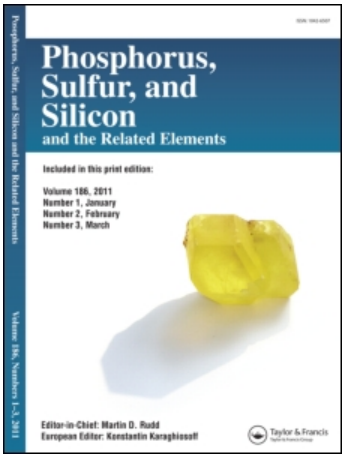

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TRANSMISSION OF CHIRALITY FROM SULFUR TO CARBON

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TRANSMISSION OF CHIRALITY FROM SULFUR TO CARBON

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The sulfinyl group is characterized by the presence of ligands very different from each other from the stereoelectronic point of view: the lone-pair, the oxygen and two aryl or alkyl groups. This accounts for the generally high stereoselectivity met with in reactions involving chiral or prochiral groups α or β to the sulfur moiety.

Transmission of chirality from sulfur to carbon has been observed i) in the α-hologenation of sulfoxides, ii) in the addition of nucleophiles and electrophiles to α, β unsaturated sulfoxides, iii) in the formation of allenic sulfoxides, and iv) in the reduction of alkylidensulfinamides and of β-ketosulfoxides.

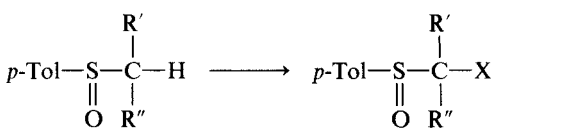
The high degree of asymmetric induction allows in most cases to rationalize the absolute configuration of the reaction products in terms of mechanism and steric factors.

In a recent review,[1] Kagan and Fiaud say that "An increasing amount of recent data (optical yields greater than 90%) demonstrate that versatile and efficient non-enzymatic asymmetric systhesis are indeed possible. The most serious obstacle continues to be the lack of basic understanding of factors mediating asymmetric induction. The optimization of optical yield remains essentially empirical, requiring many experiments. Nevertheless some concepts are slowly emerging from the large amount of experimental data, and it is to be hoped that the element of mystery about asymmetric induction may be gradually diminishing."[1] Keeping in mind such philosophical aptitude, we will deal mainly with experimental results, even if sometimes we will make some unwarranted assumptions about the topology of transition states.

Much interest has been aroused by the stereochemical features of sulfoxides, compounds which have a pyramidal structure in which the sulfur occupies the apex. The structure can be regarded as a tetrahedron if the lone pair of sulfur is taken into account as a fourth substituent. When R′ is different from R″ the sulfur atom becomes a chiral centre. Since the activation parameters for pyramidal inversion generally are in the range of $\Delta S^{\neq} = -8 + 4$ e.u. and $\Delta H^{\neq} = 35$–42 Kcal/mol, in most cases the thermal stereomutation of sulfoxides occurs at about 200°C.[2]

As pointed out by Montanari, the sulfinyl group is peculiarly characterized with respect to any other chiral group by the presence of at least three kinds of ligands very different from each other from the stereoelectronic point of view: the lone-pair, the oxygen and only two aryl or alkyl groups. This accounts for the high conformational preference of sulfoxides as well as the high stereoselectivity met with in reactions involving chiral or prochiral groups α or β to the sulfur moiety.[3]

Transmission of chirality from sulfur to carbon has been observed in the α-halogenation of sulfoxides[3] having at least one hydrogen on the α-carbon which can be converted into α-halogenosulfoxides by eletrophilic halogenating agents such as $PhICl_2$, N-chlorobenzotriazole and Br_2 in the presence of a base, generally pyridine.[4,5]

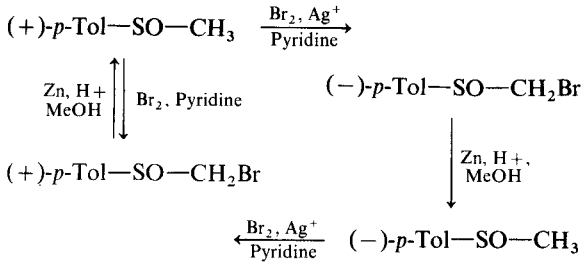


X = Cl, Br

R = R′ = H
R = H, R′ = CH_3
R = R′ = CH_3

† Plenary Lecture. Symposium *Chirality in Organic Chemistry*, Wageningen, The Netherlands, March 1980.

To obtain informations on the stereochemistry of such reactions α-halogenation has been carried out on optically active sulfoxides. When (R)-(+) methyl *p*-tolyl sulfoxide is halogenated with bromine, (S)-(+) bromomethyl sulfoxide is obtained.[6] However when the reaction is repeated in the presence of at least two moles of silver (I) nitrate the stereochemical path of the reaction is opposite and the (−) bromosulfoxide is obtained.[6] Therefore one of the two reactions must occur with inversion. We have shown[6] that the inversion is at work in the reaction in the presence of Ag^+, *inter alia* by the conversion of both bromomethyl sulfoxides into the sulfoxide by treatment with Zn in MeOH.



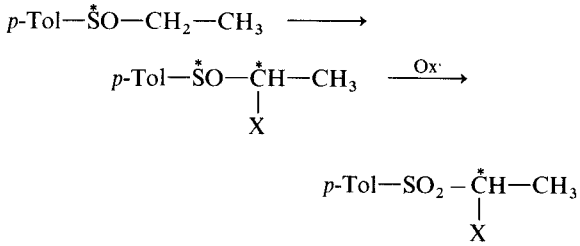
The inversion at sulfur in this case is 99%, so that this reaction is almost stereospecific.

Halogenation of ^{18}O-labelled sulfoxides proceeds with complete retention of the isotopic cotent, both in the presence and in the absence of metallic ions. Since it seems very unlikely that C—S bonds are involved in the reaction, the inversion of chirality occurs without any substitution of the original ligands at the chiral centre. When the methyl derivative is replaced by the ethyl or isopropyl derivatives, α-halogenation is always accompanied by prevailing inversion of chirality at sulphur either in the presence or in the absence of silver ions. The extent of inversion depends on the complexity of the alkyl chain (Pr^i > Et) and on the nature of the halogen (Br > Cl). It reaches 97% in the brominations of isopropyl *p*-tolyl sulfoxide and is in any case increased by working in the presence of $AgNO_3$.

α-Halogeneration of optically active alkyl *p*-tolyl sulfoxides

Alkyl	% Inversion at sulfur Br_2	$Br_2/AgNO_3$
CH_3	14	99
C_2H_5	81	93
$C_3H_7^i$	97	100

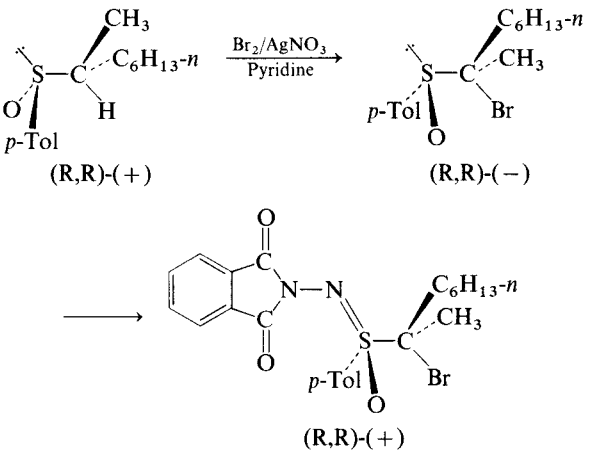
Conversion of ethyl *p*-tolyl sulfoxide into the corresponding halogenoderivative introduces a second chiral centre at the α-carbon, whose chirality is related to that at sulfur.

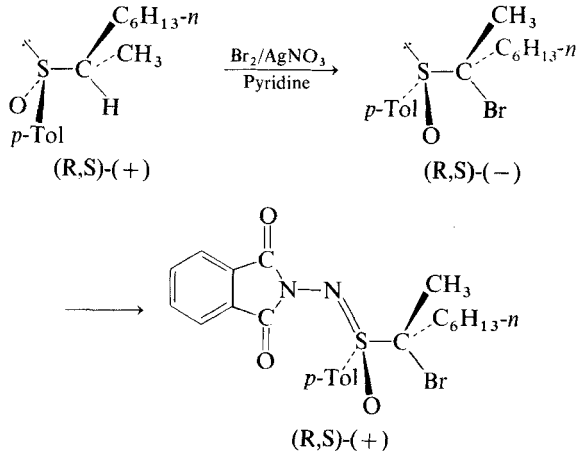


X = Cl, Br.

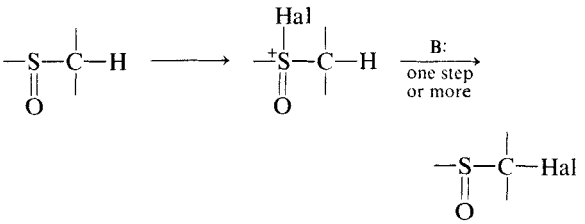
Indeed either in the presence or in the absence of silver nitrate only one of the two possible diastereoisomers is obtained.[6]

In order to establish the relationship between the stereochemical courses at sulfur and at the α-carbon, halogenation of diastereomeric (R,R)-(+) and (R,S)-(+)-2octyl *p*-tolyl sulfoxides of known chirality both at sulfur and at the α-carbon, was examined. The reaction with Br_2 and $AgNO_3$ in pyridine afforded (R,R)-(−) and (R,S)-(−) bromosulfoxides, which in their turn were converted into the corresponding sulfoxomides, whose configurations (R,R)-(+) and (R,S)-(+), respectively, were determined by X-ray analysis. This means that in this case, and probably in all of the alkyl aryl sulfoxides examined, inversion of chirality at sulfur is accompanied by inversion of chirality at carbon.[6]





All available evidence consistently indicates that the halogenation of sulfoxides in the presence of bases proceeds through the initial formation of a halooxosulfonium salt intermediate, whose base-promoted collapse eventually leads to the α-halosulfoxide.

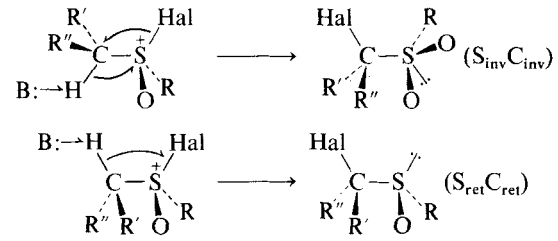


A sizable deuterium isotope effect, $k_H/k_D = 5.5$ has been found,[7] indicating that proton abstraction occurs in the rate determining transition state.

Kinetic studies cannot provide information about the step in which halogen is attached to the α-carbon, since this occurs after the rate-determining step.

Fundamentally two types of mechanism have been proposed for the α-halogenation of sulfoxides. In the one suggested by Montanari,[3,8] hydrogen abstraction and halogen migration occur in the same transition state. Such concertedness has been assumed specifically in view of the close correlation between the stereochemical course at sulfur and α-carbon; $S_{inv}C_{inv}$ or $S_{ret}C_{ret}$ stereochemical courses may be explained on the basis of two processes.

In the first, the halogen would migrate as an anion from an anti-coplanar conformation, involving inversion of configuration at both reaction centres.

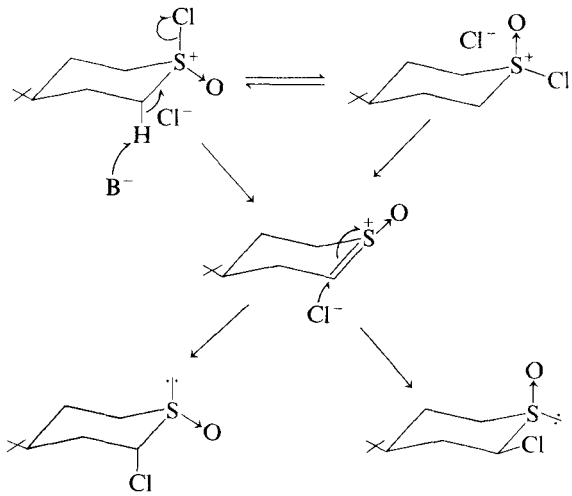


In the second the halogen would migrate as a cation from a syn coplanar conformation, producing retention of configuration at both sulfur and carbon. The competition between the two paths would be decided by the relative stability of the syn and anti conformers and ultimately by steric factors: increasing bulk of the groups at the ends of the S—C_α bond destabilizes the syn conformation required for the second process, thus shifting the balance towards the first process and its attendant $S_{inv}C_{inv}$ steric course.

The second mechanism has been proposed by Klein and Stollar and independently by Marquet and co-workers,[10] specifically for explaining the results obtained in the halogenation of six-membered cyclic sulfoxides.

It is a two-step process of elimination-addition from the halooxosulfonium ion, in which a rate determining anti β-elimination of HX to form a positively charged "sulfene" is followed by fast halide attack at the α-carbon of the sulfene to produce the halosulfoxide.

"As far as the second step of the Marquet mechanism is concerned, the observed steric course demands that chloride attack on the sulfene occurs exclusively, or very nearly so, on one of the two sides (axial attack). Even if surprising



this result is nevertheless admissible, since the faces of the "sulfene" being diastereotopic, have intrinsically different reactivities."[11]

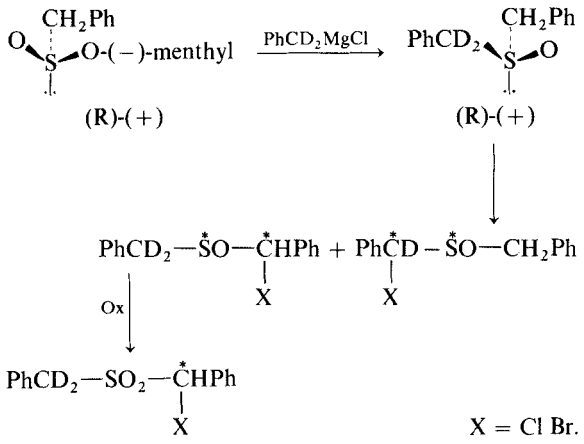
Recently Fava has studied the α-bromination of *trans*-2-thiahydrindan-2-oxide.[11]

The reaction appears to be completely regio and stereospecific and involve inversion of configuration at both sulfur and α-carbon. Also in this case, no clear-cut mechanistic choice appears to be possible.

The stereochemical outcome of α-halogenation strongly depends on the nature of the substrate, as evidenced for example in the case of benzylic derivatives.[8]

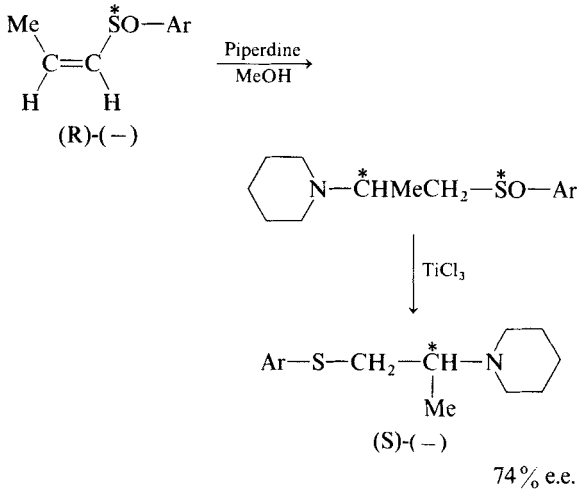
α-Halogenation is a suitable reaction for promoting asymmetric induction by isotopic dissymmetry in $[\alpha,\alpha^2H_2]$dibenzyl sulfoxide.

α-Chlorination of this compound, obtained by reaction of $[\alpha,\alpha^2H_2]$benzylmagnesium chloride with (−)-menthyl (R)-(+)toluene-α-sulfinate, afforded a single diasteromeric α-chlorobenzyl $\alpha',\alpha'\text{-}^2H_2]$benzyl sulfoxide together with a single diastereomeric α-chloro $[^2H_2]$ benzyl benzyl sulfoxide in 9:1 ratio. Similar results were obtained in the bromination reaction.[12]

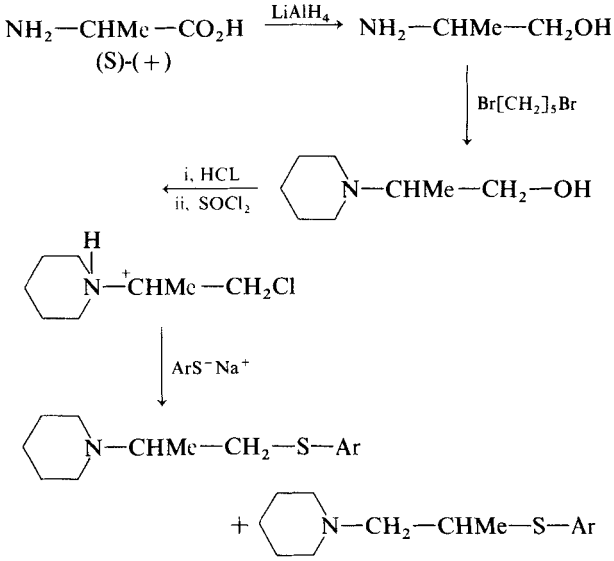


In the α-halogenation of $[\alpha,\alpha^2H_2]$dibenzyl sulfoxide the strong primary isotope effect leads to a different reactivity of the two groups, $PhCH_2$ and $PhCD_2$, enantiotopic in all essential aspects. This is accompanied by a high stereoselectivity, which gives rise to preferential substitution of one of the two diastereotopic hydrogen (or deuterium) atoms. The net result is that one of the four possible diastereomeric α-halogeno-sulfoxides is preferentially formed. Apart from enzymatic processes, this reaction thus provides the first example of an asymmetric induction by isotopic dissymmetry.

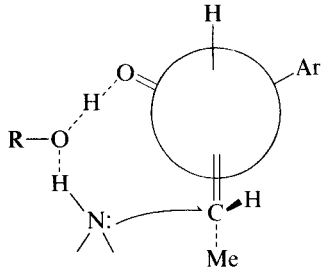
Transmission of chirality from sulfur to carbon has been observed in the additions of nucleophiles and electrophiles to optically active α,β-unsaturated sulfoxides. Treatment of optically active (−)-(R)-Z 2-propenyl *p*-tolyl sulfoxide with an excess of piperidine in MeOH gave a quantitative yield of a mixture of the diastereomeric piperidino-sulfoxides in 8:2 ration.[13]



We have shown, through reduction of the diastereomeric mixture with $TiCl_3$ to the corresponding sulfide, that the degree of asymmetric induction is 74%. The absolute configuration at carbon in the major diastereoisomer from the mixture of β-piperidino-sulfoxides has been assigned through an independent synthesis starting from (S)-(+)alanine.

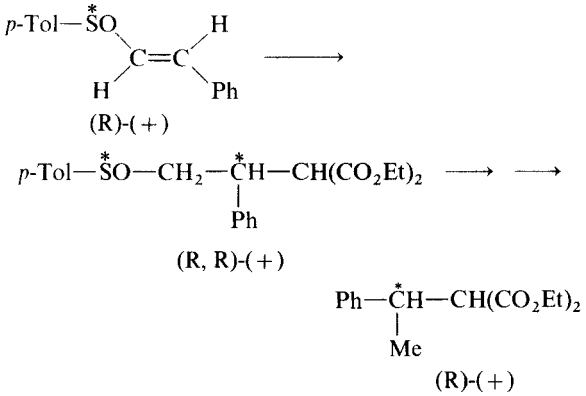


The configuration of the major diastereoisomer of β-piperidino-sulfoxide is therefore S_C and R_S. The degree of asymmetric induction is sufficiently great to warrant tentative interpretation of the steric course of the reaction, as represented in the following scheme.

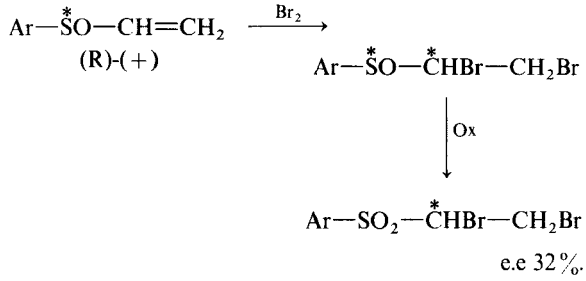


It may be presumed that the nucleophile approaches perpendicularly to the plane containing the substituents attached to the carbon-carbon double bond. We have considered the alternative approaches to the sulfoxide in its most populated conformation denoted in the scheme. The approach which is least sterically hindered (O less bulky than Ar) and which allows hydrogen bonding from amino nitrogen to sulfinyl oxygen (probably *via* and eight membered ring which includes a solvent molecule) is to be preferred. This direction is that which produces the major diastereoisomer.

Tsuchihashi and coworkers have made elegant use of β-induction in the Michael addition of diethyl malonate to chiral β-styryl sulphoxides. The reaction affords, after desulfurization and decarboxylation, (−)3-phenyl butyric acid in excellent optical yield.[14]

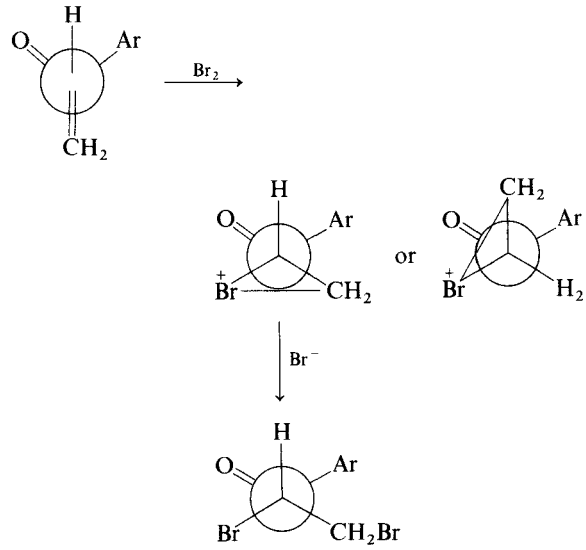


α-Induction has been observed[13] in the electrophilic addition of bromine to (+)-vinyl *p*-tolyl-sulfoxide. This reaction gave a mixture of diastereomeric dibromosulfoxides. The degree of asymmetric induction (32% e.e.) was assigned by oxidation of the mixture of diastereoisomers and comparison of the rotation of the dibromo-sulfone thus obtained with that of the sulfone obtained from oxidation of the pure major diastereoisomer.



It seems probable that the bromonium ion intermediate is symmetrical. Examination of the possible conformations of the intermediate bromonium ion formed in the reactions with the vinyl sulfoxide, leads to preference for the structures represented in the scheme, in which gauche interactions between the bromine atom and the aryl group are avoided.

Attack of bromide ion leads to the dibromide with absolute configuration S_SS_C.

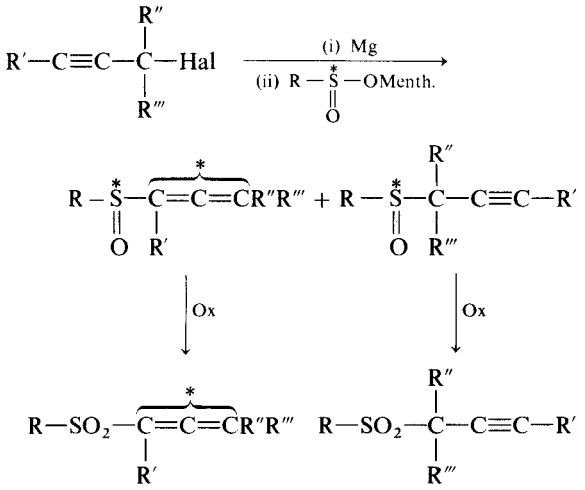


This description has been tested by the application of Brewster's rules[15] to the dibromosulfone derived from the sulfoxide. As bromine has a very high polarizability, it appears reasonable to assign

the polarizability sequence Br > $ArSO_2$ > CH_2Br > H which indeed leads to the designation of the (S)-configuration to the levorotatory enantiomer.

We have also observed the occurrence of asymmetric induction in the synthesis of chiral allenic sulfoxides.[16]

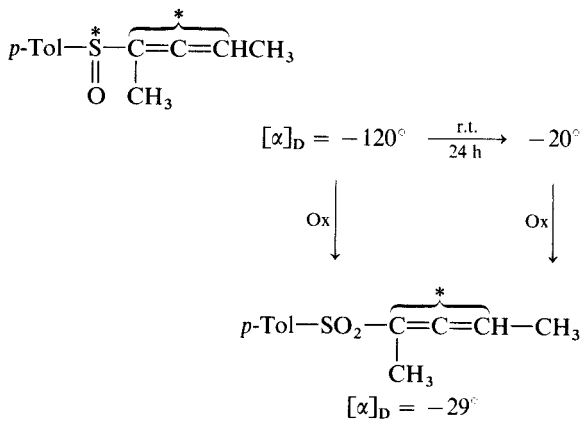
Treatment of optically pure (−)-menthyl toluene *p*-sulfinate with appropriately substituted propargyl Grignard reagents yields a mixture of optically active allenic and acetylenic sulfoxides in 15:85 to 60:40 ratio.



Oxidation of the allenic sulfoxides affords the corresponding optically active sulfones, thus indicating that there is transmission of chirality from sulfur to the allenic system. The degree of asymmetric induction obtained *via* the prop-2-ynyl Grignard reagent was as high as 60%. It has to be mentioned that induction in the direct formation of the allene system is much greater than that obtained from a simple secondary organomagnesium derivative.

A peculiar aspect of the behaviour of the allenic sulfoxides is that they mutarotate on standing at room temperature. For 1-(*p*-tolylsulfinyl)-1-methylbuta-1,2-diene the rotation changes from $[\alpha]_D$ −120° to $[\alpha]_D$ − 20°, but the recovered sulfoxide is unchanged in ^1H NMR spectrum.

Oxidation of this recovered sulfoxide gives the sulfone with the same rotation as that obtained by oxidation of a fresh sample of sulfoxide. This observation implies that epimerisation at sulfur occurs rapidly and without accompanying epimerisation of the allenic system.

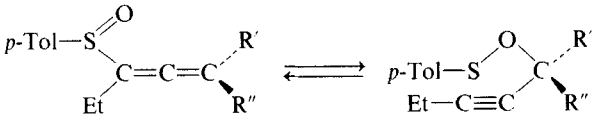


Mislow and his collaborators have defined the structural parameters which affect the ease of sulfinyl group epimerisation.[2] In simple dialkyl, alkyl aryl and diaryl sulfoxides epimerisation occurs, but at high temperatures, and pyramidal inversion is suggested. In compounds in which the C—S bond is weak, e.g. benzylic sulfoxides epimerisation is shown to occur by dissociation-recombination involving radicals which may be diverted from recombination. The third type of situation arises in allylic sulfoxides for which a low-activation [2,3] sigmatropic rearrangement involving formation of an achiral sulfenate ester can occur.

In allenic sulfoxides, the dissociation-recombination pathway can be ruled out. Vinylic and, by implication, allenic radicals do not maintain configurational integrity, and epimerisation at sulfur would be accompanied by allene epimerisation. To allow a distinction between pyramidal inversion and sigmatropic rearrangement, both of which preserve stereochemical integrity in the allene, activation parameters for sulfinyl epimerisation in allenic sulfoxide have been determined ($\Delta H^{\neq}$ 22 Kcal mol^{-1} and $\Delta S^{\neq}$ − 5.4 e.u.) These values are similar to those obtained for the racemisation of allylic sulfoxides in which it is clear that the process occurs by sulfoxide-sulfenate equilibration. The activation parameters are very different from the pyramidal inversion pathway.

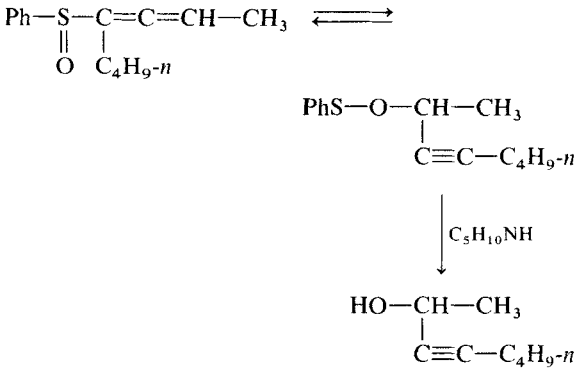
We thus prefer sulfoxide-sulfenate equilibration to pyramidal inversion, and this nicely explains the retention of configuration in the allene system while the sulfinyl group undergoes epimerisation. In this equilibration chirality is transferred specifically between the unsaturated system of the sulfoxide and the asymmetric carbon atom of the prop-2-ynyl group. Transfer of chirality in the

opposite sense has been observed previously, by Stirling and co-workers,[17] and provides further evidence for the sulfenate-sulfoxide equilibration.



Another simple line of evidence for the sulfenate-sulfoxide equilibration as the cause of epimerisation of allenic sulfoxides, is the interception of the sulfenate ester by nucleophilic attack at sulfur.

4-Phenylsulfinylocta-2,3-diene on treatment with piperidine gives the interception product, namely the propargyl alcohol and the accompanying diphenyl disulfide and thiolsulfinate.



As far as absolute configuration is concerned, it can be pointed out that empirical rules have been formulated to allow the assignment of absolute configuration to allene systems based on the sign of rotation and *vice versa*.[15]

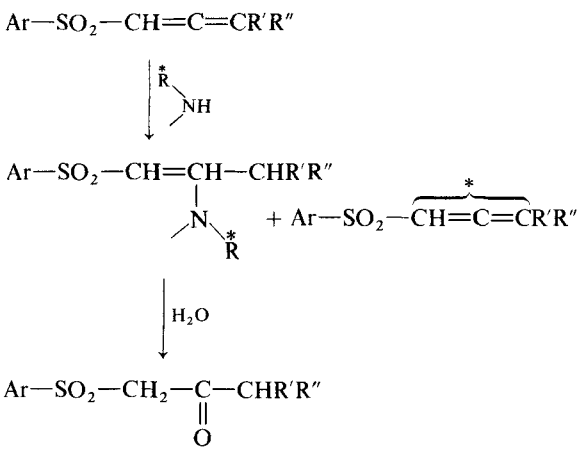
As with the application of Brewster's rules, the polarizability sequence of the substituents is required and in the case of allenic sulfones this is clearly RSO_2 > alkyl > H. The absolute configuration in allenic sulfones is therefore (−)-(R), (+)-(S).

Assignment of configuration to the allene systems of the sulfoxides follow from assignments to the allene system of the sulfones. The Andersen synthesis has been shown unequivocally to occur with inversion of configuration at sulfur in the sulfinate esters, assignment of configuration at sulfur in allenic sulfoxides can, therefore, be made.[16]

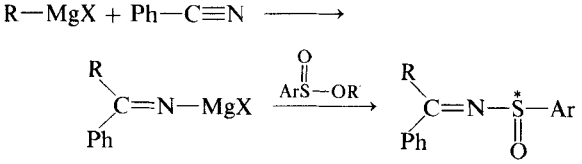
In allenic sulfones the unsaturated system is strongly activated by the sulfonyl group towards nucleophilic addition and thus furnishes a "handle" for kinetic resolution. Indeed reaction of racemic allenic sulfones with a deficiency of a chiral amine affords the corresponding enamine and allows the recovery of partially resolved starting material. The choice of the solvent is crucial, since a competitive allene-acetylene rearrangement may occur.

The value of enantiomeric enrichment of the recovered sulfones is high, up to 70%. It must be mentioned that in all cases examined that absolute configuration of the resolved allene is related to that of the resolving amines.

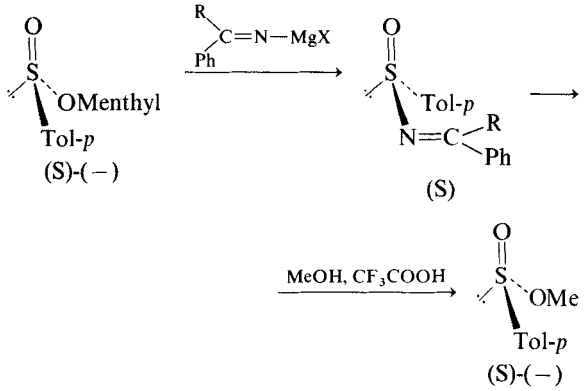
The enamine adducts are easily hydrolyzed to the oxosulfone. This allows a "catalytic kinetic resolution" of allenic sulfones by reaction with catalytic amount of a chiral base in the presence of water; the latter continuously destroys the adduct and regenerates the chiral agent.[18]



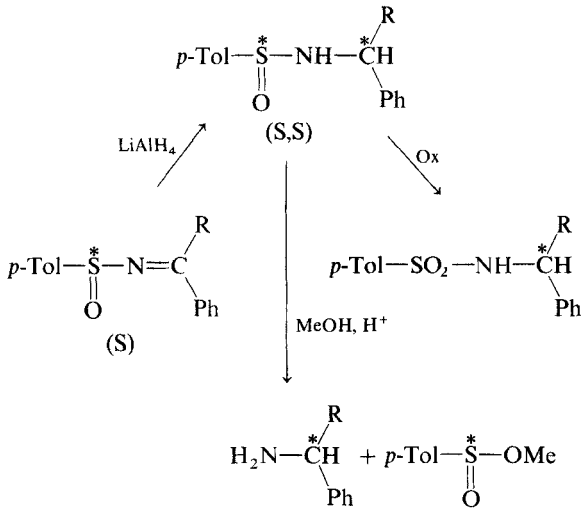
Optically active N-alkylidensulfinamides are easily accessible by treatment of a Grignard reagent with a nitrile and subsequent reaction with an optically active sulfinate. The process is stereospecific and affords sulfinamides with ee ≥ 95%.[19]



They have the (S) absolute configuration at sulfur, since it is likely that the reaction occurs with S_N2 type mechanism. This assumption has been confirmed by the synthesis of sulfinic esters of known absolute configuration through acidic methanolysis of sulfinamides.



In akylidene sulfinamides the four ligands are very different from each other: a lone pair, an oxygen, nitrogen and carbon atoms; it seemed likely by analogy with other sulfur derivatives, especially sulfoxides, that the chiral centre of N-alkyldensulfinamides could give rise to a high degree of asymmetric induction. That was the case: in the reduction by lithium aluminium hydride unequal amount of the corresponding stereomeric saturated sulfinamides are obtained, the diastereomeric ratio being in the range 9:1 to 8:2.[20]

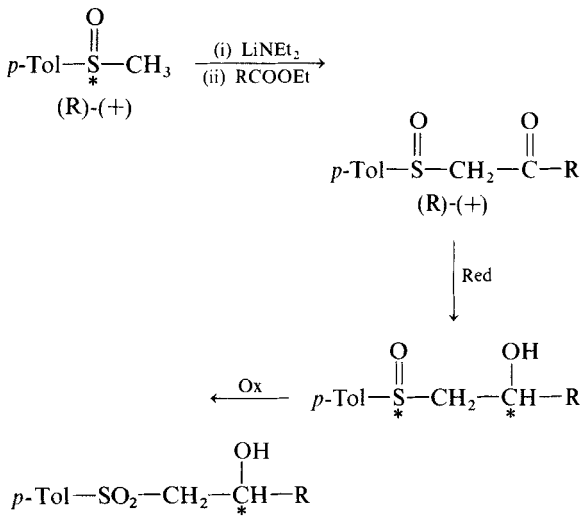


Sulfilimines can be oxidized to the corresponding optically active sulfonamides, thus confirming that asymmetric induction is occurring in the reduction. On the other hand by acidic methanolysis they afford optically active amines, with enantiomeric excess in the range 60–80%. The sign of optical rotations of optically active amines indicate that, in the cases examined, the absolute configuration of the predominating diastereomeric sulfinamide is (S,S).

The series of reactions discussed here allows the transformation of an achiral precursor, a nitrile, into a chiral amine of high, and known, optical purity. In the process asymmetry is transferred from menthol to the sulfur atom of the sulfinate ester and of N-alkylidensulfinamides and from this to the asymmetric carbon atom of the amines.

Transmission of chirality from sulfur to carbon also occurs in the reduction of β-oxosulfoxides by metal hydrides.[21]

Although β-oxosulfoxides are well known and widely used in organic synthesis, surprisingly they are virtually unknown in optically active form. Chiral β-oxosulfoxides have been prepared in our department by reaction of α-sulfinyl carbanions with carboxylic esters. Since the chirality at sulfur is not involved in the reaction, the absolute configuration of the β-oxosulfoxide can be inferred from that of the precursor, and established as (+)-(R).

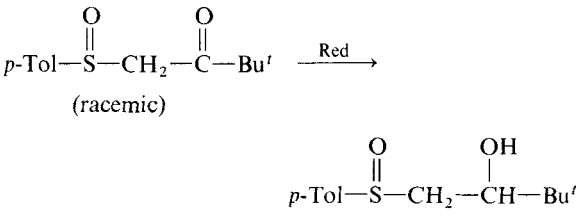


R = Et, Pr^i, Bu^t, Ph.

The optical purity of β-oxosulfoxides was shown by ^{1}H nmr analysis with the aid of chiral shift reagent Eu(tfc)$_3$ to be ≥95%. They can be easily reduced to the corresponding β-hydroxy derivatives (by sodium borohydride or $LiAlH_4$) and the latter can be oxidized to the corresponding optically active sulfones. The occurrence of 1,3 asymmetric induction was established by ^{1}H nmr analysis (with the aid of chiral shift reagents).

In the reduction with lithium aluminium hydride the transfer of chirality from sulfur to carbon is high, the e.e. of the hydroxy sulfones being in the range 60–70%, while in the reduction with sodium borohydride it is always lower (20–58% e.e.), and depends to a larger extent on the nature of the substrate.

The use of chiral and achiral alkoxy lithium aluminium hydride in the reduction of racemic oxosulfoxides was also investigated. It generally resulted only in the lowering of the stereoselectivity. A more interesting situation was encountered with the *t*-butyl *β*-oxosulfoxide: the diastereomeric ratio of the obtained alcohols depends markedly on the nature of the reducing agent, to the point that a large excess of either of the two diastereoisomers can be obtained.



Reducing agent	*Diastereomeric ratio*
$LiAlH_4$	83:17
$LiAlH_3$ (OBornyl)	70:30
$LiAlH_3$ (OMenthyl)	55:45
$LaAlH(OMe)_3$	43:57
$LiAlH_2$(OEphedrinyl)$_2$	29:71
$LiAlH(OBu^t)_3$	26:74

The synthesis of *β*-oxosulfoxides and their reduction to *β*-hydroxy sulfoxides, followed by desulfurisation, affords alcohols of high, known optical purity, whose chirality at carbon can be controlled by the appropriate choice of the chirality at sulfur in the starting sulfoxide and, in some instances, also by the nature of the reducing agent.

The examples cited in this review as well as others reported in literature[22–27] demonstrate that asymmetric transfer from chiral sulfur moieties is a valuable tool for the synthesis of a variety of optically active non-sulfur compounds.

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