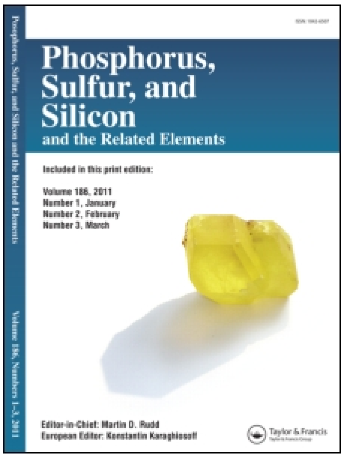

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Sulfine Chemistry

Binne Zwanenburg[a]
[a] Department of Organic Chemistry, University of Nijmegen, ED Nijmegen, The Netherlands

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SULFINE CHEMISTRY

BINNE ZWANENBURG
Department of Organic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

Abstract

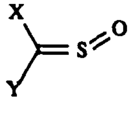
Sulfines (thione *S*-oxides) are non-linear sulfur-centered heterocumulenes with the general structure XY=SO. In the introduction the various approaches to the synthesis of sulfines and their reactions are briefly reviewed. In a separate section attention is given to the preparation of sulfines using of the reaction of sulfur dioxide with α-silyl carbanions (the modified Peterson reaction). This method provides an access to chiral sulfines, which are interesting partners in asymmetric cycloaddition reactions with dienes.

The preparation of α-oxo sulfines from α-methylene ketones, or the corresponding silyl enol ethers, and thionyl chloride is also treated in some detail. These α-oxo sulfines readily undergo cycloaddition reactions with dienes to yield various sulfur-containing heterocycles.

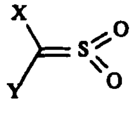
INTRODUCTION

Heterocumulenic compounds formally derived from sulfur dioxide by replacement of one oxygen atom by a carbon atom are nowadays known as sulfines.[1] The name sulfine for thione *S*-oxides was proposed by Sheppard and Dieckmann[2] in 1964 to indicate the structural relationship with thione *S*-dioxides which are known as sulfenes.[3]

Sulfine:



Sulfene:



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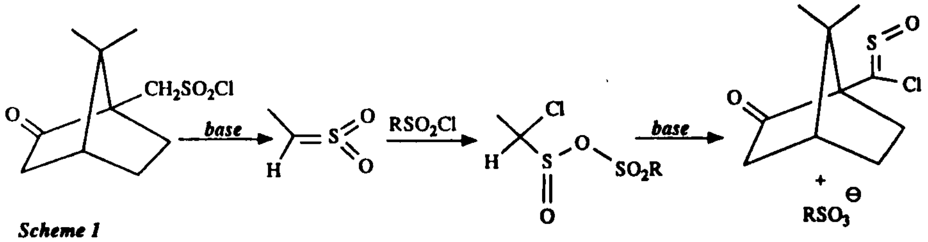
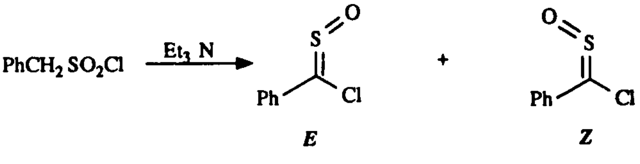
The first stable sulfine was isolated in 1923 by Wedekind et al.[4] from from a rather peculiar reaction of camphor-10-sulfonyl chloride with pyridine or triethylamine. The sulfine structure was confirmed about forty years later by King and Durst[5] using spectroscopic methods. In the early sixties evidence was accumulated that this formation of chlorosulfines proceeds via the intermediacy of a sulfene and a sulfinic sulfonic anhydride[6,3a] as is depicted in Scheme 1.



Scheme 1

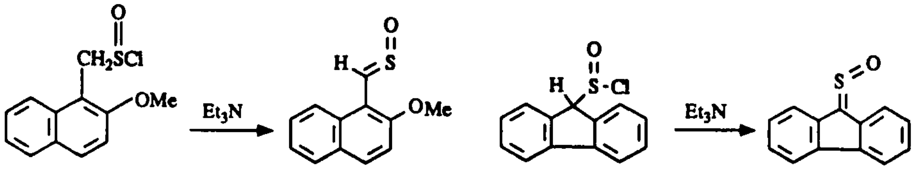
During the re-investigation of Wedekind's early chlorosulfine work King and Durst[7] observed an important structural property of sulfines, namely that these compounds can exist as stable geometrical isomers (Scheme 2). The assignment of the *E*- and *Z*- geometry could be made by means of proton NMR spectroscopy [^{1}H-NMR of the *E*-isomer: $\delta{\sim}8.3$ (2H), $\delta{\sim}7.5$ (3H) ppm, for the *Z*-isomer: $\delta{\sim}7.5$ ppm (5H)] and dipole moment measurements (for the *E*-isomer: $\mu=2.63$D, for the *Z*-isomer: $\mu=3.97$D). This observation of geometrical isomerism is in full accordance with the non-linearity of sulfines predicted from their structural relationship with sulfur dioxide. *E*- and *Z*-isomers are now known for a large variety of substituted sulfines.[1]



E *m.p. 5°C* *Z* *m.p. 38°C*

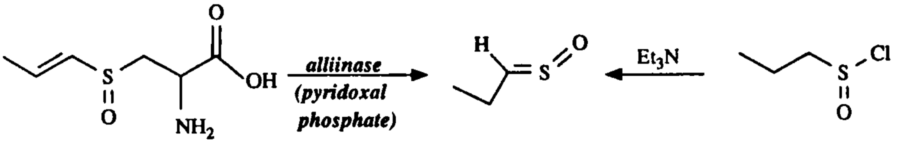
Scheme 2

The renewed interest in the chemistry of sulfines in the early sixties led to some general methods for the synthesis of these heterocumulenes.[1] Dehydrohalogenation of sulfinyl chlorides was employed to prepare the first stable thioaldehyde *S*-oxide[8] and thioketone *S*-oxide[2], as shown in Scheme 3.



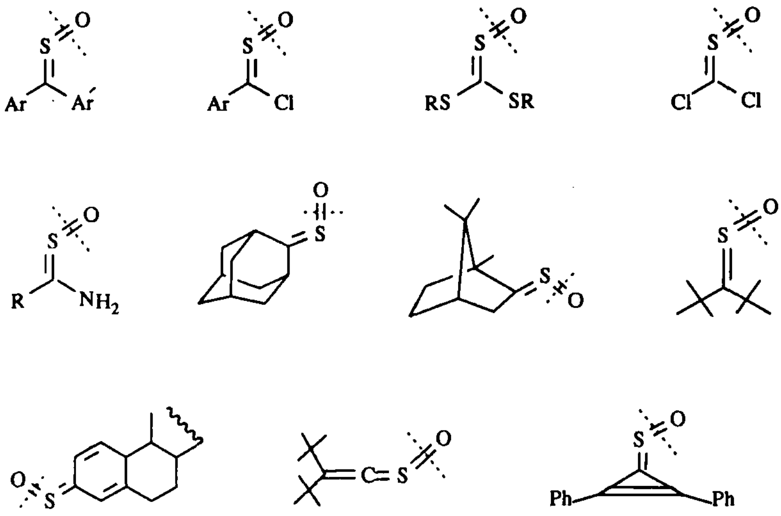
Scheme 3

This 1,2-elimination of sulfinyl chlorides was also used for the preparation of dimethylsulfine, several monoalkylsulfines, chlorophenylsulfine, cyanophenylsulfine, phenylsulfine and di-t-butylsulfine (loc. cit., cf.ref. 1). It is of interest to note that the principle lachrymatory factor in freshly cut onions has been characterized as ethylsulfine[9] (Scheme 4). In nature this sulfine is formed by the action of the enzyme *alliinase* upon (+)- *S*-(1-propenyl)-L-cysteine *S*-oxide, which is present in onions (0.2% by weight).



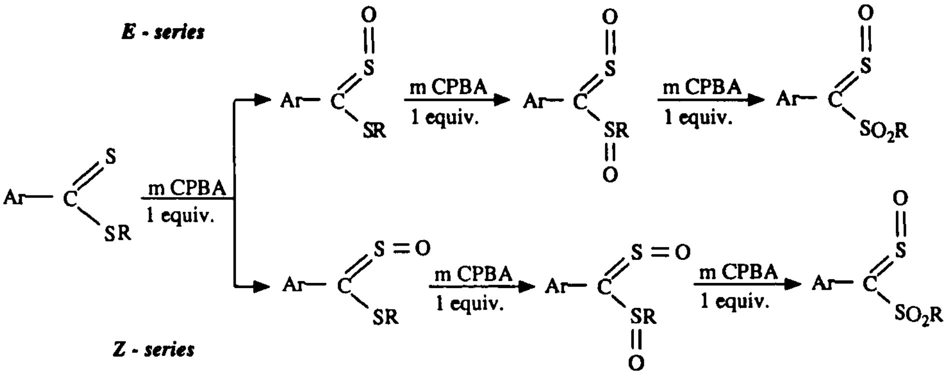
Scheme 4

The oxidation of thiocarbonyl compounds is a versatile and generally accepted synthesis of sulfines. The first examples dates back to 1938 when Kitamura[10] described the oxidation of thioamides with hydrogen peroxide to give the corresponding *S*-oxides to which, at that time, the incorrect imino sulfenic acid structure [RC(=NH)SOH] was assigned. In 1960 Walter[11] provided convincing evidence for the actual structure of the oxidation products (aminosulfines). The first report[12] of an oxidation of (aromatic) thioketones appeared in 1966. A large variety of thiocarbonyl compounds including fluorenethione, xanthione, thiaxanthione, adamantanethione, thiocamphor, thiacyl chlorides, trithiocarbonates, thiophosgene, thioketenes, have been converted into the corresponding *S*-oxides[1a,b] (Scheme 5). In most cases peroxycarboxylic acids, e.g. mCPBA, are the oxidizing agents of choice. In some special cases ozone and singlet oxygen can be used.[1a] The oxidation method is practically limited to non-enethiolizable thiocarbonyl compounds.[1a] When an appreciable amount of enethiol is present oxidation leads to vinyl disulfides.[13] When the starting thiocarbonyl compound has two different substituents at the carbon atom oxidation gives usually a mixture of *Z*- and *E*-sulfines, the ratio of which is kinetically determined.[1a,14]



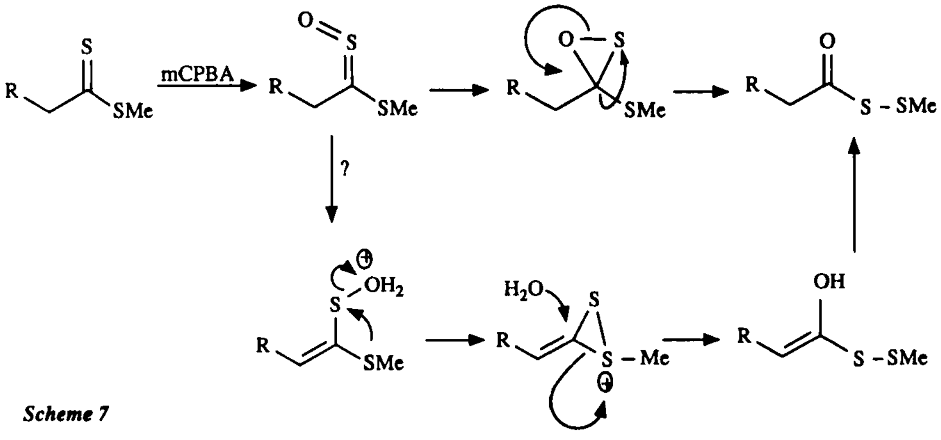
Scheme 5 Sulfines by oxidation of thiocarbonyl compounds

An illustrative example of the usefulness of the oxidation method is shown in Scheme 6. A series of structurally related sulfines can be obtained by stepwise oxidation of dithiocarboxylic esters. The first equivalent of peracid oxidizes the thiono-function to the *S*-oxide. After separation of the *Z*- and *E*-isomers, further treatment with peracid results in oxidation of the thiolo-sulfur to sulfoxide and sulfone as indicated.[1a,b,15]



Scheme 6

Rather surprisingly, the oxidation of aliphatic dithioesters with mCPBA also gave the corresponding sulfines[16] (Scheme 7). These sulfines readily undergo a rearrangement reaction (at room temperature) to give dithioperoxyesters. It was suggested that this rearrangement proceeds via the intermediacy of an oxathiirane, as depicted in Scheme 7. An alternative pathway involving an initial tautomerization to a vinylsulfenic acid, as shown on the bottom line of Scheme 7, gives credit to the fact that this interesting rearrangement reaction has not been encountered for aryl substituted alkylthio-sulfines.



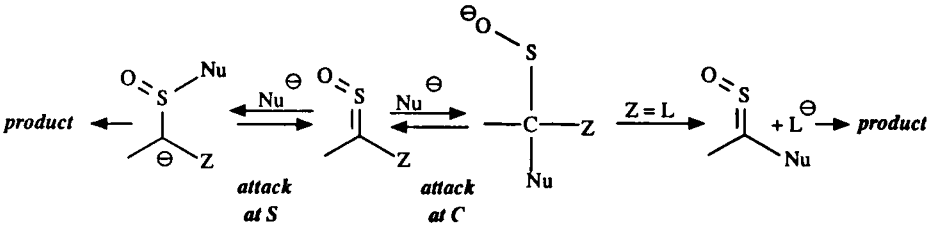
Scheme 7

There are several other methods[1] available for the synthesis of sulfines, such as the thermolysis of sulfinyl compounds, 1,3-dehydrochlorination of chlorosulfenic acids, singlet-oxygen oxidation of thiophenes, rearrangement of sulfinylcarbenes and reaction of sulfur monoxide with diazo compounds. In most cases these methods are only applicable in a limited number of cases. (the alkylidenation of sulfur dioxide will be discussed in a separate section, *vide infra*). An interesting new preparation for aliphatic sulfine, including the parent sulfine $H_2C{=}SO$, is the fluorodesilylation of α-(trimethylsilyl)alkanesulfinyl chlorides with cesium fluoride in acetonitrile.[17]

BASIC FEATURES OF SULFINES

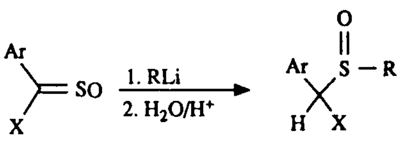
The molecular structure of sulfines, particularly the non-linearity of the CSO-system, was established by X-ray (C-S: 1.62 Å, S-O: 1.46 Å; CSO: angle: 114°).[1a] The electronic charge distribution was calculated for the parent sulfine and mono- and dihalogen substituted sulfines using *ab initio* methods.[18] The charge on sulfur and oxygen remains almost constant (S: +0.63±0.03, 0: -0.69±0.01) whereas the charge on carbon is strong influenced, when the substituents on carbon are varied. This observation is reflected in the chemical behaviour of differently substituted sulfines.[1]

For the reactions of sulfines with nucleophilic reagents two principle modes of reactions can be envisaged, *viz.* a thiophilic and a carbophilic reaction, as is depicted in Scheme 8.



Scheme 8 Reaction modes with nucleophiles.

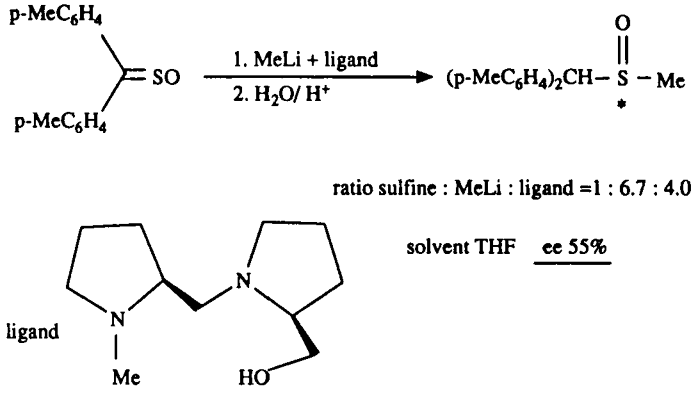
Nucleophilic reactions at the positively charged sulfur atom are observed in quite a number of cases, however, carbophilic reactions with nucleophiles are encountered less frequently and are probably limited to sulfines having a leaving group L on carbon. A typical example of a thiophilic reaction is the formation of sulfoxides upon treatment of sulfines with an alkyllithium (Scheme 9).[1a]



X = Ar, SAr, SAlk, S(O)Ar, SO_2Ar.
R = Me, Bu, Ph.

Scheme 9

The addition of methyllithium to di-*p*-tolylsulfine in the presence of Mukaiyama's chiral ligand leads to optically active sulfoxides with a reasonable enantiomeric excess (Scheme 10).[19]

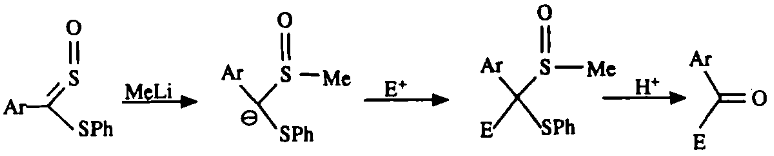


ratio sulfine : MeLi : ligand =1 : 6.7 : 4.0

solvent THF ee 55%

Scheme 10 *Asymmetric addition of MeLi*

The reaction of phenylthio substituted sulfines with methyllithium forms the basis for the use of these sulfines in nucleophilic acylation reactions[20] (Scheme 11). The initially formed carbanion can be treated with a variety of electrophiles. The dithioacetal monoxide thus formed gives the corresponding carbonyl compounds upon acidolysis. Reactions with Michael acceptors, such as acrylonitrile, can also be accomplished[20] under slightly modified conditions. An example of a carbophilic reaction is the displacement of the chlorine atom in chloro-phenyl-sulfine by a phenolthio group upon treatment with thiophenol in the presence of triethylamine.[21]



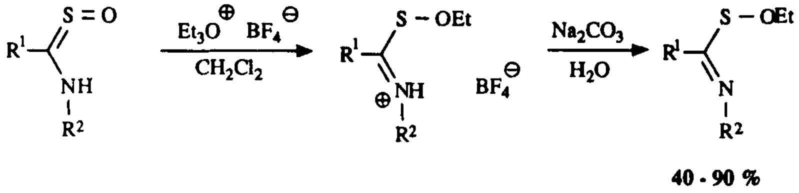
Electrophiles: RCH_2Br ; PhCOCl ; CO_2 ; PhCH=O

Products : E = RCH_2- ; PhC=O ; -COOH ; Ph-CHOH

Scheme 11

It is of interest to note that this displacement reaction takes place with retention of the geometrical configuration of the sulfine.

A reaction at the negatively charged sulfine oxygen atom was accomplished with the hard electrophilic reagent triethyloxonium fluoroborate. Aminosulfines were particularly suited as substrates as the desired O-alkylation products were readily formed[22] (Scheme 12). The iminium salts obtained gave the ethyl α-imino sulfenates shown upon treatment with sodium carbonate. Interestingly, these compounds are the esters of iminosulfenic acid, structures originally, but incorrectly, proposed for thioamide *S*-oxides by Kitamura[10] in 1938.

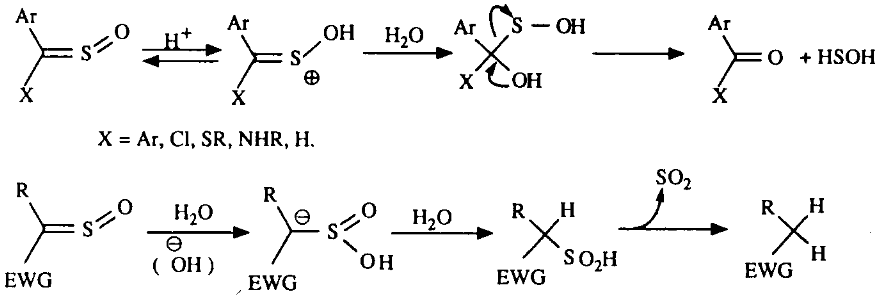


R^1 = Ph, p- Tol, CH_3 ; R^2 = H, Ph, p- ClC_6H_4

Scheme 12

These sulfenic esters do not rearrange to α-imino sulfoxides.[22] The imino sulfenate derived from thiobenzamide S-oxide (R^1=Ph, R^2=H) dimerized to give a 1,4,2,5-dithiadiazine, a new heterocyclic system,[23] even on standing at -20°C.

The hydrolysis of sulfines depends on the nature of the substituents at carbon. Ordinary sulfines, such as diarylsulfines, chlorosulfines, aminosulfines and alkylthio-sulfines undergo acid-catalyzed hydrolysis to the corresponding carbonyl compounds.[1a] Initial protonation of the sulfine oxygen with subsequent attack of water at carbon, explains this conversion[1a] (Scheme 13). A reductive hydrolysis of the sulfine function to a methylene group is observed however,for sulfines substituted with an electron-withdrawing group[24] (Scheme 13). Water now reacts nucleophilically at the sulfine sulfur atom. Expulsion of sulfur dioxide from the sulfinic acid formed then leads to the methylene compounds.



X = Ar, Cl, SR, NHR, H.

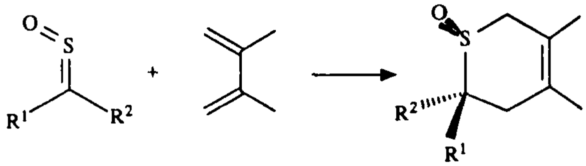
EWG = e.g. $ArSO_2$, RC(=O), $(EtO)_2P(O)$.

Scheme 13 ***Hydrolyses of sulfines.***

A typical behaviour of many types of sulfines is the loss of elemental sulfur to give the corresponding carbonyl compounds under thermal, and particularly, photochemical conditions.[1a] It has been shown that this loss of sulfur proceeds via an intermediate oxathiirane.[1a] Remarkably, this reaction has not been observed for sulfines having an electron-withdrawing substituent at carbon, the group of sulfines that also show deviant behaviour in the hydrolysis reaction.

An important and well documented reaction of sulfines is the cycloaddition with dienes and 1,3-dipoles.[1a,b] A great variety of differently substituted sulfines, especially those with electron withdrawing substituents, react with dienes to give dihydropyran S-oxides[1a,25] (Scheme 14). The stereochemical relationship of the sulfine substituents is retained in the cycloadduct. This stereospecific behaviour is in accordance with concerted [4+2] cycloaddition reactions.

In the recent literature[26] an example of a non-stereospecific cycloaddition was reported, viz. for the reaction between phenylsulfine (*Z*+*E* PhCH=SO) and dimethylbutadiene. No good explanation is avaiblable as yet, for this deviant behaviour.

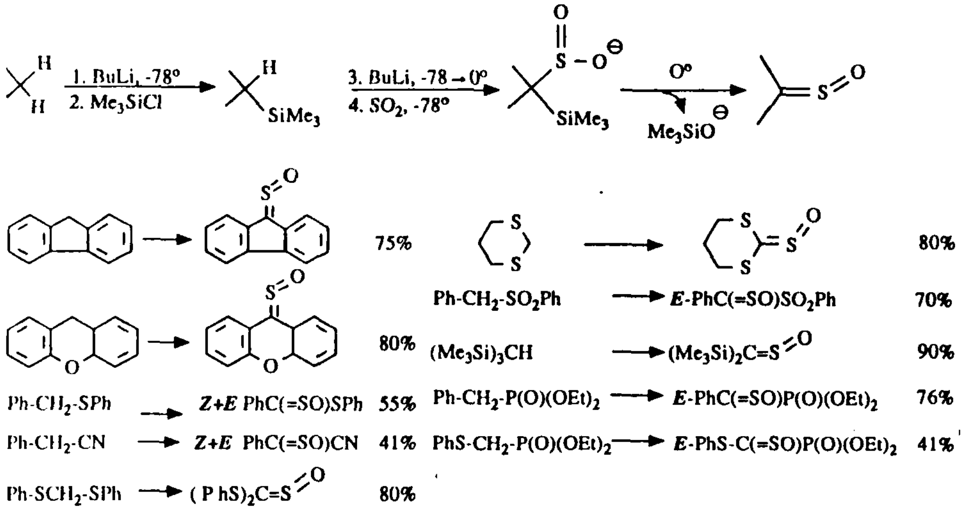


Scheme 14

Different types of 1,3-dipoles have been investigated, e.g. diazoalkanes, nitrilimines, nitrilylides and nitriloxides. These reaction have reviewed in detail in ref. 1a,b.

SYNTHESIS FROM SULFUR DIOXIDE

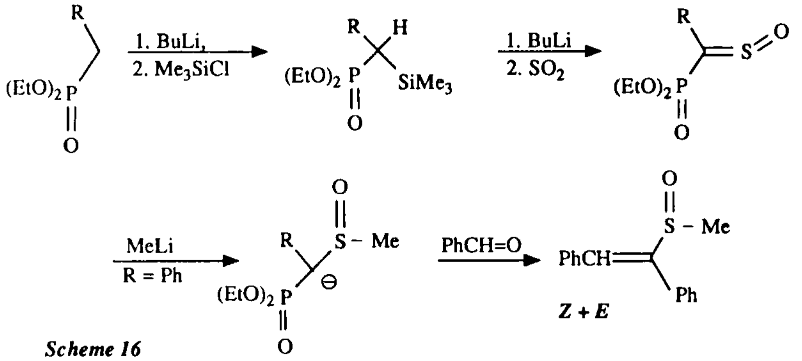
An interesting approach to the synthesis of sulfines is the replacement of one oxygen atom in sulfur dioxide by an alkylidene group. A modification of the Peterson olefination reaction[27] *viz.* the alkylidenation of sulfur dioxide using α-silyl carbanions, is an excellent and fairly general method for the synthesis of sulfines[1a,b;28,29] (Scheme 15). The attractive features of this synthesis of sulfines are: *i* that the required α-silyl carbanions can usually easily be obtained from



Scheme 15

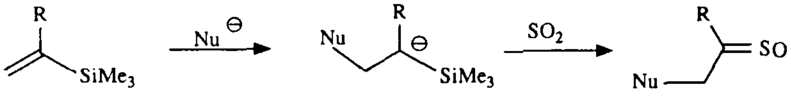
readily available active methylene compounds, *ii* that the method is experimentally simple as in many cases it can be performed without isolation of intermediate products (one-pot procedure) and, *iii* that new types of sulfines can be prepared which are not accessible by the oxidation of thiocarbonyl compounds. It is often essential to add the α-silyl carbanion to an excess of sulfur dioxide in order to avoid a complicating side reaction of the α-silyl carbanion with already formed sulfine.[28] In some cases the final elimination step leading to the sulfine is facilitated by the addition of thionyl chloride.

An illustrative example[29] of the modified Peterson reaction is the sulfination of the methylene group in a phosphonate ester (Scheme 16). Methylation of this (diethoxyphosphoryl)sulfine with methyllithium produces a Wittig-Horner type intermediate, which on reaction with benzaldehyde leads to α,β-unsaturated sulfoxides in good yields.[29]



Scheme 16

An alternative method for the preparation of α-silyl carbanions is the β-addition of appropriate nucleophiles to vinylsilanes (Scheme 17).[30] Organolithium compounds are especially suitable nucleophiles for this purpose. The best results are obtained for R is $PhSO_2$ (MeLi: 74%, PhLi: 72%). It should be noted this heteroconjugated addition leads to sulfines with a hydrogen atom at the α-carbon atom which are difficult to prepare, if at all, via the oxidation of the corresponding thiocarbonyl compounds because of the complication due to enethiolization.

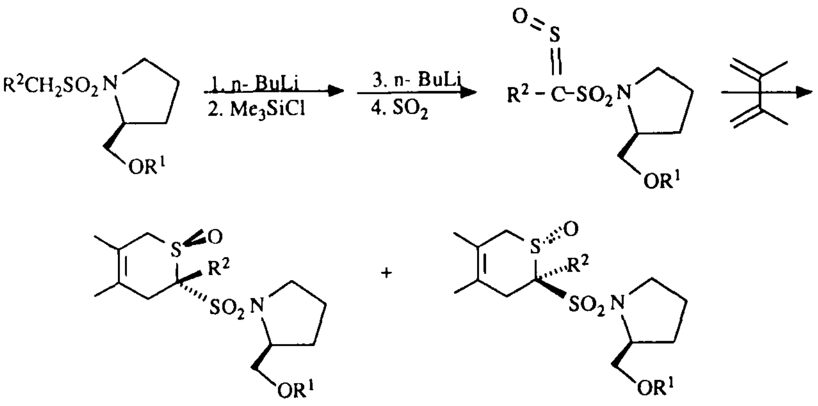


R = $PhSO_2$, Nucleophile: t- BuLi (51%), n- BuLi (50%), MeLi (74%), PhLi (72%)
R = PhS , " " (73%), " (15%)
R = Ph , " " (29%)

Scheme 17

CHIRAL SULFINES

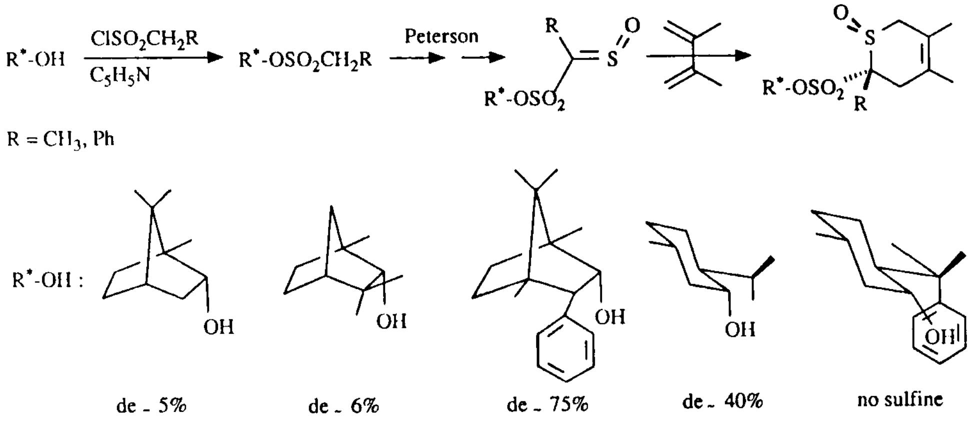
The Peterson approach offers a unique possibility to attach a chiral substituent to sulfines, simply by starting with a chiral active methylene compound. Chiral sulfines are of interest in connection with the asymmetric cycloaddition reactions with dienes. The synthesis of a chiral sulfine[31] derived from proline is depicted in Scheme 18. By reaction of a prolinol alkyl ether with an appropriate alkanesulfonyl chloride the required chiral substituent is introduced as well as an electron-withdrawing function to ensure sufficient dienophilicity of the sulfine to be prepared. The [4+2] cycloaddition reaction is a stereospecific process,



Scheme 18

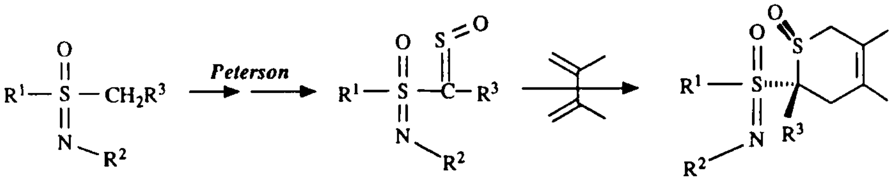
therefore two diastereomeric cycloadducts are possible (the prochiral centers in the sulfine are coupled). In case of an asymmetric induction they will be formed in unequal amounts. The diastereomeric excess obtained for the various substituents R_1 and R_2 range from 2 to 40%, the best results are obtained when R_2 is a chlorine atom and when the reaction is performed at -78^{0}C. The explanation for the moderate d.e. values is that the inducing chiral center is probably too far away form the dienophilic site.

Chiral inductors derived from terpene alcohols were also attached to the sulfine function following an approach similar to that described above. The chiral sulfonates were converted into the corresponding sulfines and subjected to a cycloaddition reaction with 2,3-dimethyl-butadiene (Scheme 19).[32] The diastereoselectivity was disappointingly low, except for (+)-3-*endo*-hydroxy-2-*endo*-phenylbornane which gave a d.e. of 75%.



Scheme 19

Excellent optical yields were obtained for the cycloaddition reaction of sulfoximino sulfines which have the inducing chiral center in close proximity to the sulfine function (Scheme 20).[33] Various substituents R_1, R_2 and R_3 were investigated, in all cases d.e.'s of 100% were found. The overall chemical yield varied from 40 to 70%. For one of the adducts the structure was determined by X-ray analysis (Scheme 21), which allows the reconstruction of the approach of the diene to the sulfine function.



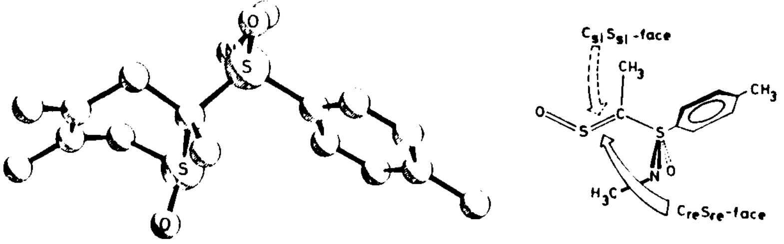
R^1	Ph ,	Ph ,	Ph
R^2	Me ,	Tos ,	Me
R^3	Me ,	Me ,	Cl

starting material: optically pure and racemic

optical yield: 100%

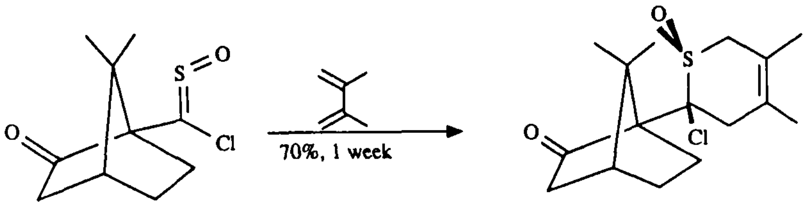
Scheme 20

From the structure shown in Scheme 21 it can be deduced that the diene has reacted from the $C_{si}S_{si}$-face of the sulfine. Assuming that the *p*-tolyl ring is positioned in a plane perpendicular to the bisecting plane of the sulfoximino group, two rotamers about the single bond between the sulfine-carbon atom and the sulfoximo-sulfur atom-with minimized steric and electrostatic interactions are conceivable, *viz.* one with the CSO function *syn* with respect to the *p*-tolyl group and one having the sulfine function placed *anti* to the *p*-tolyl group. The donor-acceptor complex of the sulfine and the diene preceding the cycloaddition reaction will most likely arise from an approach of the diene to the sulfine rotamer which has the least hindered $C_{si}S_{si}$-face. Inspection of molecular models clearly reveals that a diene reaction of the rotamer with the CSO function *anti* to the *p*-tolyl group encounters the least steric hindrance (Scheme 21). In other words, it is suggested that the steric hindrance exerted by the N-methyl group of the sulfoximino function is responsible for the high diasteroselectivity.[33b]



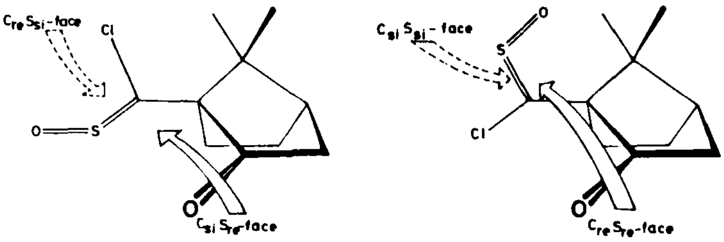
Scheme 21 *X - ray of the cycloadduct derived from E - p-Tol-S(O)(NMe)C(=SO)Me and dimethyl-butadiene. Approach from the $C_{si}S_{si}$ - face.*

It is of interest to note that the first sulfine ever prepared, *viz.* Wedekind's chlorosulfine derived from camphor (Scheme 1)[4], is a chiral sulfine and therefore a potential candidate for an asymmetic Diels-Alder reaction. Cycloaddition of this sulfine, which has the *Z*-geometry, with 2,3-dimethyl-1,3-butadiene yielded only a single diastereomer of the cycloadduct implying a complete asymmetric induction[33] (Scheme 22).



Scheme 22

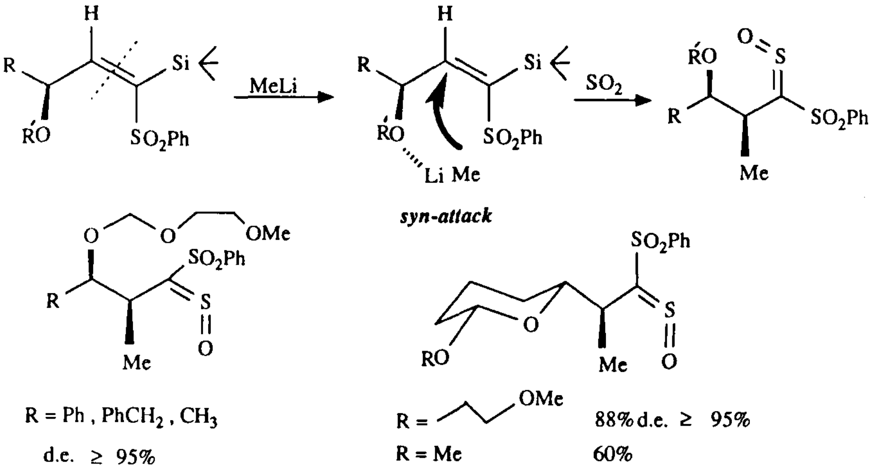
An interesting observation[33b] was made when the cycloaddition of Wedekind's sulfine was carried out in the presence of pyridine. Now two cycloadducts were isolated, one being the adduct from the *Z*-sulfine and the other the adduct derived from the *E*-sulfine, as was deduced from an X-ray analysis. This result can be readily explained by invoking an isomerization of *Z*- to *E*-sulfine under the influence of pyridine. Such an isomerization proceeds by an addition-elimination reaction as was suggested previously.[1a] From the X-ray structural information it can readily be reconstructed that the diene has approached the *Z*-sulfine from the C_{re} S_{si}:-face and the *E*-sulfine from the C_{si} S_{si}-face, Studies of molecular models revealed that the least steric hindrance for these diene approaches is encountered in the C_1-C_{10} rotamers of the sulfines that are pictured in Scheme 23. (In both cases diene approach from the rear side).[33b]



***Scheme 23** Approaches of diene to Wedekind's sulfine.*
(In both cases attack from the rear side is observed)

The heteroconjugate addition as shown in Scheme 17 can also be used to prepare chiral sulfines in the following manner.

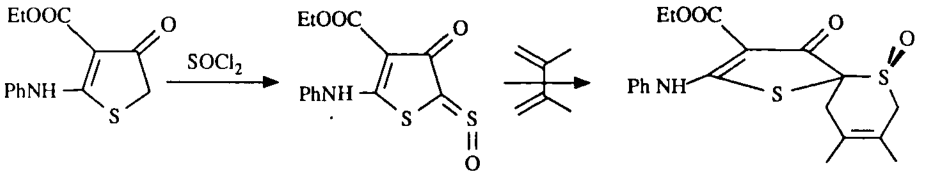
The β-addition of methyllithium to a vinylsilane takes place intramolecularly in a completely stereocontrolled fashion, when the organolithium reagent is coordinated with an appropriately positioned ether function. Such a diastereoselective *syn*-attack of an alkoxy substituted vinylsilane was first demonstrated by Isobe *et al.*[34] The stereocontrolled heteroconjugate additions shown in Scheme 24 take place with almost quantitative optical yields.[35] The Diels-Alder reactions with the chiral sulfines, prepared in this manner, show a high diastereoselectivity (d.e 's > 95%).[35]



Scheme 24 *Heteroconjugate addition*

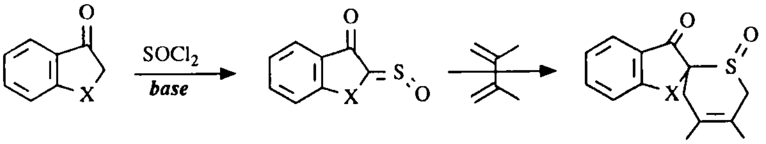
α-OXO SULFINES

In 1981 Faull and Hull[36] reported the formation of a sulfine by reaction of a dehydrothiophanone with thionyl chloride (Scheme 25), although the evidence for the sulfine structure was not unambiguous. The reaction was therefore repeated and the product subjected to a typical sulfine reaction, *viz.* the cycloaddition with a diene. An X-ray analysis[37] of the adduct proved unequivocally the formation of the α-oxo sulfine shown in Scheme 25.



Scheme 25

This finding was the start of investigations to establish whether this attractive preparation of α-oxo sulfines, from a methylene ketone and thionyl chloride, could be extended to other ketones. Treatment of 3-oxo-dihydrobenzothiophene with thionyl chloride in ether gave, in a fast reaction, the corresponding α-oxo sulfine, which crystallized from the reaction mixture within a few minutes (Scheme 26).[37] However, the oxo sulfines from the corresponding sulfone (Scheme 26) could not be isolated probably due to their high sensitivity towards reductive hydrolysis (cf Scheme 13). Trapping with dimethylbutadiene gave the expected cycloadduct[38] as shown in Scheme 26. This direct method seems to be limited to ketones with a sufficiently active methylene group[39]. The first step in

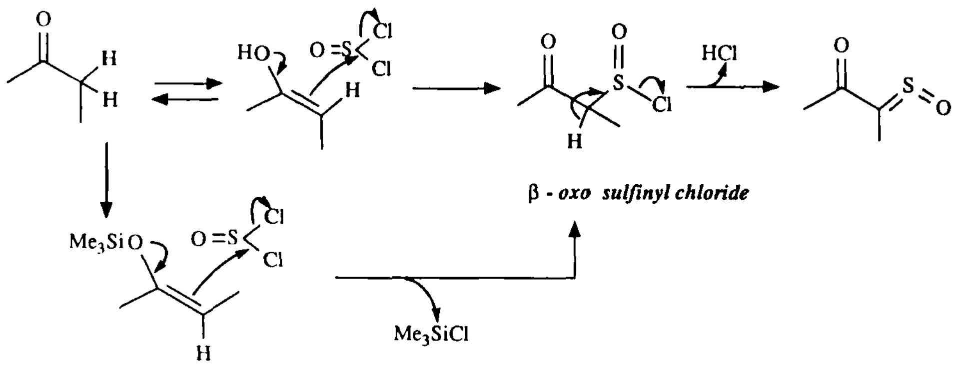


(base : 2,6 - lutidine)

X =S	67%	86%
" SO_2	not isolable	55%
" CH_2	not formed	-

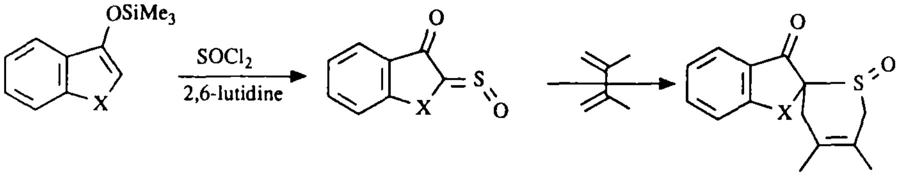
Scheme 26

this sulfine synthesis is the reaction of the enol form of the ketone with thionyl chloride to give a β-oxo sulfinyl chloride, which either spontaneously or means of base, eliminates hydrogen chloride to give the α-oxo sulfine. (Scheme 27)



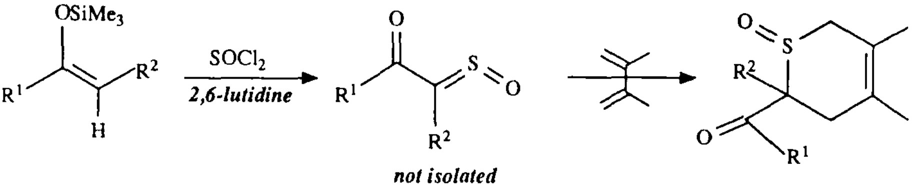
Scheme 27

Apparently, the enol content of the ketone plays an essential role in this sulfine formation. Therefore, it was decided to consolidate the enol structure through the enol silyl ether. Gratifyingly, a variety of enol silyl ethers react smoothly with thionyl chloride to produce α-oxo sulfines.[40,38] The sulfines needed to be trapped as their Diels-Alder adducts in almost all cases (Scheme 28 and 29).



X		
X = CH_2	48%	85% (one pot)
= $(CH_2)_2$	33%	75% (" ")
= OCH_2	not isolable	70% (" ")

Scheme 28



R^1	R^2	*temp. (°C)*	*time (h)*	*yield cycloadduct (%)*
EtO	EtOOC	-20	1	53
MeO	Ph	20	24	59
Ph	$PhSO_2$	-20	24	48
Ph	Ph	20	40	35
Ph	H	-78	0.5	84

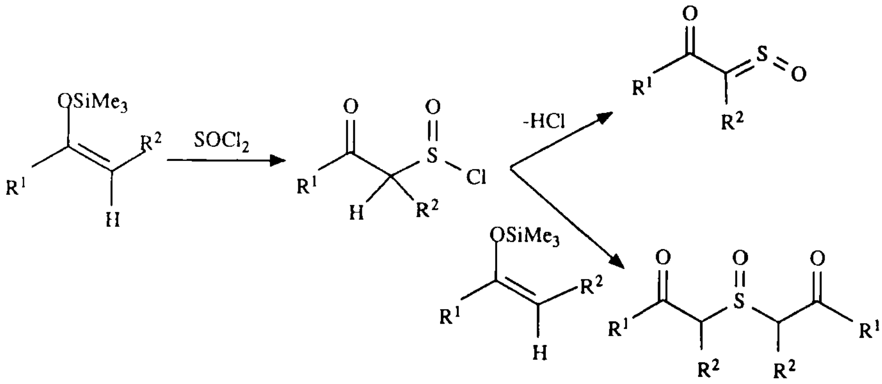
Scheme 29

The addition of a hydrogen chloride, scavenger preferably 2.6-lutidine, is necessary in practically all cases. Mechanistically it may assumed[38,40] that the enol silyl ether reacts with the electrophilic reagent thionyl chloride as depicted in Scheme 27, producing a β-oxo sulfinyl chloride which is essentially the sulfine precursor.

It should be emphasized that the α-oxo sulfines readily undergo reductive hydrolysis to give the carbonyl compounds, which are the starting materials for the enol silyl ethers. Consequently, the preparation of α-oxo sulfines must be carried out under strictly dry conditions. This sensitivity of α-oxo sulfines to water may be the reason why this simple reaction of enol silyl ethers with thionyl chloride has been overlooked in the past.

The reaction of enol silyl ethers with thionyl chloride is a general and facile entrée to a variety of α-oxo sulfines, as is demonstrated by the examples shown in Schemes 28 and 29. Benzoylsulfine can be obtained from acetophenone and bis-(ethoxycarbonyl)sulfine from diethyl malonate.

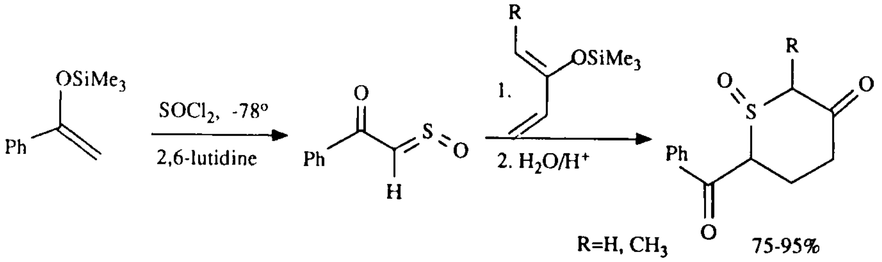
Since enol silyl ethers also react with sulfinyl chlorides there is the potential danger that the intermediate β-oxo sulfinyl chloride also reacts with the enol silyl ether to give a β,β^1-dioxo-sulfoxide as depicted in Scheme 30. This unwanted side reaction can be avoided by adding the enol silyl ether to a solution of thionyl chloride in dichloromethane (also containing a diene as trapping agent). Not all enol silyl ethers are equally sensitive to the addition procedure, in some cases, however, dramatic effects were observed.



Scheme 30

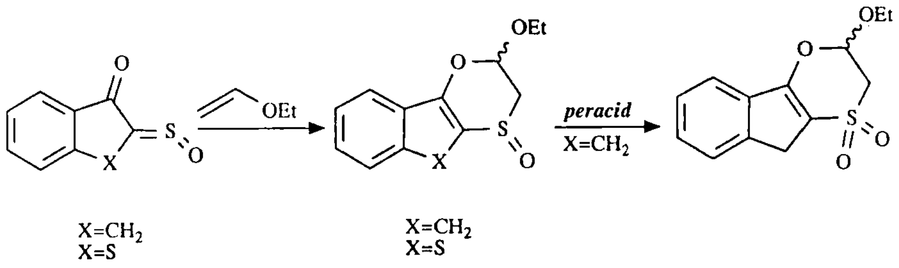
A chiral α-oxo sulfine can be obtained from, for example, the menthyl phenylacetate. Conversion into the corresponding enol silyl ether (a ketene acetal) and subsequent addition to a solution of thionyl chloride in dichloromethane, also containing 2,3-dimethyl-1,3-butadiene and 2,6-lutidine, gives a diastereomeric mixture of cycloadducts with a d.e. of 20%. However, by modifying the experimental conditions and choosing better chiral inductors, it is expected that the optical yield can be improved considerably.

α-Oxo sulfines can also be trapped[41] with 2-siloxy dienes, an example is shown in Scheme 31. These 2-siloxy dienes also can serve as starting materials in the reaction with thionyl chloride, however, no self-trapping was observed. Instead, trapping with dimethylbutadiene was readily accomplished as usual.



Scheme 31

α-Oxo sulfines also show another interesting property, namely, that they can serve as the 4π component in [4+2] cycloaddition reactions with electron-rich olefins, like ethyl vinyl ether[38] (Scheme 32). The regiochemistry of this cycloaddition was proven by oxidation of the adduct to the corresponding sulfone, the NMR spectrum of which is only in accordance with the regioisomer shown. A similar reaction was accomplished with the α-oxo sulfines derived from cyclohexanone.[41]



Scheme 32

The α-oxo sulfine obtained from 1-thiochromanone 1,1-dioxide via its enol silyl ether was found to react with isobutene and norbornene as the 2π component in a [4+2]-cycloaddition reaction.[42]

The chemistry of α-oxo sulfines and their trapping products is currently actively explored in the author's laboratory.

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