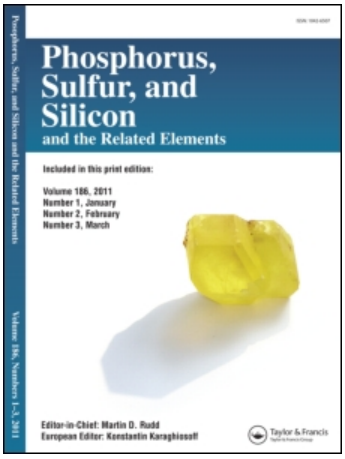

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

New Approaches for Asymmetric Synthesis of Sulfoxides

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To cite this Article Kagan, Henri B. , Rebiere, Francois and Samuel, Odile(1991) 'New Approaches for Asymmetric Synthesis of Sulfoxides', Phosphorus, Sulfur, and Silicon and the Related Elements, 58: 1, 89 — 110
To link to this Article: DOI: 10.1080/10426509108040627
URL: http://dx.doi.org/10.1080/10426509108040627

Phosphorus, Sulfur, and Silicon, 1991, Vol. 58, pp. 89–110
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NEW APPROACHES FOR ASYMMETRIC SYNTHESIS OF SULFOXIDES

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Abstract. Recent progress in asymmetric oxidation of sulfides is passed in review, and the various possibilities of using chiral sulfites for asymmetric synthesis of sulfoxides are discussed

INTRODUCTION

The preparation of various types of chiral sulfoxides with high enantiomeric excess is still of great interest. There are many applications of chiral sulfoxides, namely, as chiral auxiliaries in asymmetric synthesis or as chiral synthons[1-4]. Natural products with biological activities sometimes have a sulfinyl moiety with a well defined configuration at sulfur. Also some interest is expected for the use of chiral sulfoxides in material science, for example in liquid crystals with ferroelectric properties[5].

The main known methods of preparation of chiral sulfoxides fall under the following categories.

1) Resolution of racemic sulfoxides.

2) Chemical modification of chiral sulfoxides. This approach needs a good stereochemical control at sulfur for avoiding racemization or epimerization.

3) Transformation by the Andersen method of a diastereochemically pure chiral sulfinate into a sulfoxide[6]. The reaction involves a substitution step with an organometallic reagent, usually with full inversion of configuration[7].

4) Asymmetric oxidation of sulfides.

The Andersen method remains the main route to chiral sulfoxides, especially sulfoxides of the type p-tolyl-S(O)-R. The

reason is the easy preparation of crystalline R_S (1R)-menthyl p-tolylsulfinate from the mixture of epimeric diastereomers by a combination of *in situ* epimerization (catalyzed by HCl) and slow crystallization[1].

Asymmetric oxidation of prochiral sulfides was for a long time of minor preparative interest because of the low ee's obtained with chiral peracids. Since 1984 new methods were set up, and their progress will be summarized in the next section.

ASYMMETRIC OXIDATION OF SULFIDE

Biochemical oxidation of sulfides specifically gives sulfoxides with very high enantiomeric excess : see ref.8 for a review and ref.9 for recent results using chloroperoxidase.

A breakthrough in asymmetric oxidation of sulfides by chemical systems occured in 1984 when it was found that tertiobutylhydroperoxide in presence of some of the modified Sharpless reagents led to sulfoxides with ee's close to 90%. We discovered that the combination $Ti(OiPr)_4$/diethyl tartrate (DET)/H_2O = 1:2:1 is a very good chiral controller in asymmetric oxidation of some sulfides[10,11]. Independently Modena et al proposed the combination $Ti(OiPr)_4$/DET = 1:4 for the same purpose[12]. Both systems are efficient for asymmetric oxidation of many aryl methyl sulfides (ee = 85-88%). A survey of the results that we obtained in the 1984-86 period has already been presented[17], and in what follows we summarize the main trends of our reagent.

The water-modified titanium reagent is prepared by sequential addition of $Ti(OiPr)_4$, DET and water in methylene chloride at room temperature. After 30 min of stirring, sulfide is added and the temperature is cooled down to -20°C. tBuOOH (1.1 mol eq) is then added at this temperature. Oxidation takes place usually after a few hours. Titanium alcoholates are destroyed by hydrolysis and titanium dioxide is removed by filtration on celite. The sulfoxide is easily removed by flash-chromatography on silicagel, and the reaction can be performed on several grams scale[11]. We obtained many results following this procedure[10,11,13,14-17]. Some representative ones are listed in

Table I

Asymmetric oxidation of sulfide R^1-SO-R^2 by t-BuOOH in presence of $Ti(OiPr)_4$/(R,R)-DET/H_2O = 1/2/1[a]

Entry	R^1	R^2	Isolated yield (%)	ee[b,c] (%)	Ref
1	p-Tolyl	Methyl	90	89	11
2	p-Tolyl	n-Butyl	75	20	11
3	1-Naphthyl	Methyl	88	90	11
4	2-Naphthyl	n-Propyl	78	24	11
5	Phenyl	Cyclopropyl	73	95	14
6	Phenyl	CH_2Cl	60	47	14
7	2-Pyridyl	Methyl	63	77	11
8	t-Butyl	Methyl	72	53	11
9	n-Octyl	Methyl	77	53	20
10	$(CH_2)_2CO_2Me$	Methyl	84	63	16
11	S-Methyl	Methyl	60	41	16
12	S-i-Propyl	i-Propyl	43	52	16
13	p-Tolyl	O-Methyl	88	36	16
14	p-Tolyl	N-Diethyl	60	35	16

a) Reaction performed at 5 mmol scale. (Sulfide) = (Reagent) = $2*10^{-1}$M in CH_2Cl_2 at -20°C.

b) Measured by ^1H NMR with $Eu(hfc)_3$ or (R)-(3,5-dinitrobenzoyl)-1-phenyl-ethylamine.

c) All sulfoxides have (R) configuration except entries 11, 12 and 14.

Table I. A significant improvement in the enantioselectivity of the process is to replace tBuOOH by cumene hydroperoxide[19,20]. Some data are gathered in Table II. Oxidation by cumene hydroperoxide followed by crystallization allowed to improve ee's up to 100%. In that way methyl p-tolyl sulfoxide, methyl O-anisyl sulfoxide and methyl n-octyl sulfoxide could be isolated at 10 g scales with overall yields of respectively 76%, 80% and 40%[20]. A recent article in Organic Syntheses described an example of asymmetric oxidation and discussed the preparative aspects of our system[21]. 1,3-Dithiane 2-substituted 1-oxides were prepared with ee's up to 80% using cumene hydroperoxide as oxidant[12].

We explored some aspects of the reaction mechanism of this asymmetric oxidation[11,15,17,18]. We just mentioned here that we found a very simple picture (Scheme 1) for predicting absolute configuration of sulfoxides[15,17,18]. It is mainly based on steric discrimination between the two groups ("large" and "small") connected to sulfur, although electronic factors (π-systems) play also some role. Thus a triple bond versus a methyl group gives quite high ee[20].

Our procedure had many applications in literature, inter alii see refs[23-27]. The Modena procedure (large excess of diethyl tartrate) has been applied by the authors to various problems[28-30].

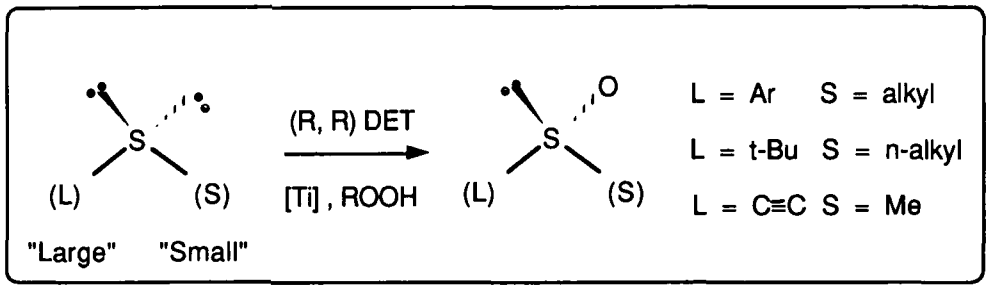
Another approach for asymmetric oxidation of sulfides has been developed by Davis et al[31]. It involves oxygen transfert from chiral oxaziridines derived from some terpenes. Ee's in the range of 90-95% have been found in many cases. Despite some impressive progress during the last five years in asymmetric oxidation of sulfides there remains some limitations. Let us consider our titanium/cumene hydroperoxide system for example. It is very convenient for many aryl methyl sulfides but ee's remain in the range of 80% for dialkyl sulfoxides. Moreover there is no hope for the preparation of sulfoxides with high ee if the two chains connected to sulfur are similar (eg C_9 and C_{10}). It was also found that diaryl sulfides are not oxidized in our standard conditions. Consequently it was interesting to find a new approach to chiral sufoxides with high enantiomeric excess which

TableII

Ee(%)[a,b] in asymmetric oxidation of some sulfides by the reagent ($Ti(OiPr)_4$/(+)-DET/H_2O=1:2:1) using various hydroperoxides[20].

Entry	Sulfides	t-BuOOH	PhC(Me)2OOH	Ph3COOH
1	Me-S-Phenyl	88[d]	93	
2	Me-S-(p-Tolyl)	89[d]	96[c,d]	16[c]
3	Me-S-(o-Anisyl)	74	93[c,d]	
4	Me-S-$(CH_2)_7CH_3$	53	80	32
5	Me-S-(p-Cl-Phenyl)	78	91[c]	
6	Me-S-Benzyl	35	61[c]	

a) See note b in table I.
b) Reaction performed at -23°C for 20h in CH_2Cl_2 in presence of 1 mol eq of Ti reagent. All sulfoxides have R configuration.
c) Ee calculated from maximum specific rotation.
d) Ee confirmed by HPLC on chiral phase.



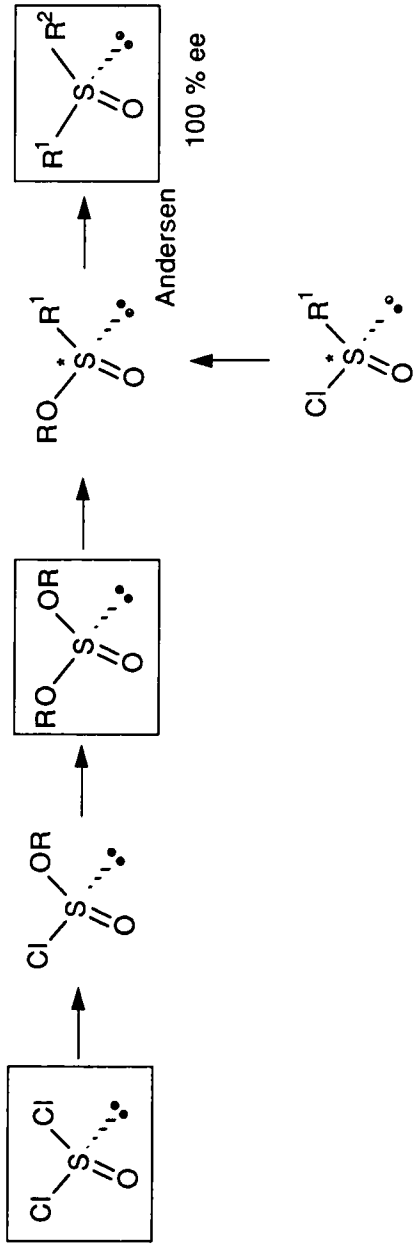
Prediction of absolute configuration of sulfoxides obtained by asymmetric oxidation with water- modified Ti reagent[15,16,17]

Scheme 1

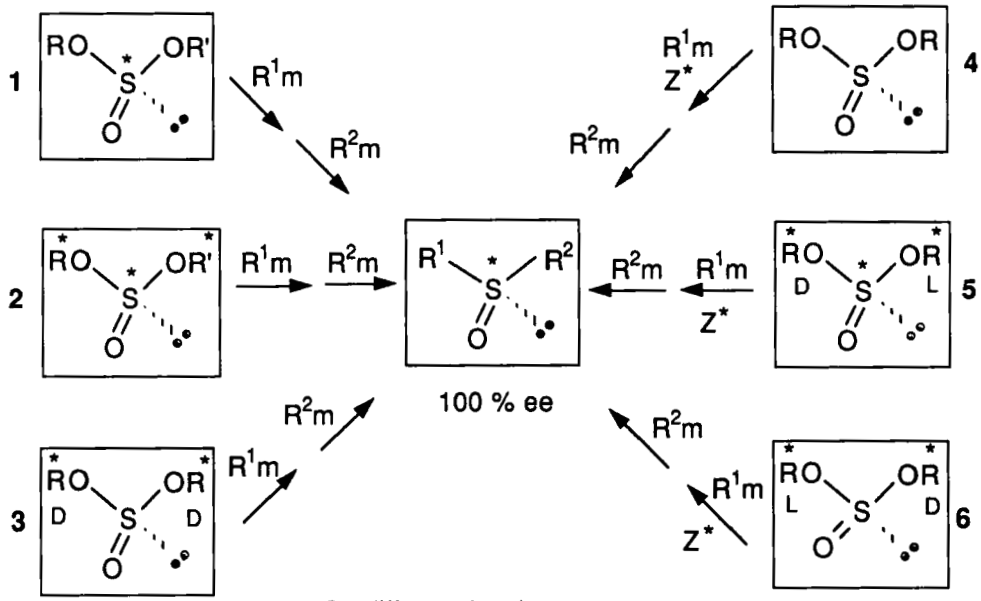
will be complementary to the one involving asymmetric oxidation. This is the topic of the next section.

FROM SULFITES TO CHIRAL SULFOXIDES

Sulfites are compounds known since a long time (for a review see ref 32), and sulfur can be an asymmetric center therein; this has been recognized for the first time in the fifties with cyclic sulfites derived from steroids. We therefore envisaged to start from sulfites with an asymmetric sulfur and to make two successive stereoselective displacements in order to get a chiral sulfoxide : RO-S(O)-OR' $\rightarrow \rightarrow$ R^1-S(O)-R^2. The starting material in sulfite chemistry is thionyl chloride, a low cost compound. As shown in Scheme 2 it can be transformed successively into a chlorosulfite and then into a sulfite. Then an organometallic R^1m should, in principle, be able to displace one alkoxy group and to lead to sulfinate. The second substitution by organometallic R^2m presents no difficulty and is part of the well-known Andersen method[6]. A chemical problem linked with the overall process of Scheme 2 is to transform sulfite into sulfinate and not into symmetrical R^1-S(O)-R^1. For this, it is necessary to find conditions where sulfinate is less reactive than sulfite towards R^1m reagent. Let us assume that this condition is fulfilled. It remains to solve a stereochemical problem : how to produce a chiral sulfinate with an asymmetric sulfur atom ? In Scheme 3 are analyzed all the possibilities of conversion of a sulfite into a chiral sulfoxide (assuming as usual that nucleophilic substitution at sulfur occurs with full inversion of configuration[2,7]). Cases **1** and **2** represent sulfites where there is already an asymmetric sulfur. If the chemical reactivity of OR and OR' groups are different enough one can expect a transfer of chirality leading ultimately to a chiral sulfoxide. In sulfite **3** the two chiral leaving groups are identical but should have different reactivities since they have diastereotopic relationships. In cases **4 - 6** one cannot expect any discrimination between leaving groups since sulfites are achiral (meso compounds). However stereoselective mono substitution should occur in principle if one combines an organometallic reagent with a chiral auxiliary (acting as catalyst or as co



Scheme 2



1, 2 : different leaving groups
3 : diastereotopic leaving groups
4-6 : enantiotopic leaving groups

Classification of the conversion of sulfite into chiral sulfoxides

Scheme 3

reagent). We decided to explore the various possibilities of Scheme 3 and we present here some results already obtained[33] (and mainly unpublished[34]). We concentrated our efforts at a first stage mainly on case **2**, which represents a sulfite with two different chiral leaving groups. This will be developed in the following sections, after reporting the few cases already described in literature of transformation of sulfites into chiral sulfinates or sulfoxides.

Early reports of conversion of sulfites and related compounds into chiral products (Scheme 4).

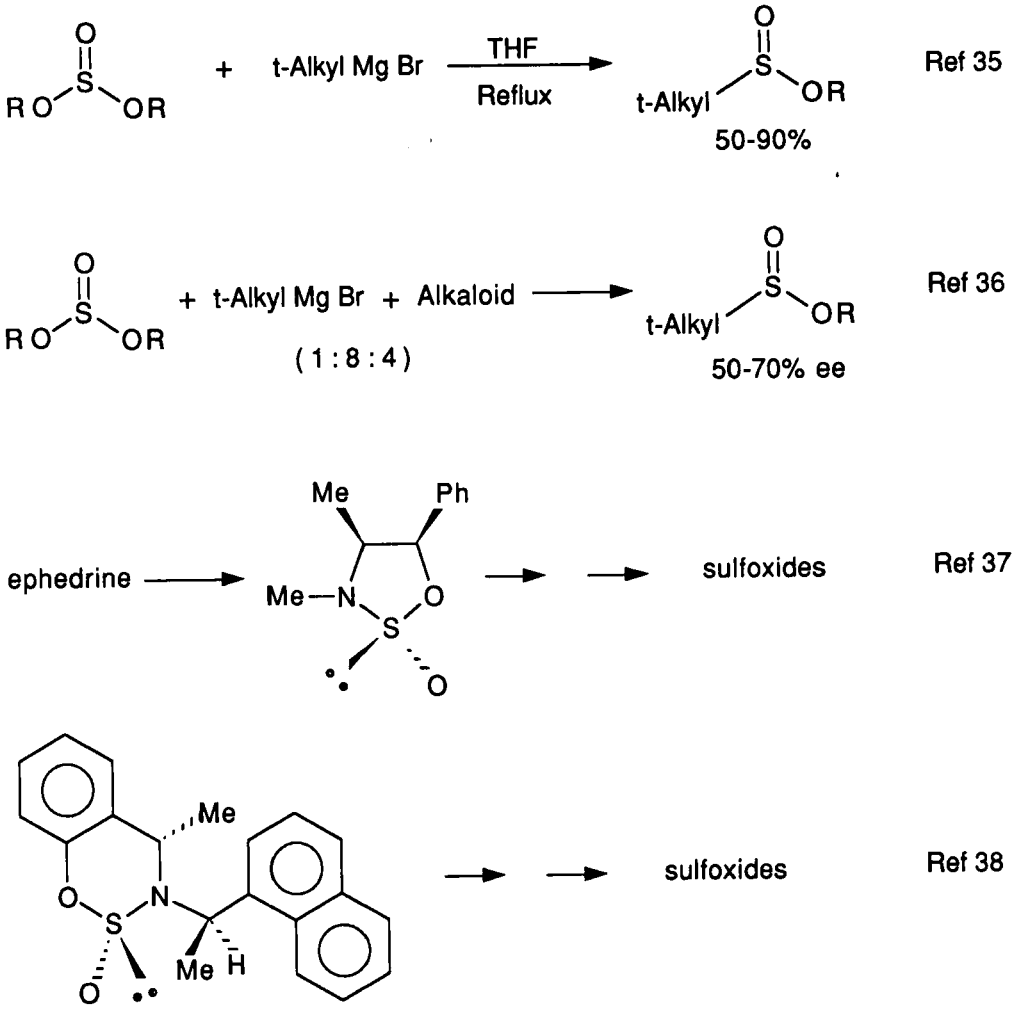
Mikolaczyk and Drabowicz found in 1974 that tertiary alkyl magnesium halides are able to transform symmetrical sulfites into tertiary alkyl sulfinates[35]. In 1988 these authors modified the experimental conditions and obtained chiral sulfinates (ee's up to 70%) by addition of alkaloids[36]. This asymmetric synthesis corresponds to case **4** in Scheme 3. Case **2** in Scheme 3 is unknown in literature but a similar process has been described for aminosulfites by Wudl and Lee[37] and by Hiroi et al[38]. In these examples the S-O bond is cleaved preferentially to the S-N bond.

Preparation of a chiral cyclic sulfite

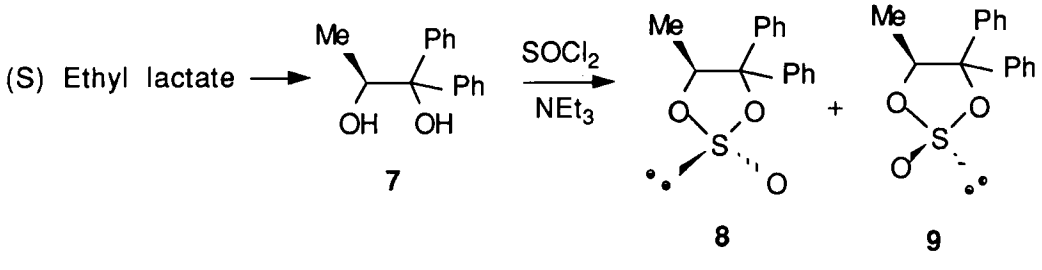
We decided to try to prepare cyclic sulfites deriving from easily available chiral 1,2 diol. Lactic acid is one of the cheapest chiral compounds. Various chiral diols could be prepared from ethyl lactate by addition of a Grignard reagent. We selected the diol **7** for the synthesis of cyclic sulfite (Schema 5), and we were pleased to determine the experimental conditions giving a large preference (90 : 10) for one diastereomer **8** (trans stereochemistry, see below). It was obtained stereochemically pure with an overall yield of 70% after crystallization. Sulfite **8** is a stable compound and represents an excellent starting material for the chemistry we intended to do.

Selective cleavage of cyclic sulfite **8**

In order to transfer efficiently the chirality from sulfur of **8** into a sulfoxide it was necessary to overcome several difficulties :



Scheme 4



Scheme 5

i) The first organometallics R^1m should avoid overeaction with intermediate sulfinate.

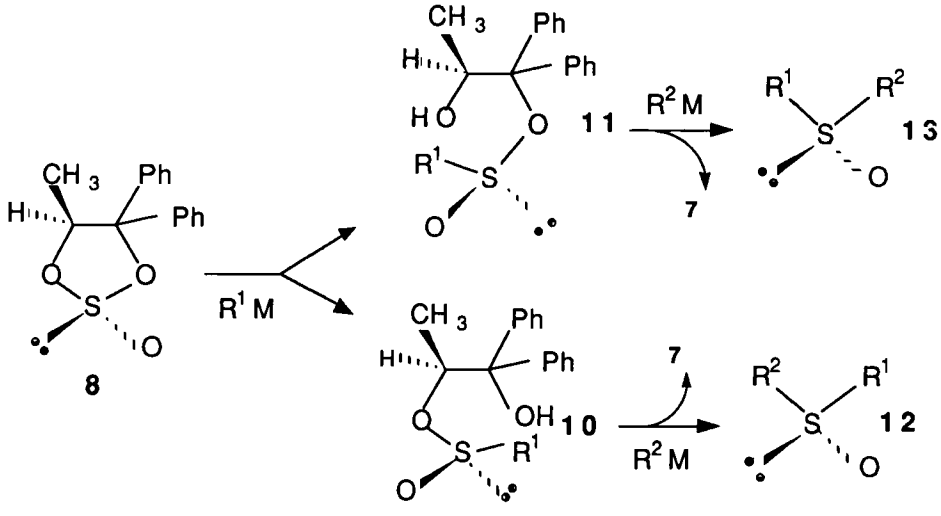
ii) Sulfinate must be generated by a selective cleavage involving only one of the both potential leaving group.

iii) The substitution reaction at sulfur should occur with the highest possible stereospecificity (inversion seems the most probable, as found in many sulfur compounds[2]).

We were encouraged by the report of Mikolaczyk and Drabowicz[35] to start our experiments. By using ter butyl magnesium halide, we expected a good yield of sulfinate. Indeed we were delighted to see that ter butylsulfinate is obtained in good yields, moreover the regioselectivity in the cleavage is excellent (90:10) affording mainly **10** (70% yield in pure compound, after crystallization). ^1H nmr shows the absence of the diastereomer of **10** at sulfur on the crude material; this epimer was prepared separately by addition of t-BuMgBr on cyclic sulfite **11**. Ter-butylsulfinate **10** is a stable compound easy to store, which is a very good starting material for asymmetric synthesis of many sulfoxides **12** (R^1 = t-Bu) as it will be detailed in the next paragraph. Mesitylmagnesium bromide gives the same chemistry as t-BuMgBr, sulfinate **10** (R^1 = mesityl) was isolated in 65 % yield (after crystallization) as a single diastereomer).

Surprisingly linear alkyl or vinyl Grignard reagents (R^1 = Et, n-octyl or vinyl) led with a high selectivity (> 90:10) to the alternate sulfinate **11**. MeMgI is a little less regioselective (80:20). Up to now all the sulfinates have been isolated as crystalline compounds which are easy to get stereochemically and chemically pure by crystallization in good yields (~60-80%). Sulfinates **11** cannot be stored, by contrast with **10**, presumably because of some instability given by the vicinity of a sulfite function and a benzylic carbon atom.

A mixture of sulfinates **10** or **11** (50:50 to 70:30) is produced by the reaction of some reagent such as $PhCH_2MgCl$ or $PhCH_2MgBr$. The usual experimental conditions for the preparation of sulfinate **10** or **11** is to allow **8** to react with R^1MgX in THF at -78°C. Organolithium reagents are less regioselective and sometimes afford symmetrical sulfoxides R^1-



Scheme 6

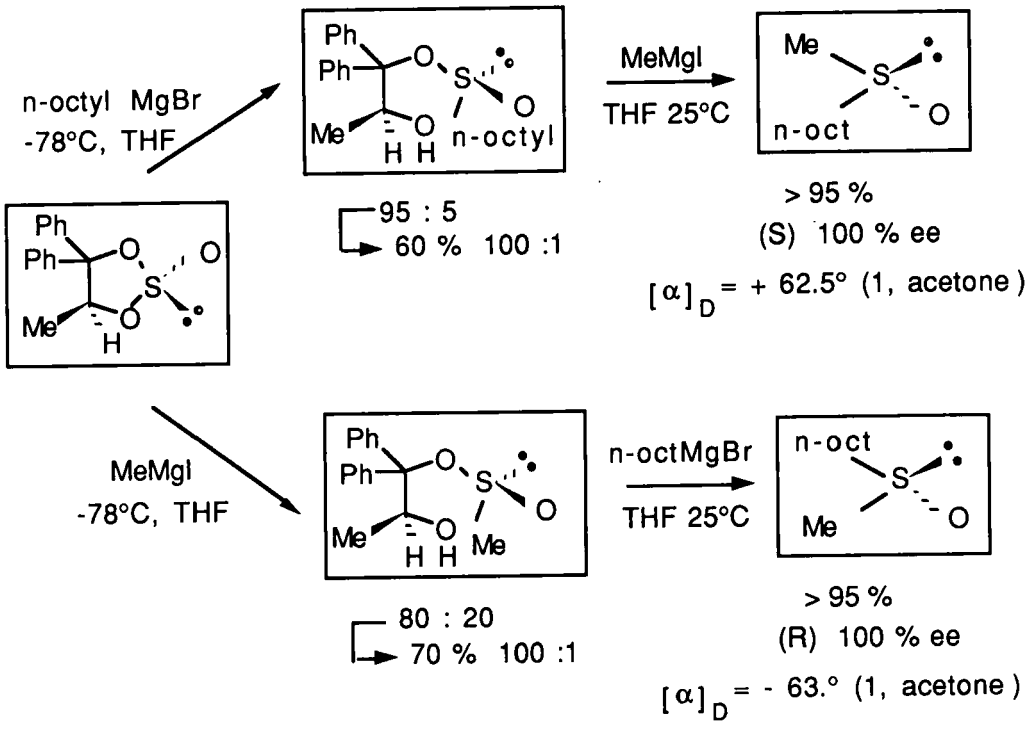
S(O)-R^1. By looking at the above data one can conclude that when R^1 is bulky the regioselective cleavage mainly gives sulfinate **10** while when R^1 is small the sulfinate **11** is the main product. A mixture of sulfinates is obtained if R^1 is of intermediate size. A gratifying behavior of cyclic sulfite **8** is its ability to react with all kinds of Grignard reagents giving sulfinates and no symmetrical sulfoxides, at the difference of acyclic sulfites.

Transformation of sulfinates **10,11** into chiral sulfoxides

The first attempts were studied on ter-butylsulfinate **10**. All kinds of organometallics (2 mol eq) react with **10**, producing enantiomerically pure sulfoxides **12** (R^1 = t-Bu). Sulfoxide **12** is recovered in a quantitative yield by flash-chromatography, the chiral auxiliary **7** is also recovered unchanged in excellent yield. Examples of synthesis of various sulfoxides are listed in Table III. Grignard reagents or organolithiums are equally suitable for the reaction, which is also working perfectly well with sulfinate **11** (leading to sulfoxides **13**, enantiomers of **12**). The absolute configuration of some of the final sulfoxide was known, allowing to assign absolute configuration at sulfur of sulfinate (as indicated in **10** and **11**, Scheme 6). These assignements are based assuming inversion of configuration during the substitution step.

How to obtain both enantiomers of a sulfoxide

(S) Lactic acid is the enantiomer which is commercially available (as well as simple derivatives as ethyl esters). It is therefore important to devise a process which will start from cyclic sulfite **8** and will generate each enantiomer of a sulfoxide. A simple solution to this problem is to permute R^1 and R^2 in organometallics involved in the two substitution steps. This has been realized in asymmetric synthesis of methyl n-octyl sulfoxide (Scheme 7). The method should apply in all cases where R^1 and R^2 are both small (as in the previous example) or bulky (eg t-Bu and mesityl). Unfortunately if one group is bulky and the other small (eg t-Bu and Me) the group permutation will necessarily lead to the same sulfoxide **12**, since the inversion in the order of introduction of the groups is "on offset" by the change in the side



Scheme 7

of the cleavage of sulfite **8** during the sulfinate synthesis. Fortunately (R) isobutyl lactate has been recently marketted (Fluka). Diol (R) **7** is easily derived from that ester, giving access to enantiomer of sulfite **8**, and then to sulfoxides **13**.

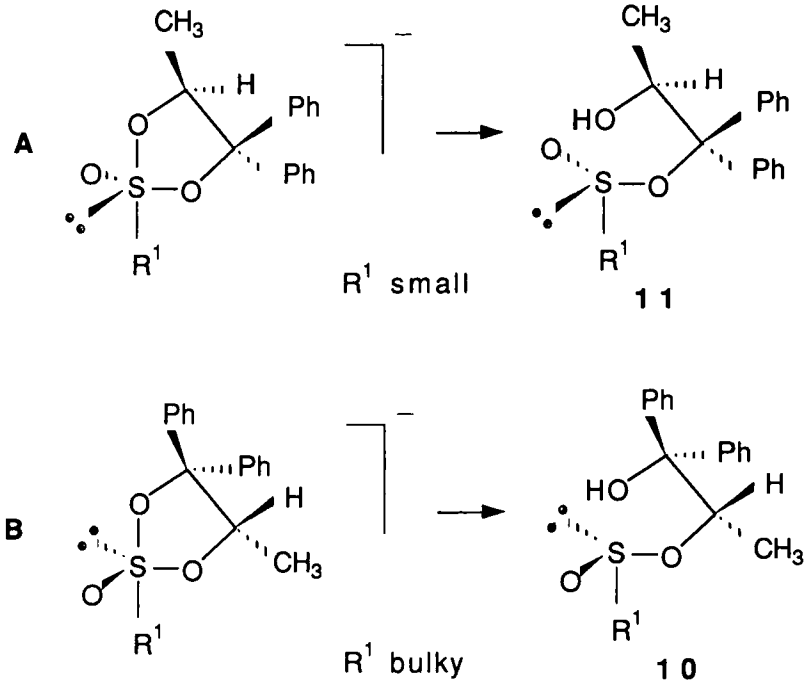
In conclusion we set up conditions for the synthesis of the desired enantiomer of a given sulfoxide. A wide variety of sulfoxides is now available by this approach, the only drawback being the low chemical yield observed where some organometallics (like $PhCH_2MgCl$) react with **8**, giving mixtures of sulfinates **10** and **11** in a ratio close to 1:1.

Stereochemistry of cyclic sulfite **8**

As explained above, absolute configuration at sulfur of sulfinates **10** and **11** was assigned by correlation with absolute configuration of sulfoxides **12** and **13**. If one also assumes inversion of configuration at sulfur in the step leading to sulfinates formation, the obvious conclusion is that sulfite **8** has R_S configuration, hence a trans stereochemistry. This assignment has been recently confirmed by X-ray structure of **8**[39].

Preferential orientation in the cleavage of sulfite **8**

The selective formation of either sulfinate **10** or **11** has been interpreted by the formation of a trigonal bipyramidal transition state or intermediate (**A**, Scheme 8) where the bulky group ($O\text{-}CPh_2$) placed itself in the equatorial position. In this species the incoming and leaving groups are both in apical positions and the ring cleavage in sulfite **8** will occur giving a secondary alcohol and hence sulfinate **11**. When the incoming nucleophile is bulky it will severely interact with the $O\text{-}CPh_2$ moiety linked to equatorial oxygen. The alternate structure **B** where the $O\text{-}CPh_2$ group is apical becomes favored, and as a consequence the alternate sulfinate **10** will be produced. There is a good qualitative agreement between experimental data and the above picture, however it is difficult to define the borderline cases giving a mixture of sulfinates. In the X-ray structure of sulfite **8** it was observed that the $S\text{-}OCPh_2$ bond is significantly longer than the S-O(CHMe) bond[39]. This could give some additional reactivity for the



Scheme 8

former bond with evolution towards structure **B** (already favored with the bulkiness of nucleophilic reagents).

Sulfites of chiral monoalcohols in the asymmetric synthesis of sulfoxides

In Scheme 3 the various ways are analyzed to go from a sulfite to a chiral sulfoxide. We recently started to investigate the situation of chiral sulfite **3** (open system). Sulfur is not an asymmetric center since it is connected to two OR* groups where the chiral moities have the same absolute configuration. Since sulfur is tetrahedral with two additional different groups (oxygen and electron pair) the two OR* branches happen to be diastereotopic. As a consequence one expects some difference in reactivity for the two OR* groups towards an achiral nucleophile. We are presently investigating this simple and interesting possibility and we shall present some preliminary results[40] in the near future. Dimenthyl sulfite has been prepared in good yield from thionyl chloride and (-)-menthol. It slowly reacts with t-BuMgBr to give a 1:1 mixture of menthyl t-butylsulfinate epimers at sulfur. t-BuLi reacts very rapidly but leads to di-t-butyl sulfoxide. Fortunately combination of the two reagents gives a good yield of menthyl t-butylsulfinate with 70% de (reaction performed at 0°C)[40]. We are actively working for improving the diastereoselectivity and the generality of this process (by a suitable choice of the experimental conditions and of the chiral alcohol). This approach can be straightforward especially for asymmetric synthesis of various chiral sulfinates which are immediate precursors of chiral sulfoxides.

Conclusion

During the past five years asymmetric synthesis of sulfoxides by chemical paths has undergone many improvements, making this approach quite convenient and general for synthetic uses[21,22,30,31]. According to the available precursors (achiral or chiral) sulfide oxidation, Andersen method or chemistry of chiral sulfite **8** will be selected. The stoichiometric synthesis of

sulfoxides from a sulfite that we developed has some interesting features : i) The use of a cheap and recyclable chiral diol .
ii) Predictability of the absolute configuration of synthesized sulfoxides. iii) The sulfoxides are obtained enantiomerically pure (with the accuracy of the usual analytical methods) with an excellent yield. iv) Both enantiomers of a sulfoxide are available by this method. As discussed above the method has some limitations in terms of structure of the sulfoxide, nevertheless as it stands at the moment it already appears to be a useful complement to existing routes to chiral sulfoxides. For example carbanions derived from some racemic ter-butyl sulfoxides give highly stereoselective 1,4-additions on conjugated esters[41,42]. This chemistry is now available by starting from the corresponding chiral ter-butyl sulfoxides that we could easily prepare (entries 6,7, Table III). Room for progress remains still in the pratical asymmetric synthesis of sulfoxides. The synthetic scheme should be compatible with the presence of many functional groups. The use of chiral auxiliary in catalytic amounts is always the most convenient and advantageous method, and we can hope to see in the future new advances in catalytic asymmetric synthesis of sulfoxides.

Table III

Asymmetric synthesis of sulfoxides R^1-SO-R^2 from sulfinate **10** or **11** and organometallique R^2M.

Entry	Sulfinate[a]	R^2M[b]	Temp.	ee[c]	Config.	Ref
1	**10** , R^1 = t-Bu	MeLi	25°C	100%	R	34
2	**10** , R^1 = t-Bu	PhLi	25°C	100%	S	33
3	**10** , R^1 = t-Bu	n-Buli	25°C	100%	R	33
4	**10** , R^1 = t-Bu	VinylMgCl	25°C	100%	R	33
5	**10** , R^1 = t-Bu	1-PicolylLi	25°C	100%	R	43
6	**10** , R^1 = t-Bu	$PhCH_2MgBr$	25°C	100%	R	34
7	**10** , R^1 = t-Bu	$Ph(CH_2)_2MgBr$	25°C	100%	R	34
8	**10** , R^1 = Mesityl	MeLi	0°C	100%	R	34
9	**10** , R^1 = Mesityl	PhMgBr	0°C	100%	R	34
10	**11** , R^1 = Me	n-OctylMgBr	0°C	100%	S	34
11	**10** , R^1 = Et	PhLi	0°C	100%	R	33
12	**11** , R^1 = Et	$PhCH_2MgBr$	0°C	100%	R	33
13	**11** , R^1 = n-Octyl	MeMgI	0°C	100%	S	33
14	**11** , R^1 = $PhCH_2$	EtMgBr	0°C	100%	S	34

a) Stereochemically pure **10** or **11** prepared from **8** as described in text.

b) Reaction gives quantitative yield after isolation of product by flash chromatography.

c) Measured by ^1H NMR with $Eu(hfc)_3$ or R-(3,5-dinitrobenzoyl)-1-phenylethylamine[18], and by compraison with maximun optical rotation.

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