shown by nmr (CCl_4) to be a 1:1 mixture of the β-hydroxysulfoximine (14.7%) and phenyl methyl sulfone.[7] Each product was identified by comparative nmr and/or ir with available samples.

Reaction of 25 with NaH in DMSO. The salt **25** (3.60 mmol) was generated (see above) in 30 ml of dichloromethane at 0–10° for 3.5 hr. The solvent was removed *in vacuo* (below 25°) at the aspirator and then under high vacuum (0.05 nm) to give a white, noncrystalline solid. This was dissolved in 10 ml of dry DMSO, and the solution was added to a magnetically stirred suspension of 3.72 mmol of NaH (0.157 g of a 57% dispersion in mineral oil, washed with several portions of pentane) in 5 ml of DMSO under nitrogen and at 25°. After 17 hr, 100 ml of pentane was added, and the mixture was quenched in 200 ml of water. The phases were separated, and the aqueous portion was extracted several times with pentane. The combined pentane fractions were dried (K_2CO_3), and the solvent was removed *in vacuo* at room temperature. A nmr (CCl_4) of the crude reaction mixture showed that none of the oxirane **7** was present. Column chromatography on silica gel (gradiently eluted with pentane–dichloromethane) gave 0.553 g (74.3%) of *trans*-1-benzoyl-2-phenylcyclopropane (**7**), 0.096 g (12.9%) of *trans*-benzalacetophenone, and 0.2864 g (47.1%) of *N,N*-dimethylbenzenesulfinamide.

Reaction of 25 with NaH in THF. A THF solution of **25** was treated with sodium hydride, and the mixture was stirred for 12.5 hr before being worked up as described above. From an nmr (CCl_4) of the crude reaction mixture, it was found to be composed of cyclopropane **7**, *trans*-benzalacetophenone, and THF polymer. None of the oxirane **6** or starting β-hydroxysulfoximine was present. The mixture was not separated into its components.

Treatment of *trans*-Benzalacetophenone with (Dimethylamino)-methylphenyloxosulfonium Fluoroborate (3) in Dichloromethane and in the Presence of 0.5 *M* Aqueous NaOH. To a solution of 1.154 g (5.55 mmol) of *trans*-benzalacetophenone and 1.554 g (5.73 mmol) of **24**, in 75 ml of dichloromethane at 25°, was added 75 ml of 0.5 *M* aqueous NaOH. The mixture was stirred for 20.5 hr. The water and dichloromethane phases were separated, and the water portion was extracted with dichloromethane. The combined organic fractions were dried (K_2CO_3), and the solvent was removed *in vacuo* to give a pale yellow oil. Column chromatography on silica gel (eluted with 80% pentane–20% dichloromethane) gave 0.897 g (72.8%) of *trans*-1-benzoyl-2-phenylcyclopropane (mp 40–44°, lit.[8] mp 45–48°) and 0.192 g (~16%) of benzalacetophenone containing a small amount of methyl phenyl sulfone as an impurity. Each product was identified by comparative ir and nmr.

Stereochemistry of α-Halo Sulfoxides. II. Interdependent Stereochemistry at Sulfur and α-Carbon in the α-Halogenation of Sulfoxides[1]

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Abstract: α-Halogenation of alkyl aryl and dialkyl sulfoxides by electrophilic halogenating reagents follows two different stereochemical processes which involve either double retention or double inversion at sulfur and carbon. When the α carbon is a chiral or prochiral center, optically active sulfoxides afford only one of the two possible diastereomeric α-halo sulfoxides, whose optical purity and chirality depend on the nature of the substrate and the reaction conditions. Possible mechanisms of these reactions, involving stereospecific migration of the halogen from sulfur to the α carbon in a halooxosulfonium salt intermediate, are discussed. Reductive dehalogenation of α-halo sulfoxides and α-halo sulfones with zinc and sodium sulfite usually proceeds with inversion of configuration at carbon.

Conversion of methyl aryl sulfoxides into chloromethyl and bromomethyl derivatives by electrophilic halogenating reagents in pyridine is accompanied by retention of configuration at the sulfur atom, but this same reaction proceeds with inversion in the presence of a molar excess of silver(I) nitrate.[1] Both processes are highly stereoselective, and the most relevant feature is that they occur seemingly without any substitution of ligands at the chiral center. This has been explained assuming that the formation of the new sulfur–halogen bond in the halooxosulfonium salt intermediate is followed by breaking of the same bond according to two different mechanisms of retention or inversion.[1]

Preliminary results[2] indicated a close relationship between the stereochemical courses at sulfur and α carbon when the latter is a chiral or prochiral center.

In this paper we report the results of the study of the stereochemical processes at sulfur and carbon and of the factors by which they are affected.

Results

Alkyl *p*-Tolyl Sulfoxides. When in alkyl *p*-tolyl sulfoxide **1** the methyl group is replaced by the ethyl or isopropyl group, α-halogenation is accompanied by inversion of sign of optical rotation (Table I).

The sign of the Cotton effect, attributed[3,4] to the n–π* transition of the sulfinyl group, in compounds **2** and **3**, is opposite to that of products **5a,b** and **6a,b**. This, together with the reduction with zinc and methanol of (−)-bromo derivatives, **5b** and **6b** to the (−)-sulfoxides **2** and **3**, enantiomeric to the starting ones,

(1) For part I of this series, see M. Cinquini, S. Colonna, R. Fornasier, and F. Montanari, *J. Chem. Soc., Perkin Trans. 1*, 1886 (1972).

(2) (a) M. Cinquini, S. Colonna, and F. Montanari, *Chem. Commun.*, 607 (1969); (b) *ibid.*, 1441 (1970).

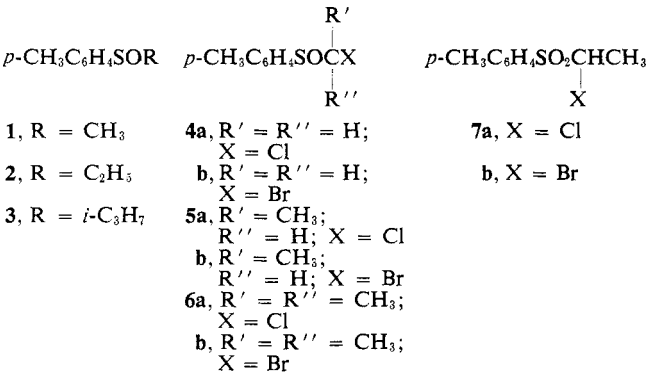
(3) (a) K. K. Andersen, W. Gaffield, N. E. Papanikolaou, J. W. Foley, and R. I. Perkins, *J. Amer. Chem. Soc.*, **86**, 5637 (1964); (b) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *ibid.*, **87**, 1958 (1965).

(4) M. Cinquini, S. Colonna, I. Moretti, and G. Torre, *Tetrahedron Lett.*, 2773 (1970).

Table I. α-Halogenation of Optically Active Alkyl *p*-Tolyl Sulfoxides

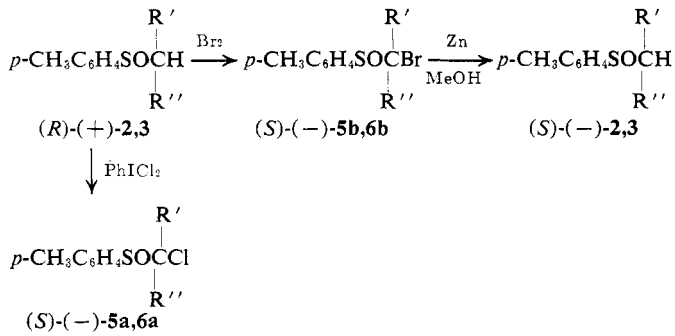
Alkyl	Sulfoxide $[\alpha]^{25}D$,[a] deg	α-Halo sulfoxide $[\alpha]^{25}D$,[a] deg (inversion, %) PhI-Cl_2[b]	$PhICl_2$-$AgNO_3$[b]	Br_2[b]	Br_2-$AgNO_3$[b]
Me	+144	+92[c]	−106[c]	+153[c] (14)	−196[c] (99)
Et	+189	−7	−153	−83 (81)	−115 (93)
i-Pr	+178	−23	−119	−84 (97)	−88 (100)

[a] In acetone, *c* 1. [b] Halogenating reagent. [c] Values taken from ref 1.



in a reaction not involving the ligands at sulfur, indicates that α-halogenation occurs in these cases with prevailing inversion of configuration at the sulfinyl group (Scheme I).

Scheme I



The amount of inversion depends on the complexity of the alkyl chain (*i*-Pr > Et) and on the nature of the halogen (Br > Cl); it reaches 97% in the bromination of isopropyl sulfoxide **3** and is further increased by working in the presence of a molar excess of silver(I) nitrate.

Conversion of ethyl *p*-tolyl sulfoxide (**2**) into the corresponding halo derivatives **5a,b** introduces a second chiral center at the α carbon. In compounds **5** the configurational homogeneity at carbon is related to that at sulfur, as indicated by the specific rotations of sulfones **7**, obtained by oxidation of sulfoxides **5** (Table II).

Moreover, the two samples of **5a** with different optical activities, obtained from **2** in the presence and in the absence of silver(I) nitrate, show identical nmr spectra, and thus have identical diastereomeric contents. The different optical activity is therefore due to different ratios of enantiomers. This conclusion follows from the fact that the nmr spectrum of the mixture of diastereomeric α-chloro sulfoxides **5a,c** obtained from **2** with *tert*-butyl hypochlorite under nonstereospecific conditions[5] shows two different quartets for the methine protons. The pure diastereoisomer **5c** was obtained by inversion of **5a** *via* triethyloxonium fluoroborate.[6]

Table II. Specific Rotations[a] of α-Haloethyl Sulfoxides **5** and Sulfones **7**

Sulfoxide	$[\alpha]^{25}D$, deg	Sulfone	$[\alpha]^{25}D$, deg
5a	−153	**7a**	−6.9
5a	−7	**7a**	−0.5
5b	−115	**7b**	−14.9

[a] In acetone, *c* 1.

The results obtained in the α-halogenation of the ethyl derivative **2** are consistent with those previously reported.[2a,7-9] When the α carbon is a prochiral center, only one of the two possible diastereomeric α-halo sulfoxides is obtained. Thus two opposite, competitive stereochemical paths at sulfur appear related to two opposite, competitive stereochemical paths at carbon. In principle, either retention and inversion of configuration at sulfur are accompanied by retention and inversion at carbon, respectively, or retention and inversion at sulfur are accompanied by inversion and retention at carbon, respectively. The first alternative is demonstrated to apply to the systems of the present study, *i.e.*, the (*S,S*)-(+)-2-octyl sulfoxide (**10**) and the (*R,R*)-(+)- and (*R,S*)-(+)-2-octyl *p*-tolyl sulfoxides (**14a** and **14b**).

(*S,S*)-(+)-Bis-2-octyl Sulfoxide. The (*S,S*)-(+)-bis-2-octyl sulfoxide (**10**) was obtained by oxidation with *N*-chlorobenzotriazole[10] of the corresponding (*S,S*)-(+)-bis-2-octyl sulfide (**9a**), prepared from (*S*)-(+)-2-octyl mercaptan (**8**) and (*R*)-(−)-2-octyl *p*-toluenesulfonate (Scheme II).[11]

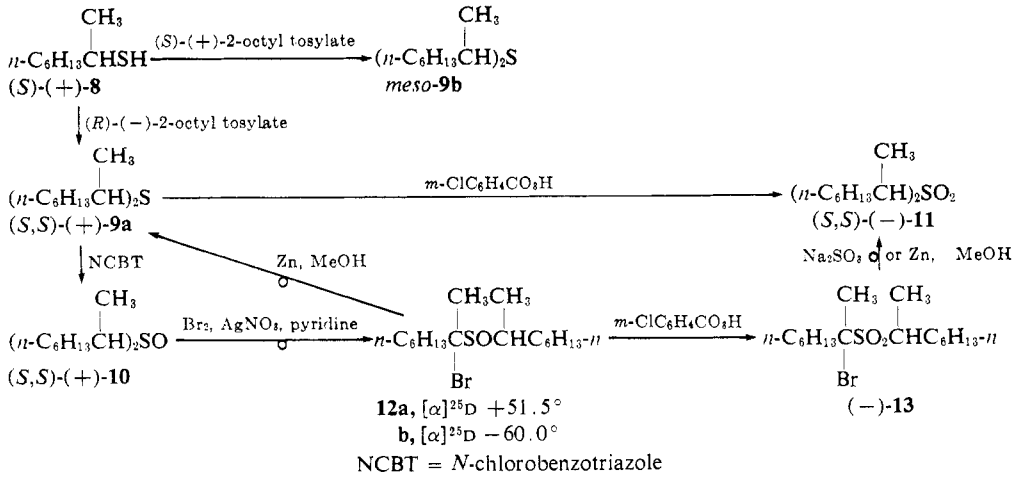
Bromination of **10** with bromine and silver(I) nitrate afforded two epimeric α-bromo sulfoxides (+)-**12a** and (−)-**12b** (Scheme II).[12]

Oxidation of **12a** and **12b** gave the same bromo sulfone **13**, whose reduction by sodium sulfite or by zinc and methanol afforded the (−)-sulfone **11**, identical with that obtained *via* oxidation of (+)-sulfide **9a**. Reduction of bromo sulfoxides **12a** and **12b** with zinc and methanol and subsequent oxidation of the (+)-sulfide **9a** gave again the (−)-sulfone **11**.

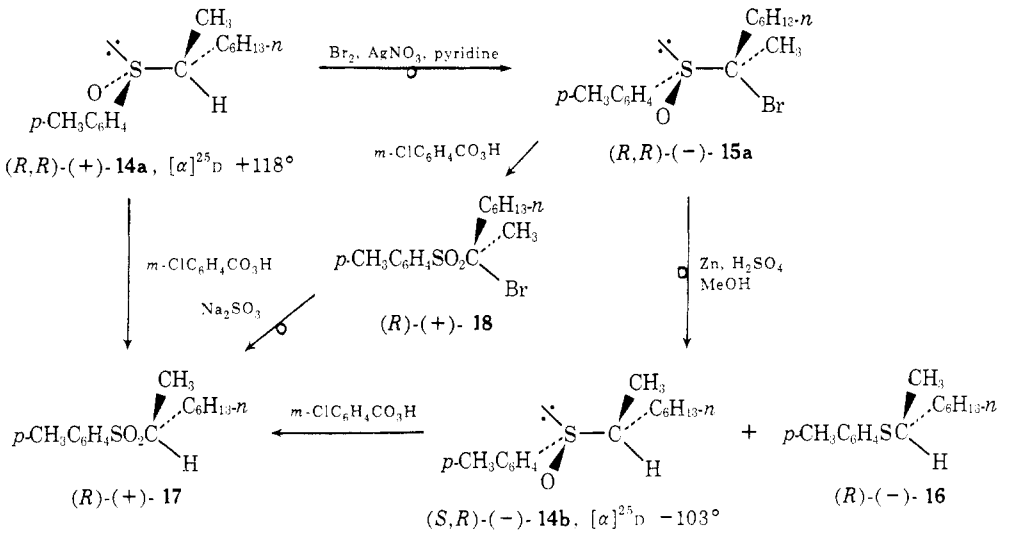
The sequence of reactions shown in Scheme II does not establish the stereochemical course of the reactions at sulfur, but indicates that the halogenation and reduction at the asymmetric carbon must have gone with overall retention. In other words, conversions **10** → **12**, **12** → **9a**, and **13** → **11** must proceed all with retention or all with inversion at carbon.

(5) S. Iriuchijima and G. Tsuchihashi, *Tetrahedron Lett.*, 5259 (1969).
(6) (a) C. R. Johnson, *J. Amer. Chem. Soc.*, **85**, 1020 (1963); (b) C. R. Johnson and D. McCants, Jr., *ibid.*, **87**, 5404 (1965).
(7) M. Cinquini and S. Colonna, *Boll. Sci. Fac. Chim. Ind. Bologna*, **27**, 201 (1969).
(8) M. Cinquini and S. Colonna, *Synthesis*, **4**, 259 (1972).
(9) M. Cinquini and S. Colonna, *J. Chem. Soc., Perkin Trans. 1*, 1883 (1972).
(10) W. D. Kingsbury and C. R. Johnson, *Chem. Commun.*, 365 (1969).
(11) *meso*-Bis-2-octyl sulfide (**9b**), obtained from (*S*)-(+)-2-octyl mercaptan (**8**) and (*S*)-(+)-2-octyl *p*-toluenesulfonate is not suitable for a stereochemical study. Its specific rotation, close to zero (see Experimental Section), is nevertheless an indication of the high degree of enantiomeric purity of **8**, and, indirectly, of the diastereomeric purity of **9a**.
(12) In sulfoxide **10** the sulfinyl group is achiral, being bonded to two 2-octyl groups with the same configuration at carbon. These carbons occupy enantiotopic positions with respect to the sulfinyl group, so that bromination leads to two epimeric bromo sulfoxides **12a,b** with identical configurations at their carbons but of opposite configurations at their sulfur atoms.

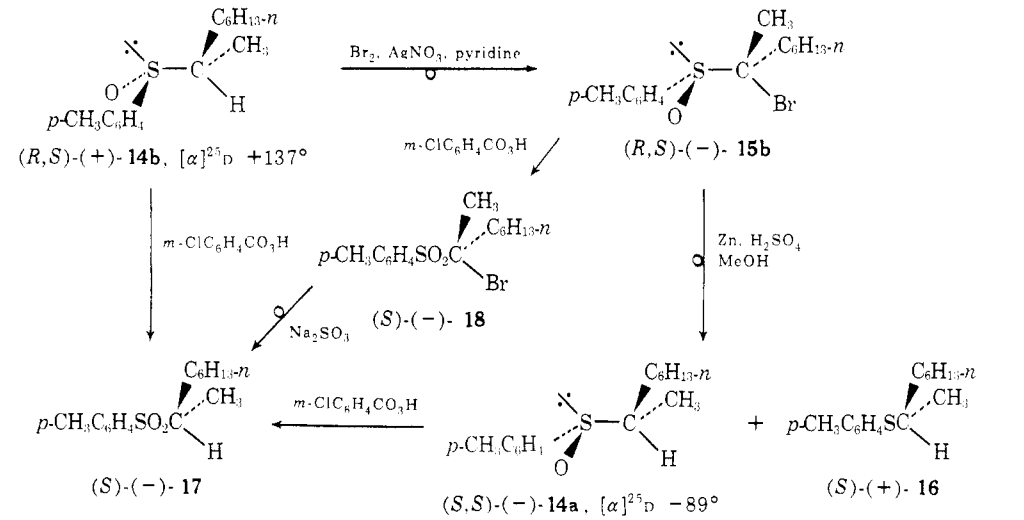
Scheme II



Scheme III



Scheme IV



2-Octyl *p*-Tolyl Sulfoxides. An analogous sequence of reactions (Schemes III and IV) was applied to the diastereomeric (*R*,*R*)-(+)-**14a** and (*R*,*S*)-(+)-**14b** 2-octyl *p*-tolyl sulfoxides of known configuration at sulfur and carbon.[3b] The inversion of sign of specific rotation met with in the conversion **14a** → **15a** and **14b** → **15b** suggests[3b] that the brominations are accompanied by inversion of configuration at the sulfur atom. This was confirmed by reduction of **15a** and **15b** to the (−)-sulfoxides **14b** and **14a**, respectively, which are obtained together with the corresponding sulfides (*R*)-(−)- and (*S*)-(+)-**16**. The sulfoxides are enantiomers of the (+)-**14b** and (+)-**14a** that served as starting materials.

Oxidation of the mixture of sulfoxide (−)-**14b** and sulfide (−)-**16** gave the sulfone (*R*)-(+)-**17**. Oxida-

tion of the mixture (−)-**14a** and (+)-**16** gave (*S*)-(−)-**17**.

The sulfones were identical with those obtained by reduction with sodium sulfite of (+)- and (−)-bromo sulfones **18** and with those obtained *via* oxidation of (+)-sulfoxides **14a** and **14b**, respectively.

The overall stereospecificity of the reactions involving the carbon atom is very high, in the range 90–100% (see Experimental Section).

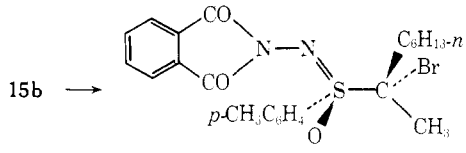
As shown in Schemes III and IV, bromination of sulfoxides and subsequent reduction of bromo sulfoxides and of bromo sulfones must occur with overall retention at carbon, *i.e.*, both reactions going with retention or both with inversion. Conversions of sulfoxides (*R,R*)-(+)-**14a** and (*R,S*)-(+)-**14b** into epimeric (*S,R*)-(−)-**14b** and (*S,S*)-(−)-**14a**, respectively, show the overall stereochemical course at sulfur to be that of inversion in the sequences **14a** → **15a** → **14b** and **14b** → **15b** → **14a**.

X-Ray Analysis of Sulfoximides. The previous results do not allow us to define the stereochemistry at carbon in the α-halogenation of sulfoxides, unless the stereochemistry of reductive dehalogenation of bromo sulfoxides or of the corresponding bromo sulfones is established.

Bordwell has shown[13] that reduction of benzylic bromo sulfones by sodium sulfite proceeds with retention of configuration at carbon, but it was questionable that we could generalize this only result to other bromo sulfones.

To solve this problem, the oily bromo sulfoxides (−)-**15a** and (−)-**15b** were transformed according to Rees[14] into the corresponding sulfoximides **19a**, mp 104–105°, $[\alpha]^{25}D$ +90° (*c* 1, acetone), and **19b**, mp 121–122°, $[\alpha]^{25}D$ +102° (*c* 1, acetone), a reaction which does not involve the α-carbon atom.

The structure of compound **19b** was determined by



19b

X-ray analysis, and the *R* and *S* absolute configurations were assigned to sulfur and carbon, respectively,[15] through the Hamilton's weighted *R* factor criterion. This means that in **14a,b** α-halogenation occurs with inversion of configuration at both sulfur and carbon. Since a prevailing or complete inversion at sulfur is encountered with suitable substrates and reaction conditions, and since any stereomutation at sulfur is related to any eventual stereomutation at carbon, it seems likely that inversion at each center constitutes a common stereochemical process in the compounds examined. The second stereochemical process which may compete with the former in the same substrates should therefore involve retention at both sulfur and carbon.

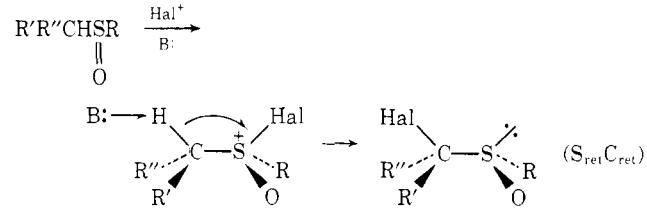
(13) F. G. Bordwell, E. Doomes, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **92**, 2581 (1970).

(14) D. J. Anderson, D. C. Horwell, E. Stanton, T. C. Gilchrist, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1317 (1972).

(15) G. D. Andreetti, G. Bocelli, and P. Sgarabotto, *Cryst. Struct. Commun.*, **2**, 171 (1973). We are deeply indebted to Professor Andreetti and to his coworkers for this structural determination. It has been also shown that compound **19a** has the expected (*R,R*) configuration: G. D. Andreetti, private communication.

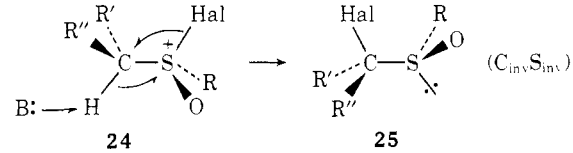
Discussion

The mechanism previously proposed[1] to explain the prevailing retention of configuration at sulfur in the halogenation of methyl aryl sulfoxides in the absence of silver(I) nitrate involves a concerted migration of an halo cation from sulfur to carbon. Since this mechanism requires the halo oxosulfonium ion to assume a syn-periplanar conformation **20**, in the case of α-alkyl



20 **21**

substituted sulfoxides it should also lead to retention of configuration at carbon, S_{ret} C_{ret}, when the latter is a chiral center. A syn-periplanar conformation **20** is unfavored by steric factors, and the experimental evidence indicating an increasing inversion at sulfur by increasing the substitution at the α carbon leads to the conclusion that this stereochemistry may be related to an enhanced stability of an anti-periplanar conformation **24**. In this the halogen could migrate as anion



24 **25**

from sulfur to carbon, while an electron pair is at the same time transferred in the opposite direction, thus leading to inversion at each center (S_{inv} C_{inv}).[16,17] This mechanism is formally similar to the diaxial–diequatorial rearrangement which takes place in alicyclic dihalides, carboxylic and sulfonic esters of halohydrins, and β-halo thioethers.[20,21] In all these compounds "it appeared that a sufficient, though not necessarily exclusive, requirement for the rearrangement was the presence in a 1,2-diaxial relationship of a good leaving group and a function capable of neighboring-group participation."[20b]

Our results indicate that inversion at sulfur is favored by the presence of silver ions that, as previously proposed,[1] seem to promote the migration of the halogen as anion, independently of the nature of the substrate. A blending of the two mechanisms explains the racemizations observed in appropriate systems, within a

(16) A less likely alternative to this mechanism seems to be the formation of a "pseudoylide," as previously proposed.[1]

(17) In both mechanisms the carbanion is assumed to be formed with retention. This may not be always the case, and formation of the carbanion with inversion would lead to the opposite configuration at carbon. Examples of reactions involving either retention or inversion of α-sulfinyl[18] and α-sulfonyl[13,19] carbanions have been reported.

(18) (a) T. Durst, R. Viau, and M. R. McClory, *J. Amer. Chem. Soc.*, **93**, 3077 (1971); (b) B. B. Jarvis, S. D. Dutkey, and H. L. Ammon, *ibid.*, **94**, 2136 (1972); (c) K. Nishihata and M. Nishio, *J. Chem. Soc., Perkin Trans. 2*, 1730 (1972), and references therein.

(19) (a) F. C. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **90**, 5298 (1968); (b) M. Gresser, *Mech. React. Sulfur Compounds*, **4**, 29 (1969); (c) S. Thyagarayan, *ibid.*, **4**, 115 (1969).

(20) (a) D. H. R. Barton and J. F. King, *J. Chem. Soc.*, 4398 (1958); (b) J. F. King, K. Abikar, D. M. Deaken, and R. G. Pews, *Can. J. Chem.*, **46**, 1 (1968); (c) J. F. King and K. Abikar, *ibid.*, **46**, 9 (1968), and references therein.

(21) We thank Professor S. Wolfe, Kingston, Canada, for the suggestion of this analogy.

diastereomeric species, which occurs in some instances, as in the ethyl derivative **2**.

The high stereospecificity of these reactions and especially the close relationship between the stereochemical courses at sulfur and carbon favor a synchronous or highly concerted process. It cannot be ruled out, however, that in other substrates a less concerted mechanism applies, that involves ion pairs capable of stereochemical reorganization. Thus competitive intermolecular reactions might intervene and lead to a reduced stereospecificity. The results on the halogenation of thianes S-oxides[22] and particularly the work by Marquet and coworkers[23] might involve such mechanisms. What remains to be explained is the extreme conformational preference that, whatever the mechanism, seems to accompany the attack by base on the halooxosulfonium salt.[2a] This feature is common to other electrophilic reactions at the carbon α to the sulfinyl group[24] or α to other functional groups of sulfur.[25] Possibly in **24** the conformational preferences are governed by the adjacent polar bonds at sulfur, in the context of the more general "gauche effect."[24]

Further comment is required on the stereochemistry of two other processes reported in this paper. X-Ray analysis of **19a,b** shows[13] that conversion of sulfoxides into phthalimidosulfoximides (likely by phthalimidonitrenes) proceeds with retention of configuration at sulfur. This confirms the stereochemistry previously suggested[26] by analogy with that of other imidation reactions of sulfoxides, particularly those leading to *N*-*p*-toluenesulfonylsulfoximides.[27,28]

Reduction by sodium sulfite of bromo sulfone **18** and likely of bromo sulfone **13** to the corresponding sulfones **17** and **11** occurs with inversion at carbon. This stereochemical course is opposite to that found[13] in the reduction of the diastereomeric α-bromo-α-phenyl ethyl sulfones. Other related facts are as follows: (i) some electrophilic reactions,[29] especially those involving sulfonyl,[13,19] and sulfinyl carbanions,[18] proceed with retention[18a,c,19b,c,29b] and other with inversion[18,19a,29c,d] at carbon, (ii) reductive dehalogenations of halo alkanes by zinc may proceed either with retention[30] or inversion[31] at carbon, and (iii) it is not clear if the mechanism of the reductions reported in Schemes I–IV is ionic or radical. Clearly, much work remains to be done to rationalize the stereochemistry of such reductions.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a Varian A-60 spectrometer; optical rotations were measured on a Perkin-Elmer 141 polarimeter and/or on a Perkin-Elmer P-22 spectropolarimeter.

Optically Active Alkyl *p*-Tolyl Sulfoxides. Optically active (*R*)-(+)-ethyl-**2**, $[\alpha]^{25}D$ +189° (*c* 1, acetone), (*R*)-(+)-isopropyl-**3**, $[\alpha]^{25}D$ +178° (*c* 1, acetone), and the diastereomeric 2-octyl *p*-tolyl sulfoxides, (*R,R*)-(+)-**14a**, $[\alpha]^{25}D$ +118° (*c* 1, acetone), and (*R,S*)-(+)-**14b**, $[\alpha]^{25}D$ +137° (*c* 1, acetone), were obtained according to the literature[3b] (lit.[3b] $[\alpha]^{25}D$ +187.5, +176.5, +118, and +137° in acetone, respectively).

Bis-2-octyl Sulfides. A. (*S,S*)-(+)-Bis-2-octyl Sulfide (9a). (*S*)-(+)-2-octyl mercaptan[32] (14.6 g, 0.1 mol), $[\alpha]^{25}D$ +28° (*c* 1, acetone) [lit.[33] $[\alpha]^{28}_{546}$ −36.9° (*c* 4.5, ethanol)] was added at 0° with stirring to a solution of sodium ethoxide (6.8 g, 0.1 mol) in absolute ethanol (150 ml). A solution of (*R*)-(−)-2-octyl *p*-toluenesulfonate,[34] obtained from (*R*)-(−)-2-octanol, $[\alpha]^{25}D$ +11.5° (neat),[34] in absolute ethanol (100 ml) was then added. The mixture was heated for 8 hr at 65°, concentrated *in vacuo*, and the residual oil dissolved in ethyl ether. The ethereal solution was washed with water, dried over sodium sulfate, and concentrated to give the crude sulfide (23.2 g, 90% yield), $[\alpha]^{25}D$ +17.5° (*c* 1, acetone), $n^{25}D$ 1.4669, which was used as such.

B. (*R,S*)-Bis-2-octyl Sulfide (9b). The meso sulfide was prepared in 87% yield as described in (A) from (*S*)-(+)-**8** and (*S*)-(+)-2-octyl *p*-toluenesulfonate. It had $[\alpha]^{25}D$ +0.3° (*c* 1, acetone).

(*S,S*)-(+)-Bis-2-octyl Sulfoxide (10). It was prepared by oxidation of the (*S,S*)-(+)-bis-2-octyl sulfide (**9a**) with *N*-chlorobenzotriazole according to Johnson's procedure[10] and purified by column chromatography (silica, eluent light petroleum–ethyl ether 7:3). It had $[\alpha]^{25}D$ +21.5° (*c* 1, acetone), $n^{25}D$ 1.4695. *Anal.* Calcd for $C_{16}H_{34}OS$: C, 70.00; H, 12.48. Found: C, 70.12; H, 12.52.

α-Halogenation of Optically Active Sulfoxides. α-Halogenation of (*R*)-(+)-ethyl-, (*R*)-(+)-isopropyl-, (*R,R*)-(+)-, and (*R,S*)-(+)-2-octyl *p*-tolyl sulfoxides, and (*S,S*)-(+)-bis-2-octyl sulfoxide was carried out with the general procedure described elsewhere.[9] Bromination of the last compound afforded two epimeric α-bromo sulfoxides (+)-**12a** and (−)-**12b** which were separated by column chromatography (silica, eluent light petroleum–ethyl ether 4:1). Specific rotations, yields, physical properties, and analytical data are reported in Table III.

α-Chlorination of Ethyl *p*-Tolyl Sulfoxide. α-Chlorination of ethyl *p*-tolyl sulfoxide with dichloroiodobenzene by the standard method[9] afforded α-chloroethyl *p*-tolyl sulfoxide **5a**, $n^{25}D$ 1.5608, in 75% yield: nmr (CCl_4) τ 2.20–2.80 (m, 4, aromatic), 5.27 (q, 1, CHCl), 7.54 (s, 3, *p*-CH_3), 8.40 (d, 3, CH_3). *Anal.* Calcd for $C_9H_{11}ClOS$: C, 53.33; H, 5.47. Found: C, 53.19; H, 5.57.

Inversion of this compound with triethyloxonium fluoroborate according to Johnson[6] afforded the diastereomeric α-chloroethyl *p*-tolyl sulfoxide **5c**, $n^{25}D$ 1.5711, in 80% yield: nmr (CCl_4) τ 2.30–2.80 (m, 4, aromatic), 5.38 (q, 1, CHCl), 7.55 (s, 3, *p*-CH_3). *Anal.* Calcd for $C_9H_{11}ClOS$: C, 53.33; H, 5.47. Found: C, 53.42; H, 5.49.

Oxidation with *m*-chloroperbenzoic acid of both diastereomers **5a** and **5c** gave in quantitative yield the α-chloroethyl *p*-tolyl sulfone (**7a**), mp 88° (from ethanol) [lit.[35] mp 84°].

Reaction of ethyl *p*-tolyl sulfoxide (**2**) with *tert*-butyl hypochlorite[5] in the presence of potassium acetate afforded a mixture of the diastereomeric sulfoxides **5a** and **5c** in a ratio 8:2 as indicated by the nmr spectrum in CCl_4.

α-Halo Sulfones. Oxidation of α-halo sulfoxides with *m*-chloroperbenzoic acid afforded a quantitative yield of the corresponding α-halo sulfones which were purified by column chromatography (silica, eluent light petroleum–ethyl ether 1:1) and/or by crystal-

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Table III

No.	Compound	$[\alpha]^{25}D$,[a] deg	$n^{25}D$ (mp, °C)	Yield, %	Anal. Calcd C	Anal. Calcd H	Anal. Found C	Anal. Found H
5a	p-$CH_3C_6H_4SOCHClCH_3$[b]	−153	1.5719	68	53.33	5.47	53.16	5.57
5a	p-$CH_3C_6H_4SOCHClCH_3$[c]	−7	1.5720	70				
5b	p-$CH_3C_6H_4SOCHBrCH_3$[d]	−115	1.5995	72	43.74	4.49	43.95	4.47
5b	p-$CH_3C_6H_4SOCHBrCH_3$[e]	−83	1.6001	76				
6a	p-$CH_3C_6H_4SOCCl(CH_3)_2$[b]	−119	(67–68)	66	55.42	6.05	55.43	6.15
6a	p-$CH_3C_6H_4SOCCl(CH_3)_2$[c]	−23	(42–43)	68				
6b	p-$CH_3C_6H_4SOCBr(CH_3)_2$[d]	−88	(79–80)	80	45.98	5.02	46.06	5.12
6b	p-$CH_3C_6H_4SOCBr(CH_3)_2$[e]	−84	(79–80)	70				
15a	p-$CH_3C_6H_4SOCBrCH_3C_6H_{13}$-$n$[d]	−63	1.6130	40	54.38	7.00	54.60	7.01
15b	p-$CH_3C_6H_4SOCBrCH_3C_6H_{13}$-$n$[d]	−73.6	1.5480	38	54.38	7.00	54.30	6.84
12a	n-$C_6H_{13}CH_3CHSOCBrCH_3C_6H_{13}$-$n$[d]	+51.5	1.4903	54	54.33	9.41	54.60	9.45
12b	n-$C_6H_{13}CH_3CHSOCBrCH_3C_6H_{13}$-$n$[d]	−60	1.4911		54.33	9.41	54.52	9.41

[a] In acetone. [b] Halogenating agent, $PhICl_2$–$AgNO_3$. [c] Halogenating agent, $PhICl_2$. [d] Halogenating agent Br_2–$AgNO_3$. [e] Halogenating agent, Br_2.

lization. α-Chloroethyl *p*-tolyl sulfone (**7a**), obtained from sulfoxide **5a** $[\alpha]^{25}D$ −153° (*c* 1, acetone), had $[\alpha]^{25}D$ −6.9° (*c* 1, acetone), mp 91–92°. The specific rotation and the melting point were unaltered after crystallization from ethanol. *Anal.* Calcd for $C_9H_{11}ClO_2S$: C, 49.42; H, 5.07. Found: C, 49.28; H, 5.02.

The same sulfone **7a** obtained from sulfoxide **5a**, $[\alpha]^{25}D$ −7.0° (*c* 1, acetone), had $[\alpha]^{25}D$ −0.5° (*c* 1, acetone), mp 88°.

α-Bromoethyl *p*-tolyl sulfone (**7b**) obtained from sulfoxide **5b**, $[\alpha]^{25}D$ −115° (*c* 1, acetone), had $[\alpha]^{25}D$ −14.9° (*c* 1, acetone), mp 94–95°. The specific rotation and the melting point were unaltered after crystallization from cyclohexane. *Anal.* Calcd for $C_9H_{11}BrO_2S$: C, 41.08; H, 4.21. Found: C, 41.17; H, 4.17.

(*R*)-(+)-2-Bromo-2-octyl *p*-tolyl sulfone (**18**), obtained from sulfoxide **15a**, had $[\alpha]^{25}D$ +11.2° (*c* 1, acetone), mp 63–64°, after purification by column chromatography (silica, eluent light petroleum–ethyl ether 1:1). *Anal.* Calcd for $C_{15}H_{23}BrO_2S$: C, 52.02; H, 6.63. Found: C, 51.92; H, 6.67.

The (*S*)-(−) enantiomer **18**, obtained from sulfoxide **15b**, had $[\alpha]^{25}D$ −10.9° (*c* 1, acetone), mp 63–64°.

(*S*)-(−)-2-Bromo-2-octyl-2′-octyl sulfone (**13**), obtained from the (−)-bromo sulfoxide **12b** and from the (+)-bromo sulfoxide **12a**, had $[\alpha]^{25}D$ −14.8° and −14.6° (*c* 1, acetone), respectively, $n^{25}D$ 1.4862. *Anal.* Calcd for $C_{16}H_{33}BrO_2S$: C, 52.02; H, 9.00. Found: C, 52.22; H, 9.07.

Reductions of α-Bromo Sulfoxides. The reduction of α-bromo sulfoxides with zinc and methanol in the presence of a few drops of concentrated sulfuric acid was carried out as previously described,[1] with reaction times of 1–3 hr, following the disappearance of the starting material by tlc analysis. The corresponding sulfides or mixtures of sulfide and sulfoxide obtained in this way were purified by column chromatography (silica, eluent light petroleum–ethyl ether 2:1).

Reduction of α-bromoethyl *p*-tolyl sulfoxide (**5b**), $[\alpha]^{25}D$ −115° (*c* 1, acetone), gave ethyl *p*-tolyl sulfoxide (**2**), $[\alpha]^{25}D$ −162° (*c* 1, acetone), 86% optically pure, in 50% yield. From α-bromoisopropyl *p*-tolyl sulfoxide (**6b**), $[\alpha]^{25}D$ −88° (*c* 1, acetone), isopropyl *p*-tolyl sulfoxide (**3**) was obtained, $[\alpha]^{25}D$ − 178° (*c* 1, acetone), 100% optically pure, in 40% yield.

Reduction of (*R,R*)-2-bromo-2-octyl *p*-tolyl sulfoxide (**15a**), $[\alpha]^{25}D$ −63° (*c* 1, acetone), afforded (*R*)-2-octyl *p*-tolyl sulfide (**16**), $[\alpha]^{25}D$ −7.0° (*c* 1, acetone) [lit.[3b] $[\alpha]^{25}D$ −10.5° (neat)] in 40% yield, and (*S,R*)-2-octyl *p*-tolyl sulfoxide (**14b**), $[\alpha]^{25}D$ −103° (*c* 1, acetone) in 50% yield. *Anal.* Calcd for $C_{15}H_{24}OS$: C, 71.37; H, 9.58. Found: C, 71.21; H, 9.36.

Oxidation of the mixture of sulfide **16** and sulfoxide **14b** with *m*-chloroperbenzoic acid gave a 95% yield of (*R*)-2-octyl *p*-tolyl sulfone (**17**), $[\alpha]^{25}D$ +8.9° (*c* 1, acetone), $[\alpha]^{25}D$ + 8.9° (*c* 1, chloroform), mp 58° (lit.[3b] $[\alpha]^{25}D$ +10.7° (chloroform), mp 59.5–60.5°). *Anal.* Calcd for $C_{15}H_{24}O_2S$: C, 67.12; H, 9.01. Found: C, 67.02; H, 8.97.

The same sulfone **17**, $[\alpha]^{25}D$ +8.6° (*c* 1, acetone), was obtained *via* oxidation of sulfoxide **14a**, as described by Mislow.[3b]

Reduction of (*R,S*)-2-bromo-2-octyl *p*-tolyl sulfoxide (**15b**), $[\alpha]^{25}D$ −73.6° (*c* 1, acetone), afforded a 42% yield of the (*S*)-sulfide **16**, $[\alpha]^{25}D$ +6.6° (*c* 1, acetone), and a 48% yield of the (*S,S*)-sulfoxide **14a**, $[\alpha]^{25}D$ −89° (*c* 1, acetone). *Anal.* Calcd for $C_{15}H_{24}OS$: C, 71.37; H, 9.58. Found: C, 71.51; H, 9.49.

The (*S*)-2-octyl *p*-tolyl sulfone (**17**), obtained by oxidation of this mixture, had $[\alpha]^{25}D$ −9.0° (*c* 1, acetone), mp 57°. *Anal.* Calcd for $C_{15}H_{24}O_2S$: C, 67.12; H, 9.01. Found: C, 67.21; H, 9.08.

The same sulfone **17**, obtained by oxidation of sulfoxide **14b**, had $[\alpha]^{25}D$ −9.1° (*c* 1, acetone).

Reduction of either (−)- or (+)-2-bromo-2′-octyl sulfoxides **12b** and **12a**, $[\alpha]^{25}D$ −60.0° and +51.5° (*c* 1, acetone), respectively, afforded as the only product the (*S,S*)-(+)-bis-2-octyl sulfide (**9a**) which was oxidized to the corresponding (*S,S*)-(−)-bis-2-octyl sulfone (**11**), $[\alpha]^{25}D$ −8.8° (*c* 1, acetone), $n^{25}D$ 1.4702. The same sulfone was obtained by oxidation of the (*S,S*)-(+)-sulfide **9a**, $[\alpha]^{25}D$ +17.5° (*c* 1, acetone), made by reaction of the (*S*)-(+)-mercaptan **8** with the (*R*)-(−)-2-octyl *p*-toluenesulfonate. It had $[\alpha]^{25}D$ −9.7° (*c* 1, acetone), $n^{25}D$ 1.4698. *Anal.* Calcd for $C_{16}H_{34}O_2S$: C, 66.15; H, 11.80. Found: C, 66.32; H, 11.99.

Reduction of α-Bromo Sulfones. Reduction of α-bromo sulfones was carried out with zinc dust in methanol in the presence of a few drops of concentrated sulfuric acid, as described[1] for the reduction of α-bromo sulfoxides, with reactions times of 12 hr. Alternatively, the reduction was carried out with sodium sulfite in methanol–water according to Bordwell.[13] In both cases the reaction products were purified by column chromatography (silica, eluent light petroleum–ethyl ether 9:1). Yields were in the range 75–90%.

Reduction of (*R*)-2-bromo-2-octyl *p*-tolyl sulfone (**18**), $[\alpha]^{25}D$ +11.2° (*c* 1, acetone), with sodium sulfite afforded (*R*)-2-octyl *p*-tolyl sulfone (**17**), $[\alpha]^{25}D$ +8.5° (*c* 1, acetone), mp 56°. Reduction of the *S* enantiomer **18**, $[\alpha]^{25}D$ −10.9° (*c* 1, acetone), afforded the (*S*)-sulfone **17**, $[\alpha]^{25}D$ −9.0° (*c* 1, acetone), mp 56°.

Reduction of 2-bromo-2-octyl-2′-octyl sulfone (**13**), $[\alpha]^{25}D$ −14.8° (*c* 1, acetone), with either zinc or sodium sulfite afforded the (*S,S*)-bis-2-octyl sulfone (**11**), $[\alpha]^{25}D$ −9.6° and −7.4° (*c* 1, acetone), respectively.

Sulfoximides. The (*R,R*)-(+)-2-bromo-2-octyl-*p*-tolyl-*N*-phthalimidosulfoximide (**19a**) was obtained in 40% yield from (*R,R*)-2-bromo-2-octyl *p*-tolyl sulfoxide (**15a**), $[\alpha]^{25}D$ −63° (*c* 1, acetone), according to Rees procedure,[14] with a reaction time of 15 hr. It was purified by chromatography (silica, eluent light petroleum–ethyl ether 7:3) and had $[\alpha]^{25}D$ +90° (*c* 1, acetone), mp 105° (from isopropyl ether). *Anal.* Calcd for $C_{23}H_{27}BrN_2O_3S$: C, 56.22; H, 5.54; N, 5.70. Found: C, 56.12; H, 5.44; N, 5.75.

The (*R,S*)-(+)-2-bromo-2-octyl-*p*-tolyl-*N*-phthalimidosulfoximide (**19b**) was similarly obtained in 44% yield from the (*R,S*)-2-bromo-2-octyl *p*-tolyl sulfoxide (**15b**), $[\alpha]^{25}D$ −73.6° (*c* 1, acetone), with a reaction time of 4 hr. It had $[\alpha]^{25}D$ +102° (*c* 1, acetone), mp 121–122° (from isopropyl ether). *Anal.* Calcd for $C_{23}H_{27}BrN_2O_3S$: C, 56.22; H, 5.54; N, 5.70. Found: C, 56.40; H, 5.48; N, 5.67.