtained in absolute ethanol on a Cary 60 spectropolarimeter. Optical rotations were measured at 25° with a Perkin-Elmer 141 polarimeter and jacketed cells. Ultraviolet spectra of absolute ethanol solutions were recorded with a Cary 14M spectrophotometer, and infrared spectra were obtained using a Beckman IR-5 spectrophotometer.

Optically pure (+)-(*R*)-methyl *p*-tolyl sulfoxide ((+)-I) (recrystallized from *n*-hexane–acetone or *n*-pentane–ether) was found to have mp 74.5–75.5°: $[\alpha]^{25}D$ +145.5° (*c* 0.795, acetone); $[\alpha]^{25}_{546}$ +180.5° (*c* 0.795, acetone); $[\alpha]^{25}D$ +168.4° (*c* 0.675, pyridine); $[\alpha]^{25}_{546}$ +208.3 (*c* 0.675, pyridine). Analytically and optically pure (−)-(*S*)-*N*-(*p*-tosyl)methyl-*p*-tolylsulfimide ((−)-II) (recrystallized from *n*-hexane–acetone) had mp 124–125°: $[\alpha]^{25}D$ −269° (*c* 1.36, acetone); $[\alpha]^{25}_{546}$ −326° (*c* 1.36, acetone); $[\alpha]^{25}D$ −260.9° (*c* 1.25, pyridine); $[\alpha]^{25}_{546}$ −315.2° (*c* 1.25, pyridine).

Preparation of *N*-Sulfinyl-*p*-toluenesulfonamide (VI). Dry benzene (100 ml), 85.5 g (0.5 mol) of *p*-toluenesulfonamide (mp 137.5–138.0°) and thionyl chloride, 178.5 g (1.5 mol) (Matheson, freshly distilled), were stirred and refluxed under dry nitrogen for 62 hr to give a homogeneous yellow solution. Excess thionyl chloride and benzene were removed by distillation. To remove the last traces of thionyl chloride, 150 ml of benzene was added and distilled, and this treatment was repeated once. The residual oil was treated with ether–pentane and cooled to −20° to achieve crystallization. The pale yellow crystals (which partially melted at room temperature) were recrystallized at −20° from benzene–cyclohexane. The yield was 24.0 g (22% yield) of pale yellow crystals, mp 49.5–51.0° (sealed, nitrogen-filled capillary) (lit. mp 52–53°[12b]). The product was further characterized by ir and nmr. *Anal.* Calcd for $C_7H_7NO_3S_2$: C, 38.70; H, 3.25. Found: C, 38.91; H, 3.06.

Preparation of *N*,*N*′-Bis(*p*-toluenesulfonyl)sulfur Diimide (VII). Thionyl chloride (89.3 g, 0.75 mol) (Matheson, not purified) was added to 50 ml of dry benzene and 42.9 g (0.25 mol) of *p*-toluenesulfonamide (mp 136.5–137.0°) over a 45-min period with stirring under dry nitrogen. This mixture was heated under reflux for 67 hr. The resulting yellow homogeneous solution was distilled to remove excess thionyl chloride and benzene. The residue, an orange oil, solidified on cooling. This product was recrystallized from benzene–cyclohexane in a drybox and gave 23.5 g of bright yellow diimide, mp 139–141° (sealed, nitrogen-filled capillary). A second crop was collected, 7.31 g, mp 136–140°. The overall yield was 66%. Since the literature melting point values for diimide were lower (120 and 119–120°),[12c,28] the product was further characterized by nmr and ir, and the adduct of the diimide and 1,3-butadiene was prepared as a derivative, mp 146–150° dec (lit. 151° dec and 175–176°).[12c,28] The diimide was alternatively prepared by the disproportionation reaction[12c] of *N*-sulfinyl-*p*-toluenesulfonamide. A solution of *N*-sulfinyl-*p*-toluenesulfonamide in dry benzene–cyclohexane at room temperature was heated with a few drops of pyridine. Within 5 min bright yellow crystals of the diimide began to form. After 0.5 hr the diimide was filtered and washed with benzene–cyclohexane in a drybox. *Anal.* Calcd for $C_{14}H_{14}N_2O_4S_3$: C, 45.39; H, 3.81. Found: C, 45.89; H, 3.93.

Preparation of (−)-(*S*)-*N*-(*p*-Tosyl)methyl-*p*-tolylsulfimide (II). Method A.[47] Phosphorus pentoxide (2.84 g, 20.0 mmol) and a solution of 6.06 g (60.0 mmol) of triethylamine (distilled from BaO and dried over KOH) in 12 ml of dry methylene dichloride was stirred under dry nitrogen until the solid had completely dissolved. The solution was then cooled to 0°. A solution of 0.616 g (4.0 mmol) of (+)-methyl *p*-tolyl sulfoxide, $[\alpha]^{25}_{546}$ +178.5 (*c* 1.61, acetone) and 1.368 g (8.0 mmol) of *p*-toluenesulfonamide (mp 136.5–137.0°) in 38 ml of dry dichloromethane was then added over a period of 20 min with stirring and cooling (ice bath). The stirring (0°) was continued for 10 hr and 40 min. With continued stirring *ca.* 15 g of ice was added along with 10 ml of water and sufficient 12 *N* sodium hydroxide to make the aqueous layer basic (pH > 12). The mixture was then extracted with two, 50-ml portions of dichloromethane. The combined organic layers were washed with dilute sulfuric acid until the aqueous layer became acidic (pH < 2). The organic layer was washed with water, dried, and filtered. Evaporation under vacuum left a yellow oil which soon solidified, 0.975 g. Chromatography of the oil on 100 g of silica gel with acetonitrile as eluent separated the sulfimide, 0.809 g (66%), $[\alpha]^{25}_{546}$ −223° (*c* 1.683, acetone), and the starting sulfoxide, 0.1005 g (16%), $[\alpha]^{25}_{546}$ +133° (*c* 0.883, acetone). The yield of sulfimide was 70%. The recovered sulfoxide was 74% optically pure. Controls indicated the sulfimide to be optically stable under the reaction conditions. Sulfimide prepared in this manner could be crystallized to optical purity, *i.e.*, $[\alpha]^{25}_{546}$ −326° (*c* 1.36, acetone), mp 125.0–125.5°, and was identical in its ir spectrum with that prepared by method B. *Anal.* Calcd for $C_{15}H_{17}NO_2S_2$: C, 58.60; H, 5.57; S, 20.86. Found: C, 58.66, H, 5.74; S, 21.04.

Preparation of (−)-(*S*)-*N*-(*p*-Tosyl)methyl-*p*-tolylsulfimide (II). Method B. A solution of 1.735 g (4.68 mmol) of *N*,*N*′-bis-(*p*-tosyl)sulfur diimide in 7 ml of pyridine (dried over molecular sieves and potassium hydroxide) was prepared in a drybox. The solution was added dropwise over a period of 5 min to 0.616 g (4.0 mmol) of (+)-methyl *p*-tolyl sulfoxide, $[\alpha]^{25}_{546}$ +178.5° (*c* 1.61, acetone), in 3 ml of pyridine under nitrogen. This solution was stirred at 0° for 3 hr and 25 min. The reaction was quenched by the addition of ice, 60 ml of water, and 40 ml of dichloromethane. Sulfuric acid (12 *N*) was then added with shaking until the aqueous layer was acidic (pH < 2). The aqueous layer was extracted with dichloromethane. The organic layer was washed with 12 *N* sodium hydroxide until the aqueous layer was basic, was washed with water, and was dried and filtered. The solvent was evaporated under reduced pressure (rotatory evaporator) leaving a solid yellow residue of 1.343 g which was chromatographed on 100 g of silica gel with elution by acetonitrile. A single fraction was collected, 1.165 g (96%), which proved to be the desired sulfimide, $[\alpha]^{25}_{546}$ −313.5° (*c* 1.682, acetone). Repeated recrystallization from benzene and from *n*-hexane–acetone gave $[\alpha]^{25}_{546}$ −326° (*c* 1.36, acetone). The reaction thus took place with 98% stereospecificity. When the reaction was carried out at 25° for 18.5 hr, the product was only 72% optically pure. When the reaction was conducted in dichloromethane, 7 ml, in the presence of pyridine (1.41 mmol), sulfoxide (2.0 mmol), and diimide (1.41 mmol) at 25° for 40 min, the product was only 44% optically pure.

Preparation of (−)-(*S*)-*N*-(*p*-Tosyl)methyl-*p*-tolylsulfimide (II). Method C. A solution of 2.03 g (9.36 mmol) of *N*-sulfinyl-*p*-toluenesulfonamide in 10 ml of pyridine (dried over molecular sieves and potassium hydroxide) was added dropwise over a period of 5 min to a nitrogen-swept flask containing a magnetically stirred solution of 0.616 g (4.0 mmol) of (+)-methyl *p*-tolyl sulfoxide, $[\alpha]^{25}_{546}$ +178.5° (*c* 1.61, acetone) or 99% optically pure, cooled to 0°. The resulting solution was stirred at 0° for 0.5 hr. A 40-ml volume of dichloromethane and 40 ml of water were added. The organic layer was washed with 12 *N* sulfuric acid until the aqueous layer was acidic (pH < 2), with 12 *N* sodium hydroxide until the washings were basic (pH > 12), and then was washed with water, dried, and filtered. The solvent was removed under reduced pressure below 50°. The residue, 0.929 g, was chromatographed on 100 g of silica gel with elution by acetonitrile. Three products were collected and identified by ir: (a) methyl *p*-tolyl sulfide, 0.017 g (3.1%); (b) (+)-methyl *p*-tolyl sulfoxide, 0.222 g (36%) $[\alpha]^{25}_{546}$ +179.3° (*c* 1.084, acetone); and (c) the desired sulfimide, 0.628 g (51.2%), $[\alpha]^{25}_{546}$ −323.4° (*c* 1.646, acetone), >99% optically pure. Thus the reaction was highly stereospecific.

Hydrolysis of (−)-(*S*)-*N*-(*p*-Tosyl)methyl-*p*-tolylsulfimide (II) to (+)-Methyl *p*-Tolyl Sulfoxide (I). Method A. A 0.307-g portion (1.0 mmol) of chromatographed and recrystallized (−)-(*S*)-*N*-(*p*-tosyl)methyl-*p*-tolylsulfimide which was 95% optically pure, $[\alpha]^{25}_{546}$ −310° (*c* 1.61, acetone) was added to 135 ml of methanol saturated with potassium hydroxide. The resulting mixture was swirled in a stoppered flask for 2 min at room temperature to dissolve the sulfimide and was then cooled to 15–17° for 24 hr. The methanol solution was poured into a mixture of 35 g of acetic acid (glacial), 125 ml of methanol, 250 ml of dichloromethane, and 500 ml of water. This mixture was shaken vigorously. The aqueous layer was removed and extracted with dichloromethane. Evaporation of the combined dichloromethane extracts left 0.197 g of a light yellow solid which was chromatographed on silica gel. The product was eluted with acetonitrile. The desired sulfoxide,

(46) The authors wish to thank Professors F. H. Westheimer and K. Mislow for valuable criticisms during the development of this work.

(47) Modified procedure based on ref 13.

0.145 g (94%), was identified by ir, $[\alpha]^{25}_{546}$ +167° (*c* 0.806, acetone), 92.5% optically pure. The hydrolysis took place with greater than 96% stereospecificity.

Hydrolysis of (−)-(*S*)-*N*-(*p*-Tosyl)methyl-*p*-tolylsulfimide (II) to (+)-Methyl *p*-Tolyl Sulfoxide (I). Method B. The sulfimide, 0.65 g, $[\alpha]^{25}_{546}$ −321° (*c* 0.900, acetone), was stirred with 10 ml of concentrated sulfuric acid for 2 min at room temperature. The clear solution was poured into 30 g of sodium carbonate (anhydrous) dissolved in 250 ml of water. The resulting clear solution (pH ~8) was extracted with three 50-ml portions of chloroform. The extracts were dried, filtered, and evaporated under reduced pressure to yield an oil which was identified by its ir spectrum as pure methyl *p*-tolyl sulfoxide, $[\alpha]^{25}_{546}$ +54° and $[\alpha]^{25}_{D}$ +45° (*c* 1.095, acetone). This rotation corresponds to an optical purity of 30%. No attempt was made to improve the stereospecificity.

Oxidation of (−)-(*S*)-*N*-(*p*-Tosyl)methyl-*p*-tolylsulfimide (II) with *m*-Chloroperbenzoic Acid to (−)-(*R*)-*N*-(*p*-Tosyl)methyl-*p*-tolylsulfoximide (III). A 0.862-g portion (5.0 mmol) of *m*-chloroperbenzoic acid, 0.424 g (4.0 mmol) of anhydrous sodium carbonate, and 0.307 g (1.0 mmol) of (−)-*N*-(*p*-tosyl)methyl-*p*-tolylsulfimide, $[\alpha]^{25}_{546}$ −320° (*c* 0.682, acetone), 98% optically pure, were added to 8 ml of acetone. The heterogenous mixture was stirred for 24 hr at room temperature. A 2.0-g portion of sodium thiosulfate and 25 ml of water was then added. After stirring for 10 min, a slight excess of 6 *N* sulfuric acid was added. After another 10 min of stirring, the mixture was made alkaline with 6 *N* sodium hydroxide (pH >12) and extracted with two 50-ml portions of dichloromethane. The combined extracts were washed with water and dried over magnesium sulfate. An off-white solid, 0.349 g, was obtained upon evaporation of the solvent. This product was chromatographed on 20 g of silica gel with elution by ether–pentane mixtures. A white solid was eluted, 0.21 g (65%), which proved to be the desired sulfoximide, $[\alpha]^{25}_{546}$ −168.5 (*c* 0.894, acetone), 97.6% optically pure. Recrystallization from dichloromethane–ether gave a white crystalline product: mp 159–160.5; $[\alpha]^{25}_{546}$ −172.5° (*c* 0.798, acetone). The oxidation thus took place with greater than 98% stereospecificity. An nmr spectrum of the product showed the *S*-methyl peak at τ 6.60 (3 H), two *p*-CH_3Ar peaks at 7.55 and 7.61 (6 H), and an aromatic multiplet centered about 2.4 (8 H). *Anal.* Calcd for $C_{15}H_{17}NO_3S_2$: C, 55.70; H, 5.30; S, 19.83. Found: C, 55.44; H, 5.34; S, 19.63.

Preparation of (−)-(*R*)-*N*-(*p*-Tosyl)methyl-*p*-tolylsulfoximide (III) by the Method of Kwart and Kahn.[18] Optically pure (+)-methyl *p*-tolyl sulfoxide, 18 g (0.117 mol), was dissolved in 100 ml of methanol, and 39 g (0.2 mol) of *p*-tosyl azide in 50 ml of methanol was added. Freshly precipitated copper powder (prepared from Zn and $CuSO_4 \cdot 5H_2O$), which had been washed with dilute sulfuric acid, water, and methanol, 12.6 g (0.2 mol), was then added. The mixture was refluxed for 1 hr. An additional 20 g (0.1 mol) of *p*-tosyl azide and 12.6 g of copper powder was then added. Another 20 g (0.1 mol) of *p*-tosyl azide was added after 2 hr of reflux. The reactants were refluxed for an additional 2.5 hr. The sulfoximide crystallized from the filtered, hot methanol solution in which it is only slightly soluble. The product was continuously extracted with acetone overnight. Upon evaporation a total of 26.5 g of nonfractionally crystallized sulfoximide was obtained (70%), $[\alpha]^{25}_{546}$ −170°, $[\alpha]^{25}_{D}$ −140° (*c* 1.165, acetone). The sulfoximide was recrystallized from acetone: mp 160–162°; $[\alpha]^{25}_{546}$ −172°; $[\alpha]^{25}_{D}$ −142° (*c* 1.060, acetone). The reaction is thus 99% stereospecific.

Hydrolysis of (−)-(*R*)-*N*-(*p*-Tosyl)methyl-*p*-tolylsulfoximide (III) to (−)-(*R*)-Methyl-*p*-tolylsulfoximide (IV). Optically pure (−)-(*R*)-*N*-(*p*-tosyl)methyl-*p*-tolylsulfoximide, 3.70 g (0.015 mol), was stirred with 20 ml of concentrated sulfuric acid for 15 min at room temperature. The resulting clear colorless solution was poured into 200 ml of water and made basic by addition of solid sodium carbonate (pH ~9). The mixture was extracted with three 100-ml portions of chloroform. The combined extracts were dried, filtered, and evaporated under reduced pressure. The light yellow oil obtained crystallized on cooling and weighed 1.92 g (99% yield): mp of 53–59°; $[\alpha]^{25}_{546}$ −39.7°; $[\alpha]^{25}_{D}$ −33.1° (*c* 1.105, acetone). The product was then recrystallized from acetone–ether: mp 56–60°, $[\alpha]^{25}_{546}$ −39.9°, $[\alpha]^{25}_{D}$ −33.4° (*c* 2.275, acetone). The product (−)-(*R*)-methyl-*p*-tolylsulfoximide is hygroscopic and was sublimed, 50° (0.05 mm), to obtain an analytical sample: mp 59–61°; $[\alpha]^{25}_{546}$ −38.9°, $[\alpha]^{25}_{D}$ −32.4° (*c* 0.885, acetone). The hydrolysis was 99% stereospecific. *Anal.* Calcd for $C_8H_{11}NOS$: C, 56.77; H, 6.55; S, 18.95. Found: C, 56.65; H, 6.31; S, 18.85.

Conversion of (−)-(*R*)-Methyl-*p*-tolylsulfoximide (IV) to (−)-(*R*)-*N*-(*p*-Tolylsulfoximide (III). The compound, (−)-methyl-*p*-tolylsulfoximide, 0.17 g (1 mmol) ($[\alpha]^{25}_{546}$ −39.9°), was refluxed with 0.05 g of sodium in 25 ml of dry benzene for 6 hr. The unreacted sodium was removed by filtration and 0.19 g (1 mmol) of *p*-tosyl chloride was added to the filtrate. The resulting solution was refluxed for 1 hr. The benzene solution was then washed with water, dried over magnesium sulfate, filtered, and evaporated leaving 0.20 g (62%) of solid product. The crude product was chromatographed on silica gel. After development of the column with benzene, the product was eluted with 1:1 benzene–ether, $[\alpha]^{25}_{546}$ −166.3°, $[\alpha]^{25}_{D}$ −137.3° (*c* 0.875, acetone). The *N*-tosylsulfoximide obtained was 97% optically pure and was identical with authentic material by nmr and ir spectra.

Conversion of (−)-(*R*)-Methyl-*p*-tolylsulfoximide (IV) to (−)-(*R*)-*N*-(*p*-Tosyl)methyl-*p*-tolylsulfoximide (III). The compound, (−)-(*R*)-methyl-*p*-tolylsulfoximide, 0.5 g (0.003 mol), $[\alpha]^{25}_{546}$ −39.7° (*c* 2.275, acetone), was dissolved in 20 ml of dry pyridine. Tosyl chloride, 0.96 g (0.005 mol), was then added to the above stirred solution. The stirring was continued for 0.5 hr at room temperature, and then the light yellow reaction mixture was poured into 150 ml of water. The precipitated product was filtered, washed with water, and oven-dried to give 0.82 g (86% yield) of dry *N*-tosylsulfoximide: mp 159.5–160.5°; $[\alpha]^{25}_{546}$ −171.3°, $[\alpha]^{25}_{D}$ −141.6° (*c* 0.885, acetone). The product, crystallized from acetone–methanol, weighed 0.60 g: mp 159.5–160.5°; $[\alpha]^{25}_{546}$ −172.5°; $[\alpha]^{25}_{D}$ −142.7° (*c* 0.825, acetone). The reaction was 99% stereospecific based on the highest observed rotation for (−)-(*R*)-*N*-(*p*-tosyl)methyl-*p*-tolylsulfoximide. This result also confirms the optical purity of (−)-(*R*)-methyl-*p*-tolylsulfoximide.

Preparation of (+)-(R_s)-*N*-(3-*endo*-Bromo-2-oxo-9-bornanesulfonyl)methyl-*p*-tolylsulfoximide ((+)-VIII). A solution of (−)-(*R*)-methyl-*p*-tolylsulfoximide, 0.2 g (0.0012 mol), $[\alpha]^{25}_{546}$ −39.9 (*c* 2.275, acetone) and 0.4 g (0.0012 mol) of optically pure (+)-3-*endo*-bromo-2-oxo-9-bornanesulfonyl chloride,[48] $[\alpha]^{25}_{D}$ +128° (*c* 0.605, $CHCl_3$) in 5 ml of dry pyridine was stirred at room temperature for 18 hr. The reaction mixture was poured into 50 ml of water and adjusted to pH 7 with 10% HCl. The colorless solid product was filtered, washed with water, and dried to give 0.45 g (83% yield) of sulfoximide VIII which was recrystallized from ether to a constant melting point: mp 155–156°; $[\alpha]^{25}_{D}$ +4.32°; $[\alpha]^{25}_{546}$ +8.92° (*c* 0.740, acetone). *Anal.* Calcd for $C_{18}H_{24}BrNO_4S_2$: C, 46.75; H, 5.23; S, 13.89. Found: C, 46.81; H, 5.32; S, 13.88.

Conversion of (−)-(*R*)-Methyl-*p*-tolylsulfoximide (IV) to (+)-(*R*)-Methyl *p*-Tolyl Sulfoxide (I). The sulfoximide, 1.6 g (0.01 mol), $[\alpha]^{25}_{546}$ −39.1 (*c* 1.2, acetone) (98% optical purity), was dissolved in 25 ml of nitromethane (dried over molecular sieves 4A). A 1.75-g portion (0.01 mol) of solid nitrosyl hexafluorophosphate was added to the stirred solution. An exothermic reaction ensued which evolved gas. The reactants were stirred for an additional 5 min. The nitromethane solution was poured into dilute sodium bicarbonate which was then extracted with chloroform. The chloroform extracts were dried, filtered, and evaporated (rotatory evaporator). The residual oil crystallized. The crude product was then chromatographed on silica gel. The product was eluted with 1:1 ether–benzene: 0.25 g (20%); mp 71–75°; $[\alpha]^{25}_{546}$ +175°; $[\alpha]^{25}_{D}$ +134°. Since the starting sulfoximide was 98% optically pure and the product is 97% optically pure, the reaction occurred with 99% retention of configuration. The ir spectrum of this material was identical with that of known (+)-methyl *p*-tolyl sulfoxide. Subsequent preparations indicated that the greater yields could be obtained (75%) if the reaction was conducted at 0° and if excess $NO^+PF_6^-$ was used.

Preparation of (−)-(*R*)-*N*-Chloromethyl-*p*-tolylsulfoximide (V). The compound, (−)-(*R*)-methyl-*p*-tolylsulfoximide ($[\alpha]^{25}_{546}$ −39°, 98% optically pure), 0.85 g (0.005 mol), was dissolved in 10 ml of water. This solution was added to a stirred solution of 50 ml of cold sodium hypochlorite. The reactants were stirred for 5 min before the oily product was extracted into chloroform. The solution was dried, filtered, and evaporated to yield 0.6 g (60%) of a viscous yellow oil, which crystallized on standing: mp 66–68°; $[\alpha]^{25}_{546}$ −266°; $[\alpha]^{25}_{D}$ −221° (*c* 1.35, acetone). This product was recrystallized from ether–*n*-hexane: mp 67–68°; $[\alpha]^{25}_{546}$ −264°, $[\alpha]^{25}_{D}$ −222° (*c* 0.63, acetone). Recrystallization from the same solvent mixture gave mp 67–68°; $[\alpha]^{25}_{546}$ −264°; $[\alpha]^{25}_{D}$ −220°

(48) (a) The sulfonyl chloride was generously provided by Dr. Edward C. Olson of The Upjohn Company; (b) F. S. Kipping and W. J. Pope, *J. Chem. Soc.*, 63, 576 (1893).

Table V. Polarimetric Data for a Typical Kinetic Run

Time, min	Rotation, deg
2	+0.249
3	+0.177
4	+0.108
5	+0.048
6	−0.013
7	−0.070
8	−0.123
9	−0.173
10	−0.221
11	−0.270
12	−0.308
13	−0.346
14	−0.384
15	−0.420
16	−0.455
17	−0.486
18	−0.517
19	−0.546
20	−0.574
21	−0.600
22	−0.625

(*c* 1.01, acetone). An nmr spectrum of the *N*-chlorosulfoximide in $CDCl_3$, showed the $-S-CH_3$ group at τ 6.76. *Anal.* Calcd for $C_8H_{10}ClNOS$: C, 47.17; H, 4.95; Cl, 17.41. Found: C, 47.25; H, 4.97; Cl, 17.49.

Melting Point–Composition Diagrams. Optically pure (+)-*N*-(*p*-tosyl)methyl-*p*-tolylsulfimide, $[\alpha]^{25}_{546}$ +326° (*c* 0.785, acetone), mp 125.3–125.6°, was obtained by reaction of (−)-(*S*)-methyl *p*-tolyl sulfoxide (from reaction of (+)-*l*-menthyl *p*-toluenesulfinate with methylmagnesium iodide[9b,49]) with *N*-sulfinyl-*p*-toluenesulfonamide in pyridine at 0°. Physical properties of the other compounds used for melting point determinations were: (−)-*N*-(*p*-tosyl)methyl-*p*-tolylsulfimide, (−)-II, $[\alpha]^{25}_{546}$ −326° (*c* 1.36, acetone), mp 124–125°; (−)-*N*-(*p*-tosyl)methyl-*p*-tolylsulfoximide, (−)-III (recrystallized to optical purity from ethyl acetate), $[\alpha]^{25}_{546}$ −172° (*c* 0.665, acetone), mp 159.5–160.5°; racemic sulfimide II, mp 123.5–124.5° (recrystallized from *n*-hexane–acetone); racemic sulfoximide III, mp 145–146° (from ethyl acetate). Samples were weighed on a Cahn electrobalance (precision of about 0.01 mg), were ground together in a small agate mortar, and were dissolved in dichloromethane. The solvent was evaporated under a stream of dry air, and the residue was ground again. Melting points were determined using the capillary method (silicone oil bath, capillary melting point apparatus made by Arthur H. Thomas Co., Philadelphia) and are accurate to within about ±0.5°. The bath temperature was raised at a constant rate of 1–2°/min. The initial thawing temperature and the final melting temperature were noted. Duplicate mixture melting point determinations were made for each sample. The resulting phase diagrams are shown in Figures 4 and 5 for the system (−)-II and (−)-III and for (+)-II and (−)-III, respectively.

Kinetics. Kinetic runs were made with (+)-(*R*)-I of maximum rotation in dry pyridine (distilled from barium oxide and stored over molecular sieves 4A) at 25°. The other reagent was either sulfur diimide VII or the *N*-sulfinyl compound VI which in pyridine is quickly converted to VII. The conversion of (+)-(*R*)-I to (−)-(*S*)-II was followed polarimetrically. The solutions were prepared and sealed in a jacketed polarimeter tube (1.00 cm) in a drybox and transferred to a Perkin-Elmer Model 141 polarimeter fitted with a sodium lamp. The yellow color of the solutions required that rotations be taken through a short sample path length (1.00 cm) at the sodium D line. Zero time was the time of mixing of sulfoxide and reagent solutions both previously thermally equilibrated to 25°. The initial rotation calculated from the resulting concentration of (+)-(*R*)-I in the reaction mixture was in agreement with extrapolation of the first few observed rotations to zero time. The magnitude of rotations observed during the reaction for the most concentrated runs varied from +0.35° to −1.14°. Rotations were recorded until they no longer changed appreciably. Final rotations observed were 90–94% of those calculated from the specific rotation of (−)-(*S*)-II of maximum rotation in pyridine ($[\alpha]^{25}D$ −260.9°) under the assumption of 100% conversion of (+)-(*R*)-I to (−)-(*S*)-II.

The concentration of sulfimide product (II) was calculated from the observed rotation α at any time by means of eq 3

$$[\mathrm{II}] = \frac{1000\alpha - l[\alpha]_{\mathrm{I}}M_{\mathrm{I}}[\mathrm{I}]_0}{l[\alpha]_{\mathrm{II}}M_{\mathrm{II}} - l[\alpha]_{\mathrm{I}}M_{\mathrm{I}}} \quad (3)$$

where l is the length of the polarimeter cell, $[\alpha]_{\mathrm{I}}$ and $[\alpha]_{\mathrm{II}}$ are the specific rotations of sulfoxide I and product II, and M_{I} and M_{II} are their respective molecular weights.

Second- and third-order rate constants, respectively, were obtained from the slopes of the least-squares straight lines for the functions F_2 and F_3 *vs.* time. The results of the calculations are

$$F_2 = \frac{1}{[\mathrm{VII}]_0 - {}^1/_2[\mathrm{I}]_0} \ln \left\{ \frac{[\mathrm{I}]_0 - [\mathrm{II}]}{[\mathrm{VII}]_0 - {}^1/_2[\mathrm{II}]} \right\}$$

$$F_3 = -\frac{1}{[\mathrm{VII}]_0 - {}^1/_2[\mathrm{I}]_0} \left[\frac{1}{[\mathrm{VII}]_0 - {}^1/_2[\mathrm{II}]} + \frac{1}{[\mathrm{VII}]_0 - {}^1/_2[\mathrm{I}]_0} \ln \left\{ \frac{[\mathrm{I}]_0 - [\mathrm{II}]}{[\mathrm{VII}]_0 - {}^1/_2[\mathrm{II}]} \right\} \right]$$

reported in Table I. The data of Table V exemplify a typical kinetic run (run 1 of Table I).

Optical Purity of *N*-(*p*-Tosyl)methyl-*p*-tolylsulfimide ((−)-II) Obtained from Reaction of (+)-Methyl *p*-Tolyl Sulfoxide ((+)-I) with *N*,*N*′-Bis(*p*-toluenesulfonyl)sulfur Diimide (VII) in Pyridine at 25°. A 0.306 *M* solution of (+)-methyl *p*-tolyl sulfoxide (98.1% optically pure) in dry pyridine and a 0.669 *M* solution of sulfur diimide VII in dry pyridine were separately equilibrated to 25°. Equal volumes (10 ml) of each were rapidly mixed. An aliquot was transferred to a 0.1-dm polarimeter cell (run 1). After 13 min (*ca.* 50% reaction) the bulk of the reaction mixture was quenched by addition of 20 ml of cold distilled water. The mixture was extracted with chloroform. The organic phase was washed with 5% HCl saturated with sodium chloride, with 10% NaOH, and finally with saturated sodium chloride solution. The chloroform solution was dried and evaporated under reduced pressure at a temperature below 40° to yield a solid. This material was chromatographed on 50 g of silica gel with elution by ethyl acetate. The recovered sulfoxide was 96.8% optically pure. The fractions containing sulfimide product were contaminated with tosylamide. Chromatography of these fractions on 5 g of silica gel gave pure (−)-sulfimide: $[\alpha]^{25}_{546}$ −307° and $[\alpha]^{25}D$ −253.2° (*c* 0.600, pyridine); 97% optically pure.

Optical Stability of (−)-*N*-(*p*-Tosyl)methyl-*p*-tolylsulfimide (II) with *N*,*N*′-Bis(*p*-toluenesulfonyl)sulfur Diimide (VII). The rotation of a dry pyridine solution, which was 0.0290 *M* in sulfimide (II) and 0.0451 *M* in sulfur diimide (VII), was observed to remain steady (0.222 ± 0.002°) over a period of 3 hr at 25°. After 72 hr the rotation was −0.205°. A similarly constituted solution, which also contained racemic methyl *p*-tolyl sulfoxide, had a constant rotation (−0.171 ± 0.006°) for 24 hr.

(49) M. M. Green, M. Axelrod, and K. Mislow, *J. Amer. Chem. Soc.*, **88**, 861 (1966); P. Bickart, M. Axelrod, J. Jacobus, and K. Mislow, *ibid.*, **89**, 697 (1967).