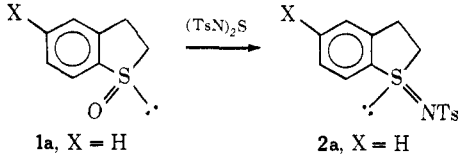
Stereochemistry of Sulfur Compounds. V. Stereochemical Reaction Cycles That Involve Cyclic Sulfoxides, Sulfimides, and Sulfoximides[1]

Frederick G. Yamagishi, Dennis R. Rayner, Evelyn T. Zwicker,[2] and Donald J. Cram*

Contribution from the Department of Chemistry, University of California at Los Angeles, Los Angeles, California 90024. *Received August 12, 1972*

Abstract: A new scheme is reported for the preparation of optically pure sulfoxides, sulfoximides, and sulfimides and is applied to cyclic sulfur compounds otherwise unavailable in optically active form. Racemic 2,3-dihydrobenzo[*b*]thiophene 1-oxide (**1a**) was converted to 2,3-dihydrobenzo[*b*]thiophene-1-imide 1-oxide (**4a**) with hydrazoic acid. Fractional crystallization of its diastereomeric *N*-*d*-10-camphorsulfonyl derivatives gave one optically pure isomer, hydrolysis of which gave (+)-**4a** of maximum rotation. Treatment of (+)-**4a** with nitrosyl hexafluorophosphate gave (−)-**1** of maximum rotation which with either *N*-sulfinyl-*p*-toluenesulfonamide or *N*,*N*′-bis(*p*-toluenesulfonyl)sulfur diimide in pyridine gave (−)-*N*-*p*-toluenesulfonyl-2,3-dihydrobenzo[*b*]thiophene-1-imide, (−)-**2a**. Although attempted base-catalyzed hydrolysis of (−)-**2a** gave only benzo[*b*]thiophene, sulfuric acid catalyzed hydrolysis of (−)-**2a** of maximum rotation gave (−)-**1a** of 26% maximum rotation. Oxidation of (−)-**2a** with potassium permanganate, nitrenation of (−)-**1a** with tosyl azide and copper, or sulfonation of (+)-**4a** with tosyl chloride in pyridine all gave (−)-**3a** of maximum rotation except the nitrenation, which was 77% stereospecific. The stereochemical course of transformation (+)-**4a** → (−)-**3a** is retention of configuration. Similar reactions were carried out with 5-bromo-2,3-dihydrobenzo[*b*]thiophene 1-oxide (**1b**). Analogies and mechanistic considerations strongly imply that the following three reactions in both the a and b series take the same stereochemical course (retention): (+)-**4** → (−)-**1**; (−)-**1** → (−)-**3**; (−)-**2** → (−)-**3**. From the symmetry properties of the five stereochemical reaction cycles implicit in the above transformations, it is concluded that (−)-**1** → (−)-**2** occurs *in pyridine* with *inversion* of configuration in both the a and b series of compounds. Similarities between optical rotatory dispersion curves of **2a**, **2b**, and *N*-*p*-toluenesulfonyl-*S*-methyl-*S*-*p*-tolylsulfimide (**6**) of known absolute configuration provided a basis for making tentative assignments of absolute configuration to all of the cyclic compounds. In benzene *without pyridine*, (+)-**1b** with *N*,*N*-bis(*p*-toluenesulfonyl)sulfur diimide gave (−)-**2b**, the reaction going with 95% *retention* of configuration. Similarly in *benzene without pyridine*, (+)-methyl *p*-tolyl sulfoxide (+)-**5** gave (+)-**6** with 94% *net retention*. Unlike the reaction (+)-**5** → (−)-**6** in pyridine that is second order in the sulfur diimide, (+)-**5** → (+)-**6** in benzene is close to first order in the sulfur diimide. The conversions of sulfoxide to sulfimide in both pyridine and benzene are 50 to 100 times faster in the cyclic compared to the open-chain system. The mechanisms are discussed.

An earlier paper[3a] described a series of stereochemical reaction cycles[3b] that involved interconversions of open-chain sulfoxide, sulfimide, and sulfoximide. Both nucleophilic and electrophilic substitution reactions at chiral sulfur were involved. This paper reports a similar study of the stereochemical course of interconversions of the same classes of compounds based on the 2,3-dihydrobenzo[*b*]thiophene and 5-bromo-2,3-dihydrobenzo[*b*]thiophene ring systems. Of particular interest was the effect of the constraints of the five-membered ring system on the stereochemical course and rate of the conversions of sulfoxides **1** to



1a, X = H
b, X = Br

2a, X = H
b, X = Br

sulfimides **2**. To make the study, a new method of obtaining optically pure sulfoxides and their derivatives had to be developed. An additional point of interest was illustration of the use of stereochemical reaction cycles as an aid to correlations of configurations and determinations of the steric courses of substitution reactions at chiral centers.[3b]

Results

Syntheses. Reduction of 2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide[4a] with lithium aluminum hydride gave 2,3-dihydrobenzo[*b*]thiophene[4b] (75%), which with sodium metaperiodate gave racemic 2,3-dihydrobenzo[*b*]thiophene 1-oxide[5] (**1a**) (100%). This material was converted with hydrazoic acid[6] to 2,3-dihydrobenzo[*b*]thiophene-1-imide 1-oxide (**4a**, 75%). Reaction of **4a** with (+)-*d*-10-camphorsulfonyl chloride in pyridine gave a crystalline mixture of diastereomers, the less soluble of which was crystallized to purity (22% overall).[7] Treatment of this material with con-

(1) This investigation was supported by U. S. Public Health Service Research Grant No. GM 12640-05 from the Department of Health, Education and Welfare.

(2) National Science Foundation Summer Undergraduate Research Participant, 1971.

(3) (a) D. J. Cram, J. Day, D. R. Rayner, D. M. von Schriltz, D. J. Duchamp, and D. C. Garwood, *J. Amer. Chem. Soc.*, **92**, 7369 (1970); (b) D. C. Garwood and D. J. Cram, *ibid.*, **92**, 4575 (1970).

(4) (a) F. G. Bordwell and W. H. McKellin, *J. Amer. Chem. Soc.*, **72**, 1985 (1950); (b) S. F. Birch, *J. Inst. Petrol., London*, **39**, 185 (1953), reported only the preparation and boiling point of this compound.

(5) S. F. Birch, R. A. Dean, and E. V. Whitehead, *J. Inst. Petrol., London*, **40**, 76 (1954).

(6) F. Misiani, T. W. Fair, and L. Reiner, *J. Amer. Chem. Soc.*, **73**, 459 (1951).

(7) Diastereomeric *N*-sulfonylsulfoximides have been previously prepared and separated by crystallization: M. Barash, *Nature (London)*, **187**, 591 (1960). Sulfoximides have been resolved through salt formation with optically active sulfonic acids: R. Fusco and F. Tenconi, *Chim. Ind. (Milan)*, **47**, 61 (1965). Racemic **4a** did not form a crystalline salt with *d*-10-camphorsulfonic acid in our hands.

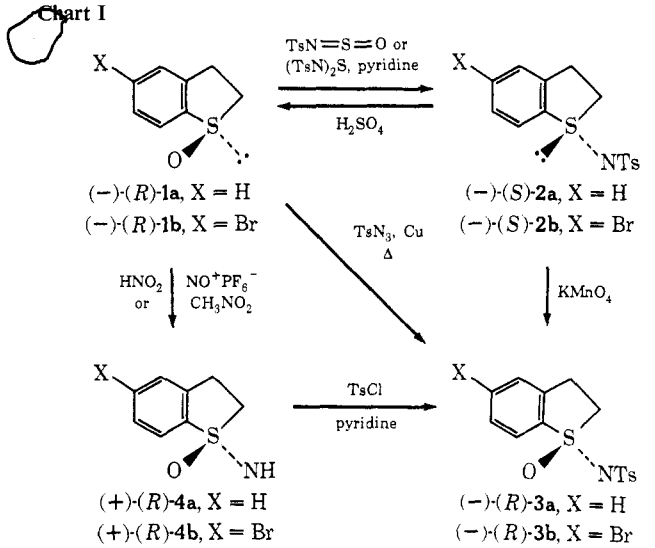
centrated sulfuric acid produced sulfoximide (+)-**4a** (64%). This material was converted to sulfoxide (−)-**1a** with nitrosyl hexafluorophosphate in nitromethane[3a] (91%), which was identical in its infrared and nmr spectrum with those of (±)-**1a** used as the primary starting material for the sequence.

With either *N*-sulfinyl-*p*-toluenesulfonamide[8] or *N*,*N*′-bis(*p*-toluenesulfonyl)sulfur diimide (DIM) in pyridine, sulfoxide (−)-**1a** gave sulfimide (−)-**2a** of essentially maximum rotation in 50 and 78% yields, respectively. Hydrolysis of sulfimide (−)-**2** with concentrated sulfuric acid at 25° gave back sulfoxide (−)-**1a** of 26% optical purity and in 74% yield. All attempts to hydrolyze (−)-**2a** to (−)-**1a** with base gave benzo[*b*]-thiophene essentially quantitatively. Oxidation of sulfimide (−)-**2a** with potassium permanganate in pyridine–water gave 31% sulfoximide (−)-**3a** of essentially maximum rotation. Nitrenation of sulfoxide (−)-**1a** with tosyl azide and copper[9] gave 24% sulfoximide (−)-**3a** of 77% optical purity. Sulfoximide (+)-**4a** was treated with tosyl chloride in pyridine to give (−)-**3a** of maximum rotation in 84% yield.

Bromination[10] of 2,3-dihydrobenzo[*b*]thiophene in acetic acid gave 5-bromo-2,3-dihydrobenzo[*b*]thiophene (97%). The position of bromination resembles that observed for 2-methylphenylmercaptoacetic acid under the same conditions.[10] Also, 6-bromo-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide[11] possesses mp 141–142°, whereas our dioxide gave mp 131.5–132.5°. Compound **4b** was prepared and resolved as was **4a**, and the interconversions of optically active **4b**, **1b**, **2b**, and **3b** were stereochemically similar to those of the a series, and in general, the yields were higher. For example, deimidation of (−)-**4b** with nitrous acid[12] gave (+)-**1b** essentially quantitatively and with complete retention of configuration. Nitrous acid is superior to nitrosyl hexafluorophosphate for the deimidation. These series of reactions provide a new way of obtaining optically active sulfoxides, sulfimides, and sulfoximides. Chart I outlines the interconversions of these compounds. In the b series of compounds, enantiomers of the compounds actually used are formulated.

Stereochemical Course of Conversion of Sulfoxides to Sulfimides. Kresze[8] and coworkers reported the formation of sulfimide from *N*-sulfinyl-*p*-toluenesulfonamide[13] or *N*,*N*′-bis(*p*-toluenesulfonyl)sulfur diimide (DIM)[14] and sulfoxides. We found that pyridine catalyzed these reactions, and in pyridine as solvent at 0°, the reactions occurred with essentially complete inversion of configuration. When run in dichloromethane with a catalytic amount of pyridine at 25°, 44% net inversion was found.[3a] Others[15b] observed that 2-(*S*),*S*(*S*)-methionine sulfoxide with *N*-sulfinyl-*p*-toluenesulfonamide *in pyridine* gave the corresponding sulfimide with *retention of configuration*. That *cis*-4-*tert*-butylthiane 1-oxide with *N*-sulfinyl-*p*-toluenesulfonamide *in benzene* went to the corresponding sulfimide with *inversion* was also reported.[16]

Chart I



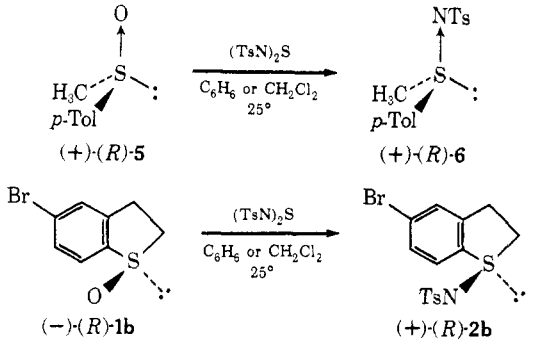
In the present work, to determine the effect of pyridine on the stereochemical course of the conversion of sulfoxides to sulfimides, we examined the reaction of (+)-(*R*)-methyl *p*-tolyl sulfoxide ((+)-**5**) with the sulfur diimide reagent (DIM) in dichloromethane without pyridine. The reaction gave predominantly (+)-(*R*)-*N*-*p*-toluenesulfonyl-*S*-methyl-*S*-*p*-tolylsulfimide ((+)-**6**), so the reaction went with predominant *retention* of configuration. The stereospecificity of the reaction varied with the relative concentrations of sulfoxide to reagent, as well as with how far the reaction was allowed to proceed. For example, at 25° with [DIM]/[(+)-**5**] = 1.8 after 54% conversion (isolated yield), the (+)-**6** produced was 53% optically pure, and the 35% (+)-**5** recovered was only 10% optically pure. Under the same conditions but much shorter time, (+)-**6** (17%) obtained was 86% optically pure, and recovered (+)-**5** (64%) was 93% optically pure. Clearly starting material was racemizing under the reaction conditions, although control experiments showed that in the absence of sulfoxide, sulfimide was not racemized by DIM, nor did (+)-**5** and (+)-**6** racemize one another without DIM present. In dichloromethane at 26°, (+)-**1b** gave (−)-**2b** (90%) with only 35% net retention of configuration. Thus the cyclic and open-chain systems behaved similarly in dichloromethane as solvent.

When benzene was substituted for dichloromethane, (+)-**5** gave (+)-**6** (55%) with DIM as reagent, and the reaction went with 94% net retention of configuration. Similarly (+)-**1b** with DIM in benzene at 25° gave (−)-**2b** (52%) with 95% net retention of configuration, and recovered (−)-**2b** (21%) was optically unchanged. Chart II traces these interconversions (the enantiomers of the **1b** and **2b** actually handled are formulated).

After these results were in hand, Christensen[15c] reported that in benzene, (+)-**5** gave (+)-**6** with retention and high stereospecificity. It was suggested[15c] that neighboring group involvement directed the stereochemical course of the methionine sulfoxide

(8) (a) G. Schultz and G. Kresze, *Angew. Chem., Int. Ed. Engl.*, **75**, 1022 (1963); (b) W. Wucherpfennig and G. Kresze, *Tetrahedron Lett.*, 1671 (1966).
(9) H. Kwart and K. A. Khan, *J. Amer. Chem. Soc.*, **89**, 1950 (1967).
(10) D. Walker and J. Leib, *J. Org. Chem.*, 27, 4455 (1962).
(11) F. G. Bordwell, B. B. Lampert, and W. H. McKellin, *J. Amer. Chem. Soc.*, **71**, 1702 (1949).
(12) T. R. Williams, R. E. Booms, and D. J. Cram, *ibid.*, **93**, 7338 (1971).
(13) J. Day and D. J. Cram, *ibid.*, **87**, 4398 (1965).
(14) D. R. Rayner, D. M. von Schriltz, J. Day, and D. J. Cram, *ibid.*, **90**, 2721 (1968).
(15) (a) B. W. Christensen and A. Kjaer, *Chem. Commun.*, 934 (1969); (b) B. W. Christensen, A. Kjaer, S. Neidle, and D. Rogers, *ibid.*, 169 (1969); (c) B. W. Christensen, *J. Chem. Soc. D*, 597 (1971).
(16) C. R. Johnson and J. J. Rigau, *J. Org. Chem.*, **33**, 4340 (1968).

Chart II



reaction[15a,b] away from its expected inversion course in pyridine to a retention path.

Kinetics. The reaction of (+)-**5** with DIM to give (−)-**6** with inversion in pyridine was found to be second order in DIM (overall third order).[3a] Accordingly, we examined the kinetic order of the reaction of (+)-**5** with DIM in benzene at 25° with ratios of [DIM]/[(+)-**5**] that varied from about 4 to 1, and per cent conversions from 6 to 37. The data (see Experimental Section) fitted an overall second-order rate constant with a probable error of 32%, and an overall third-order rate constant with a probable error of 96% during the initial stages of the reaction. The better fit for second-order behavior should be interpreted with reservations, since the extremely hygroscopic and insoluble character of DIM coupled with the far from quantitative conversion of **5** to **6** in benzene defeated determined attempts to obtain better kinetic data. We conclude the reaction in benzene is probably first order in DIM and goes with retention of configuration, but in pyridine is second order in DIM and goes with inversion. At 25° in both methylene chloride and pyridine, isothermal distillation molecular weight determinations[17] demonstrated DIM to be monomolecular (±1%).

An overall third-order polarimetric rate constant (eight points, 1 half-life) for conversion of (−)-**1a** to (−)-**2a** in pyridine at 25° by the *N*-sulfinyl-*p*-toluenesulfonamide reagent was determined (0.3 ± 0.1 M^{-2} sec^{-1}). This constant was calculated based on the assumption that the same kinetic features applied to the cyclic system as applied to the more thoroughly studied reaction,[3a] (+)-**5** → (−)-**6** (~0.005 M^{-2} sec^{-1}). Thus, the cyclic system reacts about 60 times faster than the open-chain analog. It was previously shown that with (+)-**5** in pyridine, similar kinetics were observed for the *N*-sulfinyl-*p*-toluenesulfonamide as with DIM, which the *N*-sulfinyl compound instantaneously produces in pyridine.[3a] A second difference between the cyclic and open-chain systems was that the stereospecificity of conversion of (−)-**1a** to (−)-**2a** decreases slightly faster with increasing temperature than is observed for (+)-**5** → (−)-**6**. For the cyclic system the reaction is almost completely stereospecific at 0°, but at 25° it is only about 42% stereospecific. A change from 98 to 72% stereospecific was observed when the temperature was changed from 0 to 25° in the open-chain system.

An estimated rate comparison based on overall second-order rate constants was made in benzene at 25° for (+)-**5** → (+)-**6** and (+)-**1b** → (−)-**2b** with DIM as reagent. The cyclic system gave $k = 4.68 \times 10^{-3}$ M^{-1} sec^{-1}, and the open-chain gave $k = 4.2 \times 10^{-5}$ M^{-1} sec^{-1}. Thus in benzene, the cyclic compound reacted about 110 times faster than the open-chain sulfoxide with DIM.

Optical Rotatory Dispersion Spectral Comparisons of Open-Chain and Cyclic Sulfimides. The absolute configurations of (+)-**5** as *R*[18a] and (+)-**6** as *R*[18b] have been determined by the X-ray method. Comparisons between both the ultraviolet absorption spectra and optical rotatory dispersion curves of the two cyclic sulfoxides (**1a** and **1b**) and of the open-chain sulfoxide (**5**)[3a] provide no basis for making configurational assignments to the cyclic sulfoxides. The optical rotatory dispersion curves of the three compounds provide no clue as to their relative configurations.[19] However, both the uv and ORD spectra of the three *N*-*p*-toluenesulfonylsulfimides resemble one another in some detail in the 210–260 nm region. In the uv in ethanol, open-chain sulfimide **6** gives a broad λ_{max} centered at 228 nm (log ϵ 4.36);[3a] **2a** a broad λ_{max} centered at 230 nm (log ϵ 4.25); **2b** a broad λ_{max} centered at 235 nm (log ϵ 4.30). The ORD of (−)-(*S*)-*N*-*p*-toluenesulfonyl-*S*-methyl-*S*-*p*-tolylsulfimide ((−)-(*S*)-**6**) exhibits extrema at 243 nm ([ϕ] −45,500°) and 225 nm ([ϕ] +35,500°), and [ϕ] is 0° at 234 nm. Cyclic sulfimide (−)-**2a** gives extrema at 244 nm ([ϕ] −39,000°) and 220 nm ([ϕ] +52,000°), and [ϕ] is 0° at 234 nm. The bromo cyclic sulfimide (+)-**2b** provides extrema at 248 nm ([ϕ] +39,000°) and <230 nm ([ϕ] < −50,000°), and [ϕ] is 0° at 242 nm. These similarities provide a reasonable basis for assigning the *S* configuration to (−)-**2a**, and the *R* configuration to (+)-**2b**.

Discussion

Stereochemical Reaction Cycles. The character of the stereochemical reaction cycles implicit in Charts I and II coupled with their close similarity to those of their open-chain analogs[3a] provide a secure basis for assigning the stereochemical course of these substitution reactions at sulfur.[20] The configurations of all the cyclic compounds relative to their sulfimides are assigned on this basis. The absolute configurational assignments of all the cyclic compounds are subject to the validity of the absolute configurational assignments of sulfimides **2a** and **2b** made in the last section. Their configurations relative to one another are hardly in doubt.

The reactions of the bromo and nonbrominated compounds of Chart I parallel one another, so arguments about the a and b series apply with equal force. The two series will not be distinguished here.

Tosylation of (+)-**4** to give (−)-**3** does not involve substitution at the chiral center, and so must occur with retention of configuration. Thus, the reactions, (−)-**1** → (−)-**3** and (+)-**4** → (−)-**1** each must go with the same stereochemical course. The three reactions

(17) E. P. Clark, *Anal. Chem.*, **13**, 820 (1941).

(18) (a) H. Hope, U. de la Camp, G. D. Homer, A. W. Messing, and L. H. Sommer, *Angew. Chem., Int. Ed. Engl.*, **8**, 612 (1969); (b) H. Hope and N. Kim, private communication.

(19) J. Brewster and J. G. Buta, *J. Amer. Chem. Soc.*, **88**, 2233 (1966), have pointed out the difficulties of making direct comparisons between the ORD spectra of acyclic and cyclic compounds due to the importance of conformational effects on the curves.

(20) For simplicity, Charts I and II trace the interconversions of *the enantiomers* of the cyclic bromo compounds actually used (see Experimental Section). These enantiomers will also be used in the Discussion.

taken together form a triligostatic, three-reaction cycle that involves three chiromers,[3b,21] and either two inversions or two retentions complete the cycle. The reactions, (−)-**1** → (−)-**3** and (+)-**4** → (−)-**1**, both possess the characteristics of electrophilic substitutions at sulfur. The first involves deimidation of an electron pair and the other an imidation of an electron pair. On mechanistic grounds alone, these reactions both appear to go with retention and follow the same stereochemical course observed for the same reactions in the open-chain system.[3a] Similarly, in the oxidation of (−)-**2** to (−)-**3**, the reaction is probably electrophilic at sulfur and nucleophilic at oxygen, the electron pair of sulfur acting as the nucleophile. The reaction has a high probability of occurring with retention. Again, the analogy with the open-chain analog[3a] for a similar oxidation strengthens this hypothesis. The relative configurations of all the compounds of Chart I are assigned on this basis. The absolute configurational assignments are based on the ORD correlations (see Results). Independent of this argument, the reactions (−)-**1** → (−)-**2** and (−)-**2** → (−)-**1** of Chart I must go with the same predominant steric course. The mechanistic arguments given above indicate these nucleophilic substitution reactions at chiral sulfur both occur with predominant inversion of configuration. Their open-chain analogs undergo the same reactions[3a] with the same stereochemical course.

These reactions close four stereochemical reaction cycles.[3b,21] Two of them are diligostatic, and each contains a ligand metathesis[3b,21]

$$(-)\text{-}3 \xleftarrow{R} (-)\text{-}1 \xrightarrow{I} (-)\text{-}2 \xrightarrow{R} (-)\text{-}3$$

$$(-)\text{-}3 \xleftarrow{R} (-)\text{-}1 \xleftarrow{I} (-)\text{-}2 \xrightarrow{R} (-)\text{-}3$$

Conversions

$$(-)\text{-}1 \xrightarrow{R} (-)\text{-}3 \xleftarrow{R} (+)\text{-}4 \xrightarrow{R} (-)\text{-}1$$

illustrate a three-reaction triligostatic cycle, whereas

$$(-)\text{-}1 \xrightarrow{I} (-)\text{-}2 \xrightarrow{R} (-)\text{-}3 \xleftarrow{R} (+)\text{-}4 \xrightarrow{R} (-)\text{-}1$$

illustrates a four-reaction diligostatic cycle that contains a ligand metathesis.

Since the absolute configurations of open-chain sulfoxide (+)-(*R*)-**6** are both established,[18] conversion of (+)-**5** to (+)-**6** by DIM in methylene chloride or benzene in the absence of pyridine must go with retention of configuration (Chart II). Likewise (−)-**1b** → (+)-**2b** must go with retention. These reactions coupled with those developed earlier for **5** and **6** and with those of Chart I provide a number of stereochemical reaction cycles with novel symmetry properties. One cycle that involves the bromo sulfoxide (−)-(*R*)-**1b**, the two bromo sulfimides (+)-(*R*)-**2b** and (−)-(*S*)-**2b**, and bromo sulfoximide (−)-(*R*)-**3b** is used here to illustrate. These four chiromers[3b,21] are connected by three reactions that all occur with retention of configuration, yet two of the chiromers ((+)-**2b** and (−)-**2b**) are enantiomerically related. The cycle is diligostatic (only the aryl and methylene groups are common to the four chiromers), and manipulation of the mobile ligands (O, NTs, and the electron pair) has

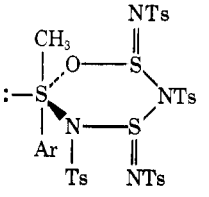
(21) D. J. Cram and J. M. Cram, *Top. Current Chem.*, **31**, 1 (1972).

$$\begin{array}{ccc} (+)\text{-}\mathbf{2b} & & (-)\text{-}\mathbf{2b} \\ R\uparrow C_6H_6 & & R\downarrow [O] \\ (-)\text{-}\mathbf{1b} & \xrightarrow{R} & (-)\text{-}\mathbf{3b} \end{array}$$

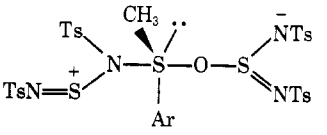
provided a ligand metathesis. The ligand metathesis is the equivalent of one inversion, and without the ligand metathesis the above cycle could not contain two enantiomers. Maps of the possible stereochemical reaction cycles have been reported.[3b,21]

Mechanisms of Conversions of Sulfoxides to Sulfimides in Pyridine. Mechanisms for conversion of sulfoxides to sulfimides with the sulfur diimide reagent (DIM) in pyridine must accommodate the following facts. (1) In pyridine the reactions occur faster than in benzene, and go with clean inversion of configuration, both with cyclic and open-chain sulfoxides. (2) In pyridine in the open-chain system, the reaction was second order in DIM. (3) The cyclic sulfoxide reacts one to two orders of magnitude faster than the open-chain sulfoxide.

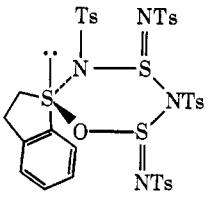
A strong argument for the reaction of open-chain sulfoxide in pyridine going through A (equatorial–equatorial or e,e substitution with inversion) was developed.[3a] It was based on the need of the entering and leaving groups to be part of the same ring system to avoid high energy reaction poducts predicted by decomposition of B (axial–axial or a,a substitution with inversion).[3a]



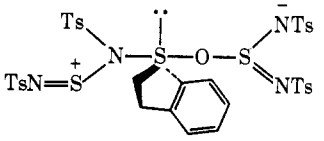
A



B



C



D

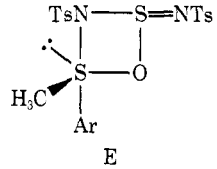
Application of the same arguments to the cyclic system's reaction in pyridine ((−)-**1a** → (−)-**2a**) provides alternative intermediates C (e,e substitution) and D (a,a substitution). Features that favor C over D are the following. (1) As in the open-chain analog, decomposition of C leads to TsNSNTs and TsNSO (known compounds) where D leads to TsNSONTs and TsNS (unknown and probably higher energy products). (2) The tetrahydrothiophene bond angles in C are less deformed spanning a and e positions than in D spanning e and e positions. (3) The leaving group in D carries a negative and the entering group a positive charge leading to charge separation in a fairly nonpolar medium. In C there is no such charge separation. (4) The leaving group in D carries a formal negative charge, is therefore electropositive, yet it is distributed in the less preferred a position for electropositive groups. A single argument favors D over C. In C the axial electron pair and the equatorial entering and leaving groups occupy positions opposite to the preferred, based on analogies with what little is known

about stable pentacoordinate sulfur compounds.[22] In such compounds, electron pairs prefer e and electronegative groups a positions when available. In D, only the leaving group (electropositive group axial) occupies an unfavored position.

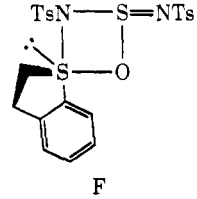
We believe the balance of evidence favors A over B and C over D, and that the e,e substitution route is highly likely. The increased rate for substitution in pyridine of the cyclic over the open-chain system we attribute to relief of strain in the five-membered sulfoxide ring system in going to the trigonal bipyramid intermediate. The smaller bond angle in the intermediate allows deeclipsing of the two sets of methylene groups in the five-membered ring. Analogies in phosphorus chemistry[23] indicate that effects of this sort provide rate enhancements of a much higher order than those observed here. Possibly, part of the rate enhancement due to angle strain release is cancelled by promoting the unshared electron pair on sulfur from an sp^3 orbital in the starting sulfoxide to an sp^3d and axial orbital in the trigonal bipyramid. Alternative intermediates B and D based on the a,a substitution route provide no explanation for the cyclic system substituting faster than the open-chain system.

Mechanisms of Conversion of Sulfoxides to Sulfimides in Benzene and Methylene Chloride. The mechanism in benzene must conform to the following facts. (1) The reaction gives high retention of configuration in both the open-chain and cyclic systems. (2) The open-chain sulfoxide's reaction with DIM follows roughly second-order kinetics toward the beginning of the reaction. (3) The cyclic reacts about 100 times faster than the open-chain system.

These facts point to trigonal-bipyramidal intermediates E and F, in which the entering and leaving groups occupy the same ring system which spans the a and e positions of the bipyramid. The tosylimide, as the more electronegative group, is placed in the a position, but the choice is arbitrary. Alternative structures with NTs e and O a also accommodate the facts. The electron pair is placed in the e position where it is close to the nucleus. The methyl is more electropositive than the aryl, and is also placed e. Intermediates E and F decompose to sulfimides and



E



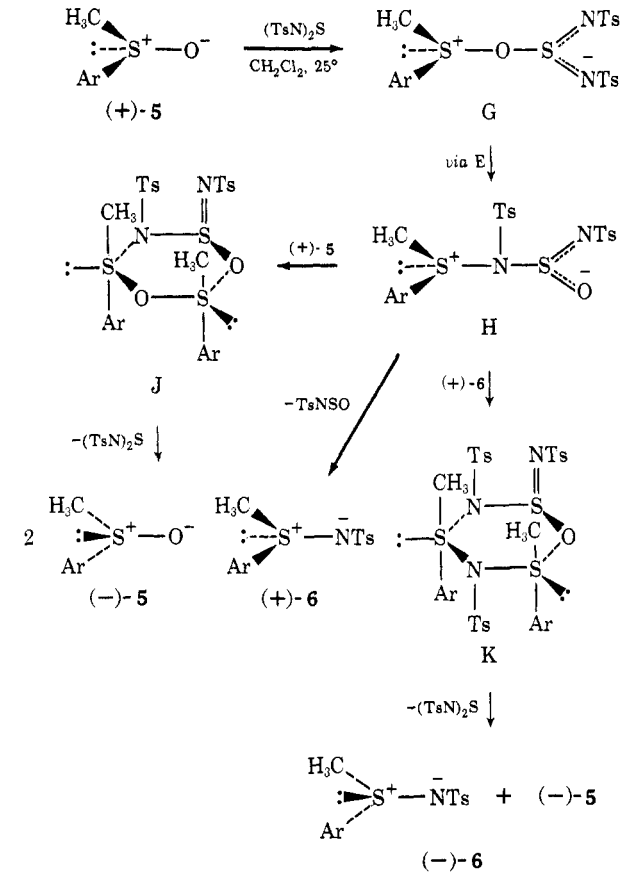
F

N-sulfinyl-*p*-toluenesulfonamide, which at 25° reacts too slowly with sulfoxide to contribute to the reaction. This overall mechanism is of an e,a variety and predicts retention of configuration.[3a] The cyclic sulfoxide probably reacts faster than the open-chain compound because methylene eclipsing strain present in the cyclic sulfoxide is somewhat lowered with lowering of the C–S–C bond angle in passing from sulfoxide to F.

In dichloromethane as solvent, the open-chain sulfoxide, after a short reaction time with DIM, gave 17% sulfimide (isolated) of which 93% was of retained and 7% was of inverted configuration. Thus when quenched, a ~1% yield of inverted sulfimide was isolated. The sulfoxide obtained (64%) was 96.5% of retained and 3.5% inverted, or a ~2% yield of inverted sulfoxide was produced. In a longer run, 54% sulfimide was produced, of which 23% was inverted, which amounts to a 12% yield of inverted sulfimide. The sulfoxide obtained (35%) was 45% inverted, which amounts to a 16% yield of inverted material. Two conclusions emerge. Inverted sulfoxide is produced faster than inverted sulfimide. Inverted sulfimide is produced at short reaction times by a process that does not involve inverted sulfoxide as intermediate.

The sequences of Chart III offer an attractive ex-

Chart III



planation of these results. Route (+)-**5** → G → E → H → (+)-**6** accounts for the conversion of (+)-**5** to (+)-**6** (retention). Route (+)-**5** → G → E → H → K → [(−)-**6** + (−)-**5**] accounts for the lack of complete stereospecificity in the reaction at short reaction times, but taken alone does not account for the greater rate of production of inverted sulfoxide than inverted sulfimide. Route (+)-**5** → G → E → H → J → (−)-**5** as a competing process provides an explanation. Thus, production of some inverted sulfimide and sulfoxide is explained by e,e multiple ligand exchange reactions at two chiral sulfur centers at the same time. Intermediates J and K resemble intermediate A, and they neatly explain the results observed in dichloromethane.

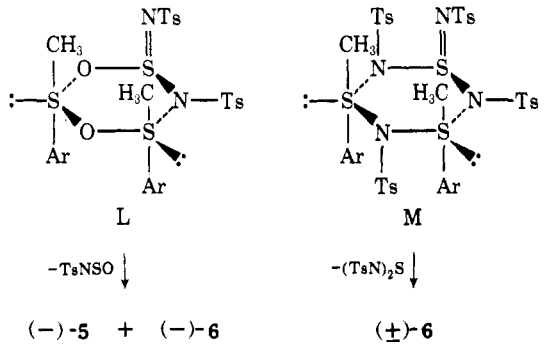
(22) (a) E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, **81**, 1084 (1959); (b) K. Kimura and S. H. Bauer, *J. Chem. Phys.*, **39**, 3172 (1963); (c) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964); (d) N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *J. Amer. Chem. Soc.*, **91**, 5649 (1969).

(23) (a) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968); (b) D. B. Boyd, *J. Amer. Chem. Soc.*, **91**, 1200 (1969).

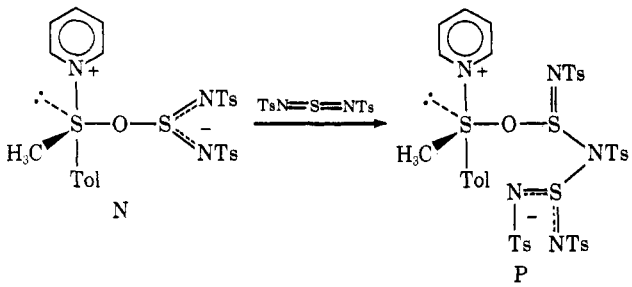
The fact that J and K do not form in benzene at rates competitive with H → (+)-6 correlates with the dipolar character of H on the one hand and the nonpolar character of benzene on the other. The reactions of H with either sulfoxide or sulfimide are bimolecular, and the lifetime of H should be longer in dichloromethane than in benzene.

Since similar results were observed in the conversion of cyclic sulfoxide to cyclic sulfimide with DIM in dichloromethane, similar competing processes are offered as an explanation.

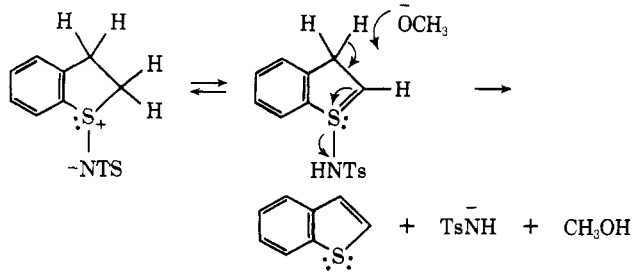
Intermediate L, which resembles A, J, and K, can be envisioned as formable from G and (+)-5. Interestingly, L would provide inverted sulfoxide (−)-5 and inverted sulfimide. No data rule out this mechanism, but the results do not require it. Similarly, M conceivably could arise from reaction of DIM with 2 mol of (+)-6. However, M contains a mirror plane, and would give (±)-6. No racemization of (+)-6 when mixed with DIM in dichloromethane was observed.



In pyridine, no inverted sulfoxide nor sulfimide of retained configuration is observed. Possibly ion pair G is formed as in the other solvents, but reacts with pyridine to form N, which in turn reacts with DIM to give P which produces A and finally inverted sulfimide.



Elimination Reaction of Sulfimide 2a with Base. Unlike the open-chain sulfimide, which hydrolyzed to sulfoxide when treated with base, cyclic sulfimide **2a** eliminated the elements of *p*-toluenesulfonamide with potassium hydroxide in methanol to give benzo[*b*]thiophene. Some mechanistic scheme such as that formulated is probably operative.



Experimental Section

General. Chemicals were reagent grade unless otherwise specified. Infrared (ir) spectra were taken in chloroform solution at concentrations of *ca.* 5% (uness otherwise noted) on a Beckman Model IR-5 spectrophotometer. Nuclear magnetic resonance (nmr) spectra were taken in deuteriochloroform (unless otherwise noted) on a Varian Associates Model A-60D or HA-100 spectrometer. Chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. Specific rotations were taken on a Perkin-Elmer Model 141 spectropolarimeter at 25.0 ± 0.5° in a 1-dm, jacketed cell. Ultraviolet (uv) spectra were obtained on a Cary recording spectrophotometer Model 14M in 0.1-mm quartz cells in absolute ethanol. Optical rotatory dispersion (ORD) curves were taken on a Cary Model 60 spectropolarimeter with 1-cm quartz cells in absolute ethanol. Melting points were taken on a Thomas-Hoover Uni-Melt apparatus and are uncorrected. Silica gel for chromatography was either Baker or Merck chromatographic grade; for thin layer chromatography (tlc) Brinkmann silica gel G on Pyrex plates or Bakerflex silica gel 1B-F plates with fluorescent indicator were used. Development was accomplished with either uv light or by spraying the plate with an alcoholic solution of phosphomolybdic acid followed by heating at *ca.* 100° for 1 min. The drybox used was a Dri-Lab Model HE-43 equipped with a Dri-Train Model HE-93 purification train, which was kept under a nitrogen atmosphere.

Starting Materials. The (+)-(*R*)-methyl *p*-tolyl sulfoxide,[3a] (+)-**5**, used gave mp 76–77°, $[\alpha]_{546}^{25}$ +179.5° (*c* 1.62, acetone). The *N*-sulfinyl-*p*-toluenesulfonamide[3a] was purified by molecular distillation (bp 120–130°, 0.45 mm) and gave an excellent C and H analysis. Analytically pure *N*,*N*′-bis(*p*-toluenesulfonyl)sulfur diimide (DIM) was prepared from analytically pure *N*-sulfinyl-*p*-toluenesulfonamide in benzene and pyridine catalyst under nitrogen and was caused to crystallize by addition of cyclohexane, mp 139–140°. Unless very pure starting material and solvents were used and the reaction was run in an absolutely dry atmosphere, the product was contaminated with *p*-toluenesulfonamide. The published method of using "undistilled" thionyl chloride gives variable results.[3a]

Preparation of (+)-(*R*)-*N*-*p*-Toluenesulfonyl-*S*-methyl-*S*-*p*-tolylsulfimide ((+)-6) in Dichloromethane at 0°. *Into an oven-dried* 50-ml flask equipped with a magnetic stirring bar and drying tube were added (+)-(*R*)-methyl *p*-tolyl sulfoxide, (+)-**5** (0.5539 g, 3.60 mmol, 99% optically pure), *N*,*N*′-bis(*p*-toluenesulfonyl)sulfur diimide, DIM (2.2651 g, 6.1 mmol), and 30 ml of dry dichloromethane in a nitrogen atmosphere drybox. The flask was removed from the drybox and placed in an ice bath (0–2°). The drying tube was replaced with a nitrogen inlet. The reaction was stirred for 3.75 hr after which it was poured into ice–water. The dichloromethane layer was separated and the aqueous layer extracted with additional dichloromethane. The organic extracts were combined and washed successively with 30 ml of 20% potassium hydroxide solution and 30 ml of brine. The extracts were then dried and filtered, and the solvent was removed *in vacuo*. The product was adsorbed on silica gel and chromatographed on 80 g of silica gel with ethyl acetate as the eluent. Care was taken to keep the evaporation temperatures below 50°. Fractions 7–14 contained pure sulfimide, (+)-**6**, 0.4382 g (39.8%), mp 121–122°, $[\alpha]_{546}^{25}$ +130° (*c* 0.93, acetone) which corresponds to 40% optical purity. The reaction was therefore 40.2% stereospecific. The sulfoxide was recovered (39%), mp 39–42°, $[\alpha]_{546}^{25}$ +2.52° (*c* 1.47, acetone) which corresponds to 1.4% optical purity.

A second run at 25° for 3 hr of 99% optically pure (+)-**5** (1.005 g or 6.5 mmol) and DIM (4.4257 g or 12 mmol) in 70 ml of dichloromethane gave after chromatography 1.07 g of (+)-**6**, $[\alpha]_{546}^{25}$ +172° (*c* 1.065, acetone) or 53% optically pure. The (+)-**5** recovered (0.35 g, 35%) gave $[\alpha]_{546}^{25}$ +18.3°, and was 10% optically pure.

A third run at 25° for 15 min made with the same ratio of the same reactants and solvents gave (+)-**5** (64%), $[\alpha]_{546}^{25}$ +166° (*c* 1.165, acetone), mp 68–73°, 93% optically pure, and (+)-**6** (17%), mp 122–123°, $[\alpha]_{546}^{25}$ +279.8°, 86% optically pure. In these experiments, care was taken not to fractionally crystallize (+)-**5** and (+)-**6** before rotations were taken.

In a control experiment, *N*-sulfinyl-*p*-toluenesulfonamide was shown not to react (rotations and tlc behavior) with (+)-**5** in dry dichloromethane at 25° for 44 hr.

Molecular Weight Determinations of *N*,*N*′-Bis(*p*-toluenesulfonyl)-sulfur Diimide (DIM). The isothermal distillation method of Signer[17] applied to DIM in dry dichloromethane at 25.0 ± 10° against triphenylmethane as standard (mp 93–94°) gave 376 as

molecular weight (371 calculated). In dry pyridine under the same conditions, a molecular weight of 367 was obtained.

Preparation of (+)-(*R*)-*N*-*p*-Toluenesulfonyl-*S*-methyl-*S*-*p*-tolylsulfimide, (+)-6, in Benzene at 27°. Sulfoxide (+)-**5** (0.2095 g, 1.36 mmol, 99% optically pure) and DIM (0.8006 g, 2.16 mmol) were dissolved in 15 ml of benzene and allowed to stir at 27° in a drybox for 2.75 hr, after which 10 ml of water and 20 ml of chloroform were added. The product was isolated as in other runs to yield 0.3528 g of a light yellow oil that crystallized on standing. The mixture was chromatographed on 30 g of silica gel (ethyl acetate, 30-ml fractions). Pure (+)-**6** was recovered from fractions 3–7, 229.1 mg (54.8%, mp 114–116°, $[\alpha]^{25}_{546}$ +302.4° (*c* 0.93, acetone)). The product was therefore 93% optically pure and the reaction proceeded with 94% stereospecificity. Its spectral properties and tlc behavior were identical with those of its enantiomer.[3a]

(±)-Dihydrobenzo[*b*]thiophene-1-imide 1-Oxide (4a). From 67 g of 2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide[4a] and 39.5 g of lithium aluminum hydride in 700 ml of dry ether was obtained, after distillation, 40.8 g (75%) of 2,3-dihydrobenzo[*b*]thiophene,[4b] which gave a good carbon and hydrogen analysis. This material when treated with 64.2 g of sodium metaperiodate in 800 ml of water at 5° for 2 hr and at 25° for 12 hr[24] gave 45 g (99%) of 2,3-dihydro[*b*]-benzothiophene 1-oxide (**1a**), mp 66–68° (from petroleum ether–benzene), lit.[5] mp 67–68°. Imidation of this sulfoxide with hydrazoic acid[6] gave **4a** (75%), mp 113–114° (from acetone). An nmr spectrum ($CDCl_3$) of the substance showed a complex aromatic multiplet (4 H), a complex multiplet centered at 3.47 ppm (4 H), and an NH singlet at 3.10 (1 H). The ir spectrum (Nujol) of the sulfoximide exhibited a medium N–H band at about 3.1 μ and strong bands at about 8.3 and 10.1 μ. *Anal.* Calcd for C_8H_9ONS: C, 57.45; H, 5.42; S, 19.18. Found: C, 57.62; H, 5.30; S, 18.95.

(+)-*N*-*d*-10-Camphorsulfonyl-2,3-dihydrobenzo[*b*]thiophene-1-imide 1-Oxide. Sulfoximide (+)-**4a**, 16.7 g (0.1 mol), was suspended in 50 ml of dry pyridine with stirring. The reagent *d*-10-camphorsulfonyl chloride, 30 g or 0.12 mol (obtained by reaction of optically pure *d*-10-camphorsulfonic acid, Eastman, with thionyl chloride followed by removal of excess of same), was dissolved in an additional 50 ml of dry pyridine. This latter solution was added dropwise to the former stirred solution over 15 min at 25°. The reactants were than stirred for an additional 4.5 hr with intermittent warming to 45°. The pyridine solution was then poured into water. The precipitated product was filtered and washed with water. The air-dried mixture of diastereomers, 36.3 g (95%), had mp 126–157° and $[\alpha]^{25}_{546}$ +45° and $[\alpha]^{25}_{D}$ +35° (*c* 1.595, $CHCl_3$). The least soluble diastereomer was then obtained by fractional crystallization of the mixture from acetone (~four times) to constant melting point and rotation, mp 183–185° dec, $[\alpha]^{25}_{546}$ +79.5° and $[\alpha]^{25}_{D}$ +66.2° (*c* 1.3, $CHCl_3$), wt 8.5 g (22% overall). *Anal.* Calcd for $C_{18}H_{23}NO_4S_2$: C, 56.66; H, 6.08; S, 16.81. Found: C, 56.71; H, 5.90; S, 16.75.

(+)-2,3-Dihydrobenzo[*b*]thiophene-1-imide 1-Oxide, (+)-4a. The pure diastereomer of (+)-*N*-*d*-10-camphorsulfonyl-2,3-dihydrobenzo[*b*]thiophene-1-imide 1-oxide obtained above, 8.5 g (0.022 mol), was stirred with 25 ml of concentrated sulfuric acid for 1.5 hr with gentle warming (<50°). The reaction mixture was poured into water and filtered to remove an insoluble gum. The filtrate was taken to pH ~9 with solid sodium carbonate, and the solution was extracted several times with chloroform. The chloroform extracts were dried and evaporated *in vacuo* leaving 2.4 g (64%) of a colorless oil. This oil was chromatographed on 100 g of silica gel. After washing the column with ether and ether–methanol (4:1), the product was eluted with ether–methanol (1:1). The oily residue was then distilled (Kugelrohr), bp ~140° (0.1 mm). The colorless oil had $[\alpha]^{25}_{546}$ +16° and $[\alpha]^{25}_{D}$ +13° (*c* 1.3, acetone) and was identical in its nmr and ir spectra with those of **4a**. *Anal.* Calcd for C_8H_9NOS: C, 57.45; H, 5.42; S, 19.18. Found: C, 57.52; H, 5.59; S, 19.04.

(−)-2,3-Dihydrobenzo[*b*]thiophene 1-Oxide, (−)-1a. Sulfoximide (+)-**4a**, 2.5 g (0.015 mol), was dissolved in 20 ml of dry nitromethane. To the above stirred solution, cooled by a water bath at 25°, was added dropwise a solution of 3.15 g (0.018 mol) of nitrosyl hexafluorophosphate in 20 ml of nitromethane. An exothermic gas-producing reaction ensued. After stirring 5 min, the reaction mixture was poured into dilute sodium bicarbonate solution. This still basic solution was extracted with four 50-ml portions of chloroform. These extracts were dried and evaporated *in vacuo*. The residue was chromatographed on 75 g of silica gel and the column washed with benzene–ether mixtures. The sulfoxide was finally eluted with ether–methanol. The product, (−)-**1a**, was distilled (Kugelrohr), bp ~115° (0.09 mm), wt 2.05 g (91%). This product was identical in its nmr and ir spectra with those of **1a** and had $[\alpha]^{25}_{546}$ −326° and $[\alpha]^{25}_{D}$ −270° (*c* 1.57, acetone). The optically pure product is hygroscopic. A second preparation of (−)-**1a** using an ice-cooled water bath gave (−)-**1a** with $[\alpha]^{25}_{546}$ −343° and $[\alpha]^{25}_{D}$ −285° (*c* 1.5, acetone). The material from the first preparation had a maximum optical purity of 95%. *Anal.* Calcd for C_8H_8OS: C, 63.12; H, 5.30; S, 21.07. Found: C, 63.24; H, 5.43; S, 20.81.

Conversion of Sulfoxide (−)-1a into (−)-*N*-*p*-Toluenesulfonyl-2,3-dihydrobenzo[*b*]thiophene-1-imide ((−)-2a) with *N*-Sulfinyl-*p*-toluenesulfonamide. Sulfoxide (−)-**1a**, 1.5 g (0.01 mol) ($[\alpha]^{25}_{546}$ −326°), was dissolved in 20 ml of dry pyridine and the solution cooled to 0°. To this solution was added *N*-sulfinyl-*p*-toluenesulfonamide,[8] 3.26 g (0.015 mol), in 10 ml of pyridine. The mixture was stirred at 0° for 3 hr, and the reaction solution was poured into 200 ml of water. The turbid mixture was extracted with several portions of chloroform, and the combined extracts were dried, filtered, and evaporated under vacuum. The solid residue was chromatographed on 75 g of silica gel, and the column was washed with benzene–chloroform mixtures. Sulfimide (−)-**2a** was eluted with pure chloroform, wt 1.5 g (50%), and had $[\alpha]^{25}_{546}$ −81° and $[\alpha]^{25}_{D}$ −65° (*c* 1.15, $CHCl_3$). The product was rechromatographed in a similar fashion to give mp 184–188° dec, $[\alpha]^{25}_{546}$ −82.7° and $[\alpha]^{25}_{D}$ −66.1 (*c* 1.26, $CHCl_3$). The product was then recrystallized from ethanol–chloroform, mp 185–188° dec, $[\alpha]^{25}_{546}$ −83.9° and $[\alpha]^{25}_{D}$ −67.2° (*c* 0.845, $CHCl_3$). *Anal.* Calcd for $C_{15}H_{15}NO_2S_2$: C, 58.99; H, 4.95; S, 21.00. Found: C, 58.93; H, 4.92; S, 21.40.

Conversion of Sulfoxide (−)-1a to Sulfimide (−)-2a with *N*,*N*′-Bis(*p*-toluenesulfonyl)sulfur Diimide (DIM). Sulfoxide (−)-**1a**, 0.35 g (0.0023 mol), $[\alpha]^{25}_{546}$ −343° (*c* 1.1, acetone), was dissolved in 5 ml of dry pyridine. This solution was cooled to 0°, DIM, 0.94 g (0.0025 mol), in 8 ml of pyridine cooled to 0° was added, and the reactants were stirred at 0° for 30 min. The reaction solution was poured into dilute potassium hydroxide solution. The precipitated product was filtered and washed with water. The wet product was then dissolved in dichloromethane, dried, and evaporated *in vacuo* leaving 0.55 g (78%) of a product having mp 181–186° dec, $[\alpha]^{25}_{546}$ −83.7° and $[\alpha]^{25}_{D}$ −67.2° (*c* 0.985, $CHCl_3$). The sulfimide was recrystallized from acetone–dichloromethane, mp 180–185° dec, $[\alpha]^{25}_{546}$ −84.5° and $[\alpha]^{25}_{D}$ −67.8° (*c* 1.045, $CHCl_3$). This material was identical in all respects with that prepared above.

Oxidation of Sulfimide (−)-2a to (−)-*N*-*p*-Toluenesulfonyl-2,3-dihydrobenzo[*b*]thiophene-1-imide 1-Oxide, (−)-3a. Sulfimide (−)-**2a** of maximum rotation, 0.3 g (0.001 mol), was dissolved in 15 ml of pyridine. This solution was added to a solution containing 0.3 g (0.002 mol) of potassium permanganate in 20 ml of water. The resulting solution was heated on a steam bath for 1 hr, poured into water, and extracted with chloroform. The chloroform extracts were washed with dilute sulfuric acid, dried, and evaporated *in vacuo* leaving a viscous oil. This oil was chromatographed on 20 g of silica gel eluting first with benzene. The product was then eluted with benzene–ether (1:1), wt 0.1 g (31%), mp 85–91°, $[\alpha]^{25}_{546}$ −44.4° and $[\alpha]^{25}_{D}$ −34.8° (*c* 1.255, acetone). The product was crystallized from methanol, mp 91–92°, $[\alpha]^{25}_{546}$ −45.3° and $[\alpha]^{25}_{D}$ −34.9° (*c* 0.435, acetone). The melting point of this material was undepressed by admixture with material of the same melting point reported below.

Conversion of Sulfoximide (+)-4a to Its *N*-Tosyl Derivative (−)-3a. Sulfoximide (+)-**4a** (prepared above), 0.50 g (0.003 mol), was stirred in 35 ml of dry pyridine with 1.0 g (excess) of tosyl chloride for 3 hr at 25°. This solution was poured into water and the product precipitated. The crude product was chromatographed on 30 g of silica gel eluting with benzene–ether (1:1). Two product-containing fractions were collected. The first, 0.3 g, had a mp 82–84°, $[\alpha]^{25}_{546}$ −44.3° and $[\alpha]^{25}_{D}$ −34.6° (*c* 1.005, acetone). The second, 0.5 g, had a mp 90–92°, $[\alpha]^{25}_{546}$ −45.2° and $[\alpha]^{25}_{D}$ −35.6° (*c* 1.055, acetone). The combined fractions were crystallized from methanol, wt 0.75 (84%), mp 91–92°, $[\alpha]^{25}_{546}$ −44.8° and $[\alpha]^{25}_{D}$ −35.1°. The product (−)-**3a** can exist in two crystalline modifications having mp 83 and 92°. *Anal.* Calcd for $C_{15}H_{15}NO_3S_2$: C, 56.05; H, 4.70; S, 19.95. Found: C, 56.08; H, 4.74; S, 20.31.

Conversion of Sulfoxide (−)-1a to Sulfoximide (−)-3a. Sulfoxide (−)-**1a**, 0.22 g (0.00145 mol) ($[\alpha]^{25}_{546}$ −343°, *c* 1.5, acetone), was dissolved in 50 ml of methanol. Copper powder (freshly precipitated), 1.27 g (0.02 g-atom), was added followed by 3.96 g (0.02 mol) of tosyl azide. The mixture was refluxed with stirring

(24) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

for 1.5 hr. A second portion of copper powder was added and refluxing was continued for another 3 hr. The hot solution was filtered. The solvent was evaporated leaving a green oil that contained product along with *p*-toluenesulfonamide (ir spectrum). The sulfonamide was removed by dissolving the oil in chloroform and washing the resulting solution with potassium hydroxide solution. The solvent was removed and the residue chromatographed on 30 g of silica gel. After the column was washed with benzene and benzene–ether (4:1), sulfoximide (−)-**3a** was eluted with benzene–ether (1:1) as an oil which crystallized, wt 0.11 g (24%), $[\alpha]^{25}_{546}$ −34.5°, $[\alpha]^{25}D$ −26.7° (*c* 0.950, acetone). The sulfoximide thus obtained is 77% optically pure. Its spectral properties were identical with those observed for (−)-**3a** prepared above.

Hydrolysis of Sulfimide (−)-2a to Sulfoxide (−)-1a with Sulfuric Acid. Sulfimide (−)-**2a**, 0.2 g (0.66 mmol) ($[\alpha]^{25}_{546}$ −82.7°), was added to 10 ml of concentrated sulfuric acid. This solution was stirred at 25° for 3 min and poured into 150 ml of saturated sodium bicarbonate solution. The solution was saturated with sodium chloride and extracted with three 100-ml portions of chloroform. The combined extracts were dried and evaporated, yielding 0.12 g of a viscous oil that was chromatographed on 20 g of silica gel. The sulfoxide was eluted with chloroform–methanol (1:1) to give 0.074 g of material and was identified by comparison of its ir spectrum ($CHCl_3$) with an authentic sample. The sulfoxide had $[\alpha]^{25}_{546}$ −85.4° and $[\alpha]^{25}D$ −71.3° (*c* 0.885, acetone), which corresponds to an optical purity of 26%.

Conversion of Sulfimide 2a to Benzo[*b*]thiophene. Racemic **2a** was prepared as follows. Into an aqueous solution of 26 g of Chloramine-T was added 13.6 g of 2,3-dihydrobenzo[*b*]thiophene, and the aqueous mixture was heated at 90° for 20 min and rapidly stirred until cool. The precipitated product was collected, washed, dried, and recrystallized from 95% ethanol to give 14.5 g (48%) of **2a** as white plates, mp 150–152°. This material exhibited spectral and thin-layer properties identical with those of (−)-**2a**.

To a solution of 30 ml of methanol saturated at 25° with potassium hydroxide was added 0.42 g of **2a**. The solution was stirred at 25° for 24 hr, 30 ml of water was added, and the mixture was extracted with three 30-ml portions of pentane. The aqueous layer was saturated with sodium chloride and extracted with four 30-ml portions of chloroform. Each organic layer was dried and evaporated under vacuum. The chloroform evaporation left no residue. The pentane evaporation gave 0.18 g of a yellow liquid whose ir spectrum and tlc behavior were identical with those of authentic benzo[*b*]thiophene.

5-Bromo-2,3-dihydrobenzo[*b*]thiophene. To a stirred solution of 205 g (1.51 mol) of 2,3-dihydrobenzo[*b*]thiophene in 600 ml of glacial acetic acid was added dropwise at 25° a solution of 241 g (82.4 ml, 1.51 mol) of bromine in 300 ml of acetic acid.[10] After addition was complete, the red solution was stirred for 3 hr, allowed to stand 10 hr, and mixed with 100 ml of a saturated aqueous solution of sodium bisulfite. The mixture was shaken with 1500 ml of ether; the ether layer was washed several times with water, dilute sodium carbonate solution, 15% sodium hydroxide soluton, and brine. The ethereal extract was dried and filtered and the solvent removed *in vacuo* to yield 332.8 g (100%) of a slightly red liquid that solidified on cooling. Sublimation of this material at 62° (0.5 mm) yielded a white, hydroscopic solid, mp 45.5–46°. The product gave an nmr spectrum of a complex aromatic multiplet at δ 7.08–7.20 (3 H) and a slightly split singlet at 3.31 (4 H). *Anal.* Calcd for C_8H_7BrS: C, 44.67; H, 3.28; Br, 37.15; S, 14.91. Found: C, 44.97; H, 3.16; Br, 37.05; S, 15.32.

5-Bromo-2,3-dihydrobenzo[*b*]thiophene 1-Oxide (1b). By the procedure used for the preparation of the parent compound **1a** (see above), 215 g of 5-bromo-2,3-dihydrobenzo[*b*]thiophene was oxidized[24] to **1b**, which was recrystallized from benzene–petroleum ether to give 197 g (85%), mp 95–97°. *Anal.* Calcd for C_8H_7BrOS: C, 41.58; H, 3.05; S, 13.87. Found: C, 41.69; H, 2.98; S, 13.69.

5-Bromo-2,3-dihydrobenzo[*b*]thiophene-1-imide 1-Oxide (4b). By the same procedure used to convert **1a** to **4a**, 196 g of sulfoxide **1b** was imidated with hydrazoic acid to give 227 g of a dark oil. This material was dissolved in benzene, and dry hydrogen chloride was bubbled through the solution for 1 hr. The voluminous solid was collected, washed with ether, and recrystallized from methanol. Four crops yielded 201.2 g (84%) of the hydrochloride salt, mp 204–206° dec. The salt was dissolved in 1000 ml of water to which sodium carbonate was added to pH 8, and the mixture was extracted with three 250-ml portions of chloroform. The combined solution was dried and filtered, and the solvent was removed *in vacuo* yielding 191.8 g (100%) of a yellow oil. This was dissolved in 600 ml of acetone and allowed to crystallize yielding 172 g (82.4%) of **4b** as a white solid, mp 97–99°. The compound's ir spectrum gave a sharp absorption at 3.02 μ and two strong, broad absorptions at 8.20 and 10.40 μ. *Anal.* Calcd for C_8H_5BrNOS: C, 39.02; H, 3.28; S, 13.03. Found: C, 38.93; H, 3.31; S, 13.30.

5-Bromo-2,3-dihydrobenzo[*b*]thiophene-1-(*N*-*d*-10-camphorsulfonyl)imide 1-Oxide. To a solution of 40.0 g (0.162 mol) of sulfoximide **4b** in 300 ml of pyridine was added dropwise 48.9 g (0.195 mol) of *d*-10-camphorsulfonyl chloride[25] in 200 ml of pyridine. After addition, the reaction was heated at 55° for 2.5 hr. Approximately 400 ml of pyridine was removed by vacuum distillation. The residual material was dissolved in 700 ml of chloroform, and the solution was washed twice with ice-cold 6 *M* sulfuric acid and twice with 200-ml portions of brine. The solution was dried and the solvent removed *in vacuo*, yielding 70.2 g (94.2%) of a yellow oil. The compound was pure by tlc (silica gel, ethyl acetate) and its ir spectrum showed a carbonyl absorption at 5.72 μ and sulfonyl absorption at 7.58 and 8.75 μ. The NH absorption at 3.02 μ was absent. Attempts to crystallize this material were unsuccessful. This diastereomeric mixture (70.2 g, $[\alpha]^{25}_{436}$ +36.3°, *c* 1.05, chloroform), was chromatographed on 2000 g of silica gel (1500-ml fractions). The column was washed with 5–70% ether–pentane mixtures, the polarity being increased after 20–25 l. had been collected. Fractions 152–215 contained diastereomer. Fractions 152–160 (A) and 180–192 (B) were combined. Addition of ether caused precipitation of a powder. Repeated crystallization of B from ether yielded a crystalline product as prisms, wt 7.48 g, mp 131–132°, $[\alpha]^{25}_{436}$ +119.7° (*c* 1.51, chloroform), which was judged to be diastereomerically pure isomer B. *Anal.* Calcd for $C_{18}H_{20}BrNO_3S$: C, 46.96; H, 4.82; S, 13.93. Found: C, 46.94; H, 4.81; S, 13.69.

Material recovered from the mother liquors was recrystallized from methanol to yield a crystalline product as hexagonal plates, wt 10.28 g, mp 118–119°, $[\alpha]^{25}_{436}$ +46.8° (*c* 1.32, chloroform), which was judged to be diastereomerically pure isomer A.

(−)-(*S*)-5-Bromo-2,3-dihydrobenzo[*b*]thiophene-1-imide 1-Oxide ((−)-4b). Isomer B (see above), 1.44 g $[\alpha]^{25}_{436}$ +120° (*c* 0.71, chloroform), was heated at 90° in concentrated sulfuric acid for 1.5 hr. The dark brown solution was poured into 50 ml of water which was taken to pH 8 with sodium carbonate and extracted with three 25-ml portions of chloroform. The organic extracts were combined, dried and filtered, and the solvent was removed *in vacuo* to yield a yellow semisolid which was chromatographed (silica gel, ethyl acetate), yielding 0.59 g (76.6%) of pure (−)-**4b**, mp 123–123.5°. The compound was recrystallized from dichloromethane–ether yielding white prisms, mp 124–125°. It had specific rotations of $[\alpha]^{25}_{436}$ −39.0° and $[\alpha]^{25}_{546}$ −24.8° (*c* 0.86, chloroform). Its ir spectrum and tlc behavior were identical with those of its racemic counterpart. *Anal.* Calcd for C_8H_5SBrNO: C, 39.02; H, 3.28. Found: C, 39.14; H, 3.46.

(+)-(*R*)-5-Bromo-2,3-dihydrobenzo[*b*]thiophen-1-imide 1-Oxide ((+)-4b). Isomer A (see above), 3.5 g, $[\alpha]^{25}_{436}$ +47° (*c* 0.70, chloroform), was similarly hydrolyzed to give 1.13 g (61%) of sulfoximide. After three recrystallizations from benzene, (+)-**4b** gave mp 121–122°, $[\alpha]^{25}_{436}$ +35.1° (*c* 1.38, chloroform). This corresponds to an optical purity of 91%. Its spectral and tlc behavior were identical with its enantiomer. *Anal.* Calcd for C_8H_5BrNOS: C, 39.02; H, 3.28. Found: C, 39.32; H, 3.33.

(+)-(*S*)-5-Bromo-2,3-dihydrobenzo[*b*]thiophene 1-Oxide ((+)-1b). From 0.60 g of sulfoximide (−)-**4b**, $[\alpha]^{25}_{436}$ −38.5° (*c* 0.86, $CHCl_3$), and 0.75 g of nitrosyl hexafluorophosphate was obtained (see preparation of (−)-**1a** for procedure) 0.65 g of a crude yellow solid, mp 101–107°. Chromatography of this material on 40 g of silica gel (ethyl acetate) gave 0.51 g (90%) of material, mp 105–107°, $[\alpha]^{25}_{546}$ +198° and $[\alpha]^{25}_{436}$ +369.7° (*c* 0.86, $CHCl_3$). After three recrystallizations of this material from benzene–hexane, material was obtained, mp 114–115°, $[\alpha]^{25}_{546}$ +246.0° and $[\alpha]^{25}_{436}$ +458.8° (*c* 0.86, $CHCl_3$). A portion of this was sublimed at 65–70° (0.05 mm), mp 113–114°, $[\alpha]^{25}_{546}$ +247.7°, $[\alpha]^{25}_{436}$ +462° (*c* 0.66, $CHCl_3$). *Anal.* Calcd for C_8H_7BrOS: C, 41.58; H, 3.05. Found: C, 41.88; H, 3.26.

Deimidation of the same sample of (−)-**4b** was also carried out with nitrous acid as follows.[12] Sulfoximide, 0.3984 g, was dissolved in 15 ml of 4 *N* sulfuric acid. Sodium nitrite (0.228 g) was dissolved in 5 ml of water and added to the acidic solution. The reaction was stirred at 25° for 1 hr after which it was extracted with three 15-ml portions of chloroform. The organic extracts were

(25) P. D. Bartlett and L. H. Knox, *Org. Syn.*, **45**, 14 (1965).

Table I. Rate Constants for the Reaction of (+)-5 with DIM in Benzene at 25.0 ± 0.2°

Run	$[(+)\text{-}5]_0$, M	$[DIM]_0$, M	Ratio[a]	n[b]	10^5k_2, M^{-1} sec^{-1}	r[d]	10^2k_3, M^{-2} sec^{-1}	r[d]	%[e]
1	0.0986	0.1000	1.01	14	10.0 ± 0.5[c]	0.990	15.2 ± 0.7	0.990	16.8
2	0.01292	0.04725	3.7	17	5.0 ± 0.2	0.983	0.15 ± 0.008	0.982	37
3	0.01305	0.0315	2.4	12	1.5 ± 0.07	0.995	0.12 ± 0.003	0.996	16.7
4	0.01301	0.01565	1.2	8	0.33± 0.07	0.983	0.25 ± 0.017	0.986	6.1

[a] Ratio = $[DIM]_0/[(+)\text{-}5]_0$. [b] n = number of data points. [c] Error is expressed as one standard deviation. [d] The correlation coefficient obtained from the least-squares treatment is r. [e] % conversion used in kinetic treatment.

combined and dried over sodium sulfate, and the solvent was removed *in vacuo* to yield 0.3858 g of an off-white solid, mp 115–116.5°, $[\alpha]^{25}_{546}$ +250.3° (*c* 0.88, chloroform). Recrystallization of (+)-**1b** from benzene–hexane gave white prisms, mp 114.5–115.5°, $[\alpha]^{25}_{546}$ +253.3° (*c* 0.88, chloroform). Therefore the reaction proceeded in quantitative yield and 99% stereospecificity. The spectral and tlc behavior were identical with material obtained above.

***N*-*p*-Toluenesulfonyl-5-bromo-2,3-dihydrobenzo[*b*]thiophene-1-imide (2b).** Sulfoxide **1b,** 0.5064 g, in dry pyridine at 0° was treated with 1.1636 g of DIM in dry pyridine to give 0.72 g (91%) of **2b** (see preparation for **2a** for procedure), mp 164–166°, which when recrystallized from acetone–hexane gave white prisms, mp 169.5–170°. Its ir spectrum showed strong absorptions at 7.75 and 8.00 (sulfonyl) and at 10.49 μ. Its nmr spectrum showed a complex aromatic multiplet at δ 7.16–7.82 (7 H), a complex multiplet for the methylene protons centered at 3.60 (4 H), and a sharp methyl singlet at 2.42 ppm (3 H). *Anal.* Calcd for $C_{15}H_{14}S_2O_2NBr$: C, 46.88; H, 3.67. Found: C, 46.72; H, 3.53.

(+)-(*R*)-*N*-*p*-Toluenesulfonyl-5-bromo-2,3-dihydrobenzo[*b*]thiophene-1-imide ((+)-2b). Sulfoxide (+)-**1b,** 0.1088 g, $[\alpha]^{25}_{546}$ +246° (*c* 0.83, chloroform, 98% optically pure), and DIM, 0.3243 g, in 10 ml of dry pyridine at 0° in an inert atmosphere for 1 hr gave (after chromatographic purification of the product on 20 g of silica gel with ethyl acetate) 0.13 g (98%) of (+)-**2b**, mp 173.5–174.5°, $[\alpha]^{25}_{546}$ +158.3° and $[\alpha]^{25}_{436}$ +353.5° (*c* 0.55, $CHCl_3$).

Recrystallization of this material did not change its properties, and it was judged to be essentially optically pure. Its spectral and tlc behavior was the same as that of **2b**. *Anal.* Calcd for $C_{15}H_{14}S_2O_2NBr$: C, 46.88; H, 3.67. Found: C, 47.11; H, 3.74.

(+)-(*S*)-*N*-*p*-Toluenesulfonyl-5-bromo-2,3-dihydrobenzo[*b*]thiophene 1-Oxide ((+)-3b). Sulfoximide (−)-**4b,** 0.149 g, $[\alpha]^{25}_{436}$ −38.5° (*c* 1.65, chloroform), and 0.2355 g of tosyl chloride in 15 ml of pure pyridine were stirred at 25° for 3 hr, poured into 20 ml of water, and stirred an additional 20 min. The product was isolated by the usual extraction procedure and was chromatographed on 20 g of silica gel with ethyl acetate as developer to give 0.24 g (~100%) of (+)-**3b**, $[\alpha]^{25}_{546}$ +114.9° and $[\alpha]^{25}_{436}$ +249.1° (*c* 0.78, $CHCl_3$). When recrystallized from methanol, (+)-**3b** was obtained as prisms, mp 142–143°, $[\alpha]^{25}_{546}$ +115.6° (*c* 1.02, $CHCl_3$). *Anal.* Calcd for $C_{15}H_{14}S_2O_3NBr$: C, 45.00; H, 3.52. Found: C, 45.10; H, 3.54.

Racemic **3b** similarly prepared from **4b** gave (~98%) mp 170–171°. *Anal.* Calcd for $C_{15}H_{14}S_2O_3NBr$: C, 45.00; H, 3.52. Found: C, 45.05; H, 3.67.

Oxidation of (+)-2b to (+)-3b. Sulfimide (+)-**2b,** 52 mg, $[\alpha]^{25}_{546}$ +173° (*c* 0.38, chloroform), was heated in 6 ml of acetic acid for about 5 min. Potassium permanganate (60.6 mg) in 2 ml of water was added, and the mixture was heated for 15 min on a steam bath. The product was isolated by the usual extraction and chromatographic procedure to give 41 mg (76%) of (+)-**3b**, $[\alpha]^{25}_{546}$ +91.5° (*c* 0.345, $CHCl_3$), 80% optically pure. The tlc and spectral properties of this material were identical with those of **3b**.

Imidation of (+)-1b to Give (+)-3b. Application of the Kwart–Kahn method of imidation[9] to 0.102 g of (+)-**1b**, $[\alpha]^{25}_{546}$ +248° (*c* 0.66, chloroform, 99% optically pure), gave 0.0078 g (4%) of (+)-**3b**, $[\alpha]^{25}_{546}$ +83.0° (*c* 0.31, $CHCl_3$), pure to tlc and identical in spectral properties with those of authentic material. The reaction was 73% stereospecific.

Conversion of Sulfoxide (+)-1b to (−)-2b in Benzene. Sulfoxide (+)-**1b**, 0.0998 g (0.432 mmol), $[\alpha]^{25}_{546}$ +248° (*c* 0.66, chloroform), and 0.172 g (0.481 mmol) of DIM were dissolved in 10 ml of anhydrous benzene. Approximately 1.2 ml was removed for a kinetic run, and the remainder was allowed to stand for 24 hr at 25°. The product was isolated in the usual way to give 0.087 g (52%) of (−)-**2b**, mp 175–176°, $[\alpha]^{25}_{546}$ −165.2° (*c* 0.66, $CHCl_3$), which corresponds to an optical purity of 94% (reaction proceeded with 95% stereospecificity). The starting sulfoxide was recovered, wt 0.0195 g, mp 101–103°, $[\alpha]^{25}_{546}$ +253° (*c* 0.096, $CHCl_3$), optically pure. The (−)-**2b** isolated exhibited tlc behavior identical with its enantiomer. *Anal.* Calcd for $C_{15}H_{14}S_2O_2NBr$: C, 46.88; H, 3.67. Found: C, 47.11; H, 3.67.

Conversion of Sulfoxide (+)-1b to (−)-2b in Dichloromethane. A solution of 0.0451 g of (+)-**1b** (0.195 mmol), $[\alpha]^{25}_{546}$ +248° (*c* 0.66, chloroform), and 0.1975 g of DIM in 10 ml of dry benzene was stirred at 26° for 3 hr and the products were isolated as usual. Sulfimide, wt 0.0675 g (90%), gave mp 153–159°, $[\alpha]^{25}_{546}$ −60.8° (*c* 0.75, $CHCl_3$), 35% optically pure. Its spectral and tlc properties resembled that of its enantiomer.

Rate of Reaction of Sulfoxide (−)-1a with *N*-Sulfinyl-*p*-toluenesulfonamide in Dry Pyridine at 25°. The optical rotation of a dry pyridine solution, 0.1269 *M* in sulfoxide (−)-**1a**, $[\alpha]^{25}_D$ −288.1° (*c* 1.35, pyridine), and 0.1339 *M* in *N*-sulfinyl-*p*-toluenesulfonamide was measured at intervals following initial preparation of the solution. A 0.1-dm, water-jacketed polarimeter cell maintained at 25° and a wavelength of 589 nm were employed. A total of eight data points were gathered, and the reaction was followed until the rotation was essentially constant (200 hr). The initial rotation decayed from α_{obsd} of −0.556° at zero time to −0.122° at 200 hr. The final rotation corresponded to a rotation expected from sulfimide (−)-**2a** of 42% optical purity. Third-order integrated rate constants[3a] were calculated for each data point based on the assumption that the sulfimide product was produced with the same stereospecificity (42%) throughout the reaction. Equation 1 was used to calculate the concentrations of sulfimide (−)-**2a** at each time. In this equation, α is the observed rotation of the solution in degrees, l is the length of the polarimeter cell, $[\alpha]_{1a}$ and $[\alpha]_{2a}$ are the specific rotations

$$[\mathbf{2a}] = \frac{1000\alpha - [\alpha]_{1a}M_{1a}[\mathbf{1a}]_0}{l[\alpha]_{2a}M_{2a} - l[\alpha]_{1a}M_{1a}} \quad (1)$$

of sulfoxide **1a** and sulfimide **2a**, and M_{1a} and M_{2a} are the molecular weights of **1a** and **2a**, respectively. Optically pure (−)-**2a** has a specific rotation of $[\alpha]^{25}_D$ −75.4° (*c* 1.19, pyridine), and after 200 hr the reacting solution gave $[\alpha]^{25}_D$ −31.5°.

Kinetics of Reaction of (+)-5 with DIM in Benzene. Rate data were obtained polarimetrically in a 1-dm, thermostated cell at 25.0 ± 0.2° at 578 nm. Grease-coated glass plugs were used to seal the cell. Benzene was refluxed over lithium aluminum hydride for several hours, distilled into an oven-dried flask, and stored over metallic sodium in a nitrogen atmosphere drybox. Sulfoxide (+)-**5** was vacuum dried overnight and stored in the drybox. Sulfur diimide, DIM, was stored in the drybox. All equipment to be used in the preparation of samples was oven dried overnight before introduction into the drybox. Solutions were prepared in the drybox by weighing out (+)-**5** and DIM into a 2-ml volumetric flask and dissolving the mixture in benzene. Zero time was taken at the point when solvent was added. The polarimetric cell was sealed in the drybox and immediately transferred to the polarimeter.

Table II. Polarimetric Control Data for Kinetic Study of Reaction (+)-**5** → (+)-**6** in Benzene at 25°

Compd	Time, min	Observed rotation, deg Initial	Final	Δ%
(+)-**5**	1215	1.546	1.547	0.06
(−)-**6**	1230	−1.444	−1.448	0.3
(+)-**5** and (−)-**6**	450	−0.067	−0.070	4.4[a]
(−)-**6** and DIM	1590	−0.420	−0.417	0.7
(+)-**5** and NSA[b]	2635	1.550	1.520	1.4

[a] Rotation readings were within the error of the instrument. [b] *N*-Sulfinyl-*p*-toluenesulfinamide, dichloromethane as solvent. No trace of **6** after run detectable by tlc.

Table I summarizes the data. Attempts were made to fit the kinetics to the integrated second-order rate expression, rate = k_2·[(+)-**5**][DIM], and to the integrated third-order rate expression, rate = k_3[(+)-**5**][DIM]^2, where k_2 is the second-order and k_3 the third-order rate constant. The data points used in each run were the maximum number obtained as the reaction proceeded that would provide a straight line when subjected to a least-squares regression treatment with correlation coefficients greater than 0.98. The average rate constants obtained were $k_2 = 0.0025 \pm 0.001\ M^{-1}\ min^{-1}$ and $k_3 = 2.3 \pm 2.2\ M^{-2}\ min^{-1}$, in which the error is expressed as the standard deviation from the mean. The probable error in k_2 was 32%, and in k_3 was 96%. At the completion of each run, the solution in the polarimeter cell was checked by tlc, and in no case were extraneous products observed. Table II indicates the results of control experiments. The 5–6% racemization observed in the overall reaction was disregarded in the kinetic treatment.

The nonreproducibility of the rate constants of Table I may arise from several sources. Since DIM was only sparingly soluble in benzene, measurements had to be made at low concentrations, and its fluffy character made it difficult to weigh in the drybox. Its extreme hygroscopic properties prohibited handling it outside of a drybox.

Estimate of Rate Constant of (+)-1 with DIM in Benzene. Application of the same polarimetric technique to the reaction of (+)-**1** with DIM in benzene at 25° at approximately the same concentrations as for (+)-**5** and DIM gave $k_2 = 4.68 \pm 1.7 \times 10^{-3}\ M^{-1}\ sec^{-1}$. Control experiments similar to those applied to (+)-**5** gave the same results.

Stereochemistry of Sulfur Compounds. VI. Multiple Termolecular Ligand Transfers between Sulfur–Carbon–Carbon, Sulfur–Sulfur–Carbon, or Sulfur–Carbon–Phosphorus Centers[1]

Donald C. Garwood,[2] Michael R. Jones, and Donald J. Cram*

Contribution No. 3024 from the Department of Chemistry, University of California at Los Angeles, Los Angeles, California 90024. *Received August 12, 1972*

Abstract: In acetonitrile at 25°, *p*-toluenesulfonyl isocyanate (*p*-tosyl isocyanate) and (+)-(*R*)-methyl *p*-tolyl sulfoxide ((+)-**1**) gave (−)-(*S*)-*N*-*p*-toluenesulfonylmethyl-*p*-tolylsulfimide, (−)-(*S*)-**2**, with net inversion of configuration, but by a mechanism that competitively racemized both starting material and product. All three components were required for the racemization reaction of (−)-**2**. Conversion of **1** to **2** was roughly first order in **1** and second order in isocyanate reagent. Reaction of (+)-(*R*)-**1** with *p*-tosyl isocyanate in acetonitrile in the presence of *tert*-butyl methyl sulfide (**3**) gave (−)-(*S*)-**2** with 80% net inversion (48% yield) and *N*-*tert*-butyl-*N'*-*p*-toluenesulfonylacetamidine (**4**). Reaction of *tert*-butyl methyl sulfoxide (**5**) with *p*-tosyl isocyanate in acetonitrile also gave **4**. In the presence of *N*-*p*-nitrobenzenesulfonyltetramethylenesulfimide (**6**), **1** with *p*-tosyl isocyanate in acetonitrile gave **2**, *N*-*p*-nitrobenzenesulfonylmethyl-*p*-tolylsulfimide (**7**) and *N*-*p*-toluenesulfonyltetramethylenesulfimide (**8**), as well as recovered **6**. Treatment of **1** with *p*-tosyl isocyanate and diethyl sulfide in acetonitrile gave mainly *N*-*p*-toluenesulfonyldiethylsulfimide (**9**) and methyl *p*-tolyl sulfide (**10**). All three components were required for reaction. By nmr a transient intermediate was detected in the same reaction when dimethyl sulfide was substituted for diethyl sulfide. Reaction of **1** and *p*-tosyl isocyanate in acetonitrile with triphenylphosphine (**11**) produced methyl *p*-tolyl sulfide (**10**) and triphenylphosphine oxide (**12**). All three components were required for reaction, and the *p*-tosyl isocyanate acted only as a catalyst. In acetonitrile, sulfimide **2**, triphenylphosphine (**11**), and *p*-tosyl isocyanate gave triphenylphosphine oxide (**12**), *N*-*p*-toluenesulfonyltriphenylphosphinimide (**13**), recovered **2**, and *p*-toluenesulfonamide (after water treatment). All three components were required for reaction. In acetonitrile, *N*-*p*-nitrobenzenesulfonylmethyl-*p*-tolylsulfimide (**7**), triphenylphosphine, and *p*-tosyl isocyanate gave **10**, **12**, **13**, *N*-*p*-nitrobenzenesulfonyltriphenylphosphinimide (**14**), *p*-nitrobenzenesulfonamide, and *p*-toluenesulfonamide (after water treatment). General cyclic, termolecular mechanisms are postulated for ligand transfers between sulfur–carbon–carbon, between sulfur–sulfur–carbon, and between sulfur–carbon–phosphorus centers.

Earlier papers reported on the molecularity and stereochemical course of the conversion of methyl *p*-tolyl sulfoxide (**1**) to *N*-*p*-toluenesulfonyl-*S*-methyl-*S*-*p*-tolylsulfimide (**2**) with *N*,*N*-bis(*p*-toluenesulfonyl)-sulfur diimide.[3] In pyridine, the reaction was overall termolecular and was interpreted as going through a six-membered ring composed of three sulfur atoms connected by nitrogens and oxygens. The inversion of configuration was explained by an equatorial–equatorial substitution on a trigonal bipyramid at chiral sulfur (see A).[3a] In benzene, the reaction was overall bimolecular and occurred with retention of configuration. The stereochemical course of substitution was explained through an equatorial–axial substitution on a trigonal bipyramid at chiral sulfur (see B).[3b] In methylene dichloride, the substitution went with predominant retention, but both starting material and product were racemized during the conversion. These latter reactions were interpreted as involving multiple ligand exchanges of the equatorial–equatorial variety between three sulfur atoms through intermediates such as C and D.

This paper reports results of a survey of the general

(1) This investigation was supported by U. S. Public Health Service Research Grant No. GM 12640-09 from the Department of Health, Education, and Welfare.

(2) National Institutes of Health Special Research Fellow, 1969–1970.

(3) (a) D. J. Cram, J. Day, D. R. Rayner, D. M. von Schriltz, D. J. Duchamp, and D. C. Garwood, *J. Amer. Chem. Soc.*, **92**, 7369 (1970); (b) F. G. Yamagishi, D. R. Rayner, D. C. Garwood, E. T. Zwicker, and D. J. Cram, *ibid.*, **95**, 1916 (1973).