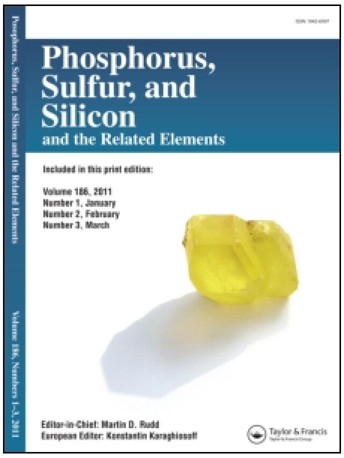

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Advances in Sulfine Chemistry

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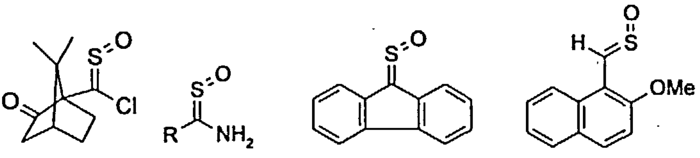
Sulfines (thione S-oxides) are nonlinear sulfur centered heterocumulenes formally derived from sulfur dioxide by replacing one oxygen by a carbon atom. In the introduction historical highlights are presented. A section is devoted to some recent developments regarding the synthesis of sulfines, viz. via oxidation by dimethyl dioxirane, and the reaction of silyl enol ethers and active methylene compounds, respectively, with thionyl chloride in the presence of a tertiairy amine base. Enethiolization of sulfines to vinylsulfenic acid is discussed in terms of its entrapment by an intramolecular reaction with an olefin. In this context also the optical integrity of sulfines having a stereogenic center at C-α is described. In the final section the Diels-Alder type cycloaddition reaction to give dihydrothiopyran *S*-oxides, with special focus on the asymmetric induction, is reported.

Keywords: thione *S*-oxides; enethiolization; vinylsulfenic acid; cycloaddition; sulfur heterocycles

INTRODUCTION

In 1923 Wedekind, Schenck and Stüsser [1] published their paper on the preparation of "Chlorosulfoxid-camphor" 1 which nowadays can be considered as the bench marker for the chemistry of sulfines. This preparation of the first thiocarbonyl *S*-oxide by treatment of camphor-10-sulfonyl chloride with pyridine or triethylamine is a peculiar reaction which mechanistically is by no means straightforward. The structure of Wedekind's product was confirmed about forty years later by King and Durst using spectroscopic evidence [2]. These authors also uncovered a very important property of sulfines, namely that they have a nonlinear structure and that therefore they exist as geometrical isomers provided that the substituents at the sulfine carbon atom are different[2]. Thus, treatment of benzylsulfonyl chloride with triethylamine gave both isomers of phenyl-chlorosulfine. The mechanism of this first sulfine synthesis proceeds via the intermediacy of a sulfene [2,3] (as was already suggested by Wedekind *et al.*) and a sulfinic sulfonic anhydride[4], but the full details remain still unclear[5]. It is of interest to note that it took more than sixty years before the actual geometry of Wedekind's Chlorosulfoxid-camphor was elucidated by an X-ray analysis[6].



1 2 3 4

CHART 1

Another important milestone in sulfine chemistry is the publication by Walter[7] in 1960 in which he proved that the actual structure of the products obtained by oxidation of thioamides using hydrogen peroxide, is a thioamide *S*-oxide **2**. The original report on aminosulfines by Kitamura [8] remained unnoticed until Walter's reinvestigation[7].

A historical marker in sulfine chemistry is for sure the publication of Sheppard and Diekmann (1964)[9] who prepared fluorenethione *S*-oxide **3** by a dehydrochlorination reaction of the corresponding sulfinyl chloride. These authors suggested for the first time[9] the name *sulfine* for thiocarbonyl *S*-oxides to indicate the structural relationship with sulfenes, which are thiocarbonyl *S,S*-dioxides[3]. In the same year the first thioaldehyde *S*-oxide **4** was prepared by Strating, Thijs and Zwanenburg[10] also employing the dehydrochlorination method.

In retrospect it is highly remarkable that oxidation of thioketones was not considered earlier for the synthesis of diarylthione *S*-oxides. Apparently, the earlier literature[11] indicating that oxidation of thioketones immediately led to the corresponding ketones, has been too discouraging. It was found however, that careful treatment of fused aromatic thioketones, such as fluorene thione and xanthione with one equivalent of monoperphtalic acid gave an immediate change of the typical thione colour and concurrent formation of the corresponding sulfines in excellent yields[12]. After this initial success, the oxidation method was elaborated to a general and convenient method for the synthesis of a large variety of sulfines[13,14]. In fact, the only limitation is the availability of the starting thiocarbonyl compounds. This oxidative method has been extensively reviewed[13,14,15,16].

A true milestone in sulfine chemistry is the finding that ethylsulfine is the principal lachrymatory factor in freshly cut onions[17,18]. The occurrence of a sulfine in nature has undoubtedly stimulated the development of sulfine chemistry in the seventies. Sulfines are usually represented as heterocumulenes formally derived from sulfur dioxide by replacing one oxygen atom by a carbon atom. This formula is not correctly referring to the electronic structure of sulfines in which sulfur has a net positive and oxygen a net negative charge[19]. The participation of d-orbitals is regarded as small if any[20].

The general features of the chemical behavior of sulfines are summarized in Chart 2. The most frequently used reaction of sulfines

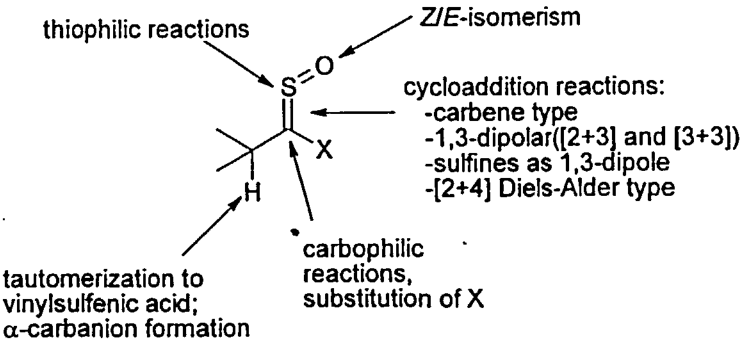
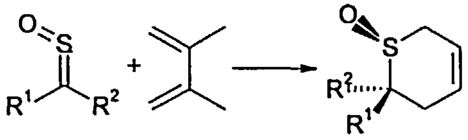


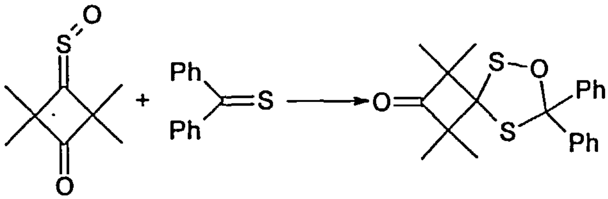
CHART 2

is the Diels-Alder type cycloaddition with 1,3-dienes to give dihydrothiopyran *S*-oxides (Scheme 1). In this respect the first reported Diels-Alder reaction of phenyl-chlorosulfine is of historic relevance[21]. This [2+4]-cycloaddition is stereospecific as the geometry of the sulfine is retained in the cycloadduct[13, 21]. Dipolar cycloadditions also have been extensively



SCHEME 1

studied[13,14]. However, a cycloaddition in which the sulfine serves as the 1,3-dipole was discovered much later by Huisgen *et al.*[22], who elegantly used thiones as super-dipolarophiles[23]. The structures of the 1,2,4-oxadithiolanes was confirmed by an X-ray diffraction analysis[22] (Scheme 2). Thiophilic addition reactions have been investigated in



SCHEME 2

great detail[13,14]. In this context the use of sulfines derived from dithioesters in nucleophilic acylation reactions is worth noting[13,24]. Carbophilic reactions can only be accomplished when a good leaving group X is present, e.g. for X is Cl displacement with sulfur nucleophiles has been accomplished[13]. The tautomerism of sulfines with vinylsulfenic acid was already discussed when the structure of the lachrymatory factor in onions was investigated[25,13,18]. Originally it was believed that this factor was 1-propenylsulfenic acid ($CH_3CH=CH-S-OH$) instead of the ethylsulfine tautomer[18,23]. Chemical evidence for the existence of tautomerism was obtained by trapping experiments of the vinylsulfenic acid tautomer (see section enethiolization) which were carried out at a more recent date[26].

Several reviews on the chemistry of sulfines have appeared over the years, covering most of the chemistry performed until the late eighties [13,14,15,16,27,28,29]. In this account special attention will be given to some recent developments with regard to the synthesis of sulfines, the phenomenon of enethiolization, special features of α-oxosulfines and new aspects of the Diels-Alder type cyclization reaction.

SYNTHESIS

The oxidation of thiocarbonyl compounds to give sulfines (see previous section) is usually performed with a peroxycarboxylic acid, such as *m*-chloroperbenzoic acid (mCPBA). There is however still a need for a mild oxidant especially for those sulfines that may decompose during the (aqueous) work-up procedure. For this purpose dimethyl dioxirane (DMDO) was investigated as it is a mild and convenient oxidant[30]. Treatment of diaryl thioketones with DMDO smoothly produced the corresponding *S*-oxides in high yield (Chart 3). Mesityl phenyl thioketone gave an *E*:*Z* mixture of sulfines in the ratio of 7:3. Most importantly, this method is also very suitable to oxidize thiocarbonyl compounds which have α-hydrogen atoms, as is exemplified by the three dithioesters shown in chart 3. It should be noted here that aliphatic dithioesters can also be oxidized with mCPBA[15], but our method seems somewhat more convenient.

Sulfines by oxidation of thiocarbonyl compounds with dimethyl dioxirane

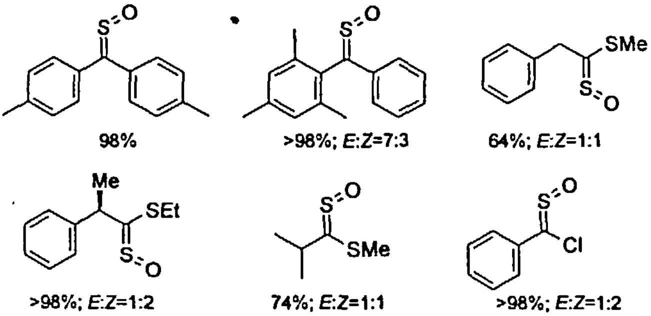
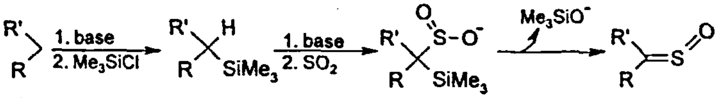


CHART 3

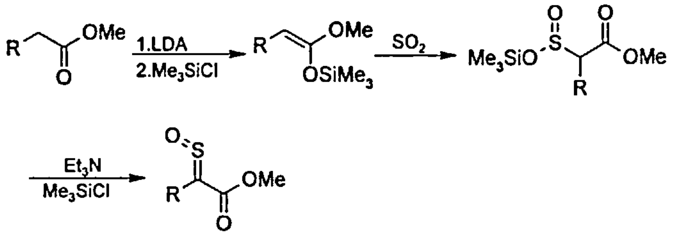
The modified Peterson reaction involving the reaction of α-silyl carbanions with sulfur dioxide is a very attractive route to sulfines, especially in those cases where the corresponding thiocarbonyl compounds are not accessible[13,14,27,28,31]. This method, which has a wide scope, is depicted in Scheme 3. An alternative method of employing



Substrates: e.g. fluorene, $PhCH_2SPh$, $PhCH_2SO_2Ph$, $(Me_3Si)_3CH$, $R_2P(=O)CH_2R$

SCHEME 3

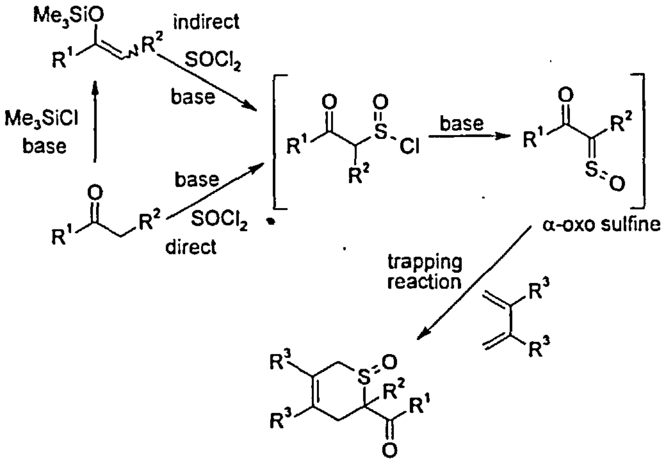
sulfur dioxide as the principal source of sulfur in sulfine synthesis is shown in Scheme 4. The first step is the reaction of a silyl enol ether derived from an ester with sulfur dioxide[32]. Subsequent treatment with a tertiary amine base, such as triethylamine, resulted in the elimination of trimetylsilylanol to give the sulfine in a poor yield (R=Ph : 17%)[30].



SCHEME 4

However, addition of a slight excess of trimethylsilyl chloride as scavenger of trimethylsilanolate improved the yield to 82% (Scheme 4). Unfortunately, the scope of this approach to sulfine synthesis is rather limited[30]. Modified versions were used to prepare sulfines from five- and six-membered lactones[30].

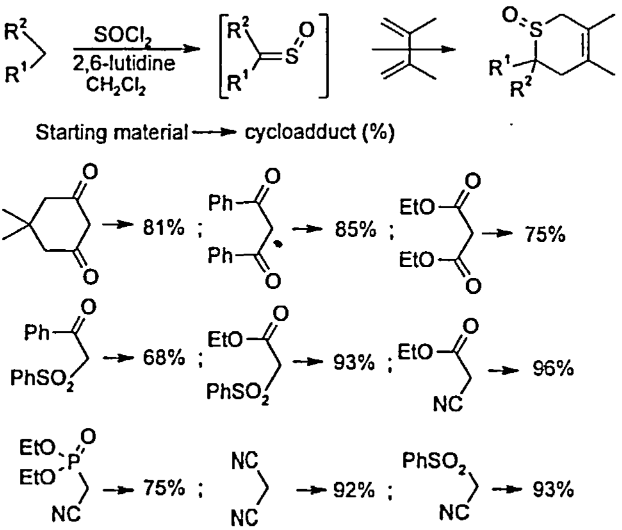
The synthesis of α-oxo sulfines has received considerable attention [27,28]. This type of sulfines readily undergoes the Diels-Alder reaction due to the presence of the electron-withdrawing carbonyl function adjacent to the sulfine unit. The *in situ* preparation of α-oxo sulfines can be achieved most conveniently from silyl enol ethers by treatment with thionyl chloride in the presence of a tertiary amine base (Scheme 5) [27,28,33,34]. In some cases the corresponding methylene compounds can be used as the starting material[27,28,35,36,37,38]. First, a β-keto sulfinyl chloride is formed which then, upon reaction with the base, leads to the α-oxo sulfine. *In situ* entrapment with a diene is in most cases required due to the decomposition of the α-oxo sulfines during the aqueous work-up (Scheme 5). This reaction with thionyl chloride, especially with silyl enol ethers, has a large scope[27,28,36,37] as can be deduced from the examples given in ref. 33.



R^1	R^2	R^3	Yield (%)
Ph	H	Me	84
Ph	Me	Me	92
Et	Me	Me	44
OMe	Ph	H	90
OMe	CH_2Ph	H	48
OEt	CO_2Et	H	75

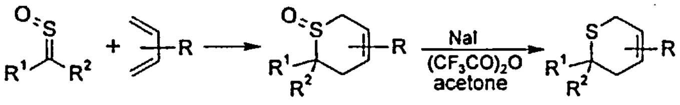
SCHEME 5

Doubly activated methylene compounds react smoothly with thionyl chloride in the presence of 2,6-lutidine as the tertiary amine base to give the corresponding sulfines in excellent yields (Scheme 6). In all cases the highly reactive sulfines were trapped *in situ* by a Diels-Alder reaction with 2,3-dimethyl-1,3-butadiene[16,37]. The methodology shown in the Scheme 5 and 6 allows the synthesis of sulfines of which the corresponding thiocarbonyl compounds are either highly unstable or unaccessible. Removing the oxygen at sulfur from the Diels-Alder cycloadducts opens avenues to prepare dihydrothiopyran derivatives formally derived from an unaccessible thiocarbonyl compound. In other



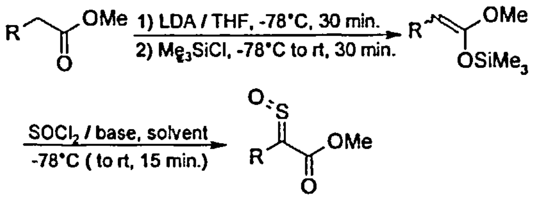
SCHEME 6

words, here sulfines serve as the synthetic equivalents of thiocarbonyl compounds (Scheme 7)[37,38].



SCHEME 7

As mentioned above sulfines having an electron-withdrawing substituent at carbon, such as an ester or a carbonyl group, are usually too unstable to be isolated as such, due to decomposition during work-up. This puts a limitation on the study of the chemical behavior of α-oxo sulfines. Therefore, an extensive study to modify the experimental conditions was made. It was then found that using diisopropylethylamine as a base at low temperature, allowed the isolation of α-oxo sulfines derived from esters by flash chromatography (Scheme 8)[39]. The α-oxo sulfine from methyl propionate could even be distilled. This experimental fine-tuning of the reaction conditions allowed the study of such sulfines in Diels-Alder reactions in the presence of catalysts (see section on cycloaddition) or other types of reagents which are not compatible with thionyl chloride.

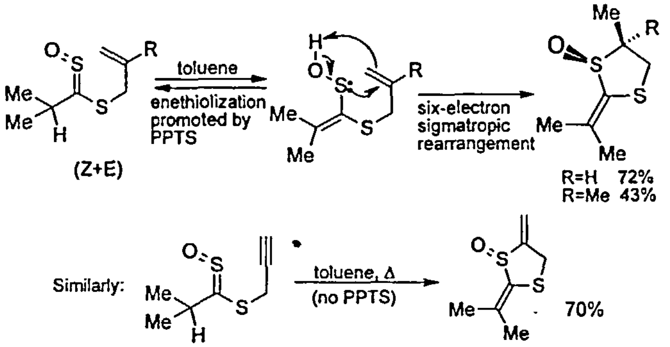


R	base	solvent	conditions	Yield (%)
Me	iPr$_2$NEt	Et$_2$O	-78°C→ rt, 15 min	66
iPr	"	"	"	89
tBu	"	"	"	85
Ph	"	"	"	96
CH$_2$Ph	"	"	"	93

SCHEME 8

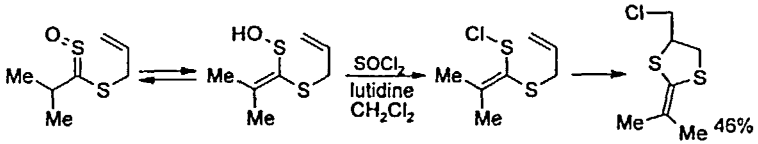
ENETHIOLIZATION

The intramolecular trapping of a vinylsulfenic acid tautomer of a sulfine was achieved [26,40] as shown in Scheme 9. The allylsulfanyl substituent reacted intramolecularly to give a five-membered ring heterocycle, the structure of which was unambiguosly established by an X-ray diffraction analysis. The enethiolization was catalyzed by pyridinium *p*-toluenesulfonate. The intramolecular reaction of the vinylsulfenic acid probably proceeds via a concerted six-electron sigmatropic rearrangement as is evidenced by the *syn* stereochemistry of the cyclization. It is also possible to perform the intramolecular entrapment of the sulfine tautomer by a prop-2-ynylsulfanyl substituent which results in a 5-methylene-1,3-dithiolane-1-oxide (see Scheme 9).



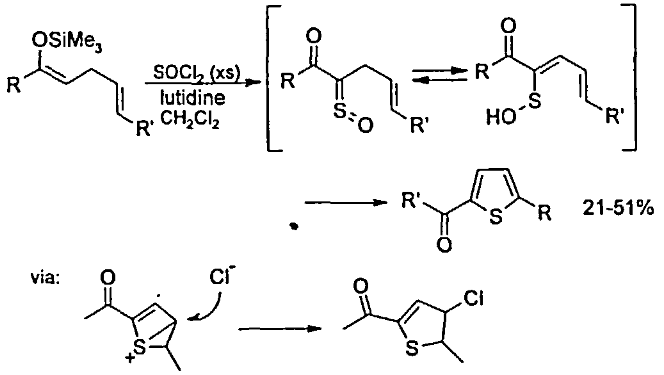
SCHEME 9

An alternative manner to trap the vinylsulfenic acid tautomer is a reaction with thionyl chloride[40] whereby a chloromethyl-1,3-dithiolane is obtained (Scheme 10). Still *et al*[34b] studied an intermolecular reaction of enethiolizable sulfines and made similar observations. The formation of the chloromethyl product proceeds via the vinylsulfenyl chloride which is formed by the reaction of the vinylsulfenic acid with thionyl chloride. A modification of this entrapment reaction of vinylsulfenic



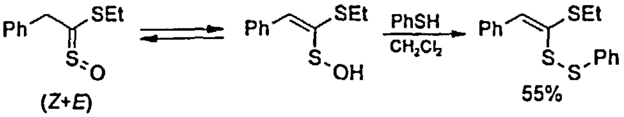
SCHEME 10

acid is depicted in Scheme 11. Here the starting material is a silyl enol ether which upon reaction with thionyl chloride first gives the α-oxo sulfine [37]. In a subsequent reaction the tautomeric form reacts with thionyl chloride to give a thiophene derivative (Scheme 11). It is assumed[37] that the intermediate vinylsulfenyl chloride reacts with the olefinic bond via an episulfonium ion as indicated in Scheme 11.



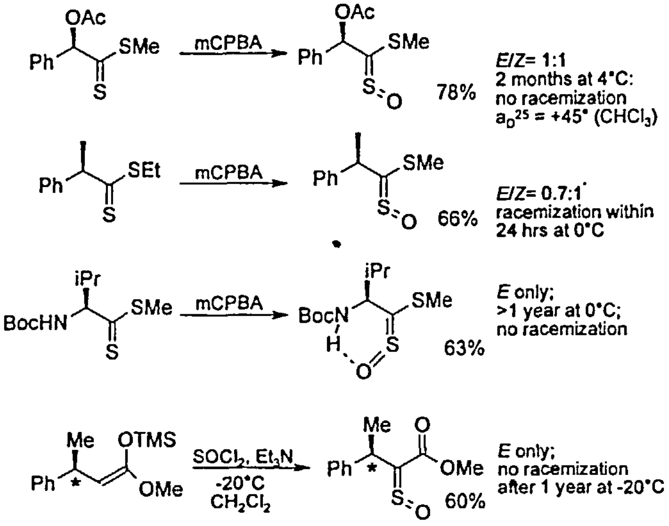
SCHEME 11

A trapping reaction of a different nature is shown in Scheme 12. Treatment of an appropriate sulfine with benzenethiol in dichloromethane gives a disulfide which clearly arises from the reaction of the vinylsulfenic acid tautomer with the thiol[37].



SCHEME 12

Information about the ease of the tautomeric interconversion can be obtained by investigating the optical integrity of chiral sulfines having a stereogenic center at C-α. Four differently α-substituted sulfines were studied for this purpose[41]. The sulfine derived from mandelic acid (top line Scheme 13) retained its optical rotation while standing at 4°C for two months, indicating that no racemization, and accordingly no tautomeric interconversion, had taken place. When stored in solution (dichloromethane) for seven months at room temperature, decomposition had occurred to give a 1:1 mixture of a dithioperoxy ester and a monothio *S*-methyl ester. In this reaction only the sulfine

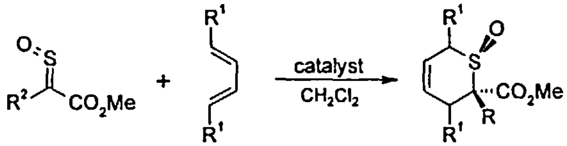


SCHEME 13

unit is involved[42] and not the α-carbon atom. The second compound (see second line, Scheme 13) was derived from L-leucine by a thionation reaction using Lawesson's reagent and a subsequent oxidation with mCPBA. This α-amino sulfine, which was obtained as a single isomer, retained its original optical rotation for a few years. The high stability of this sulfine may be attributed to the intramolecular hydrogen bonding in the *E*-configuration. On standing in solution no decomposition was observed either. The third sulfine (see third line, Scheme 13) having an α-methyl substituent racemized completely within 24 hrs on standing at 0°C. In solution again decomposition to a dithioperoxy ester was observed. The behavior of the fourth sulfine[39a] (see bottom line Scheme 13), which also has an α-methyl substituent, is completely different from that of the third sulfine, namely, neither racemization nor decomposition took place after one year at –20°C. The results with four chiral sulfines clearly demonstrate that the optical integrity and thus tautomerization strongly depends on the substituents at C-α and the sulfine carbon atom as well.

CYCLIZATION

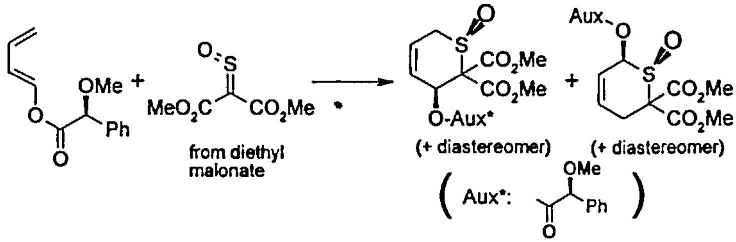
The most frequently used diene in Diels-Alder reactions with sulfines is 2,3-dimethyl-1,3-butadiene[13,14,27,28]. Even sulfines with a moderate dienophilicity react with this diene. However, 1,3-butadiene is much less reactive and the same holds for 1-acyloxy and 1-alkoxy substituted 1,3-dienes. For these dienes a catalyst would be desirable. It was found that $SnCl_4$ is an effective catalyst for Diels-Alder reactions of sulfines (Scheme 14)[39a]. The results show that the effect of the catalyst is enormous. It was very tempting to try this catalyst in the presence of a chiral ligand to achieve an asymmetric [4+2]-cycloaddition. Disappointingly no enantioselectivity was observed when ligands, such as R-(+)-1,1'-bi-2-naphtol (BINOL), were used as an addendum. Chiral Lewis acid catalysts, such as chiral shift reagents, were not effective either[39a].



R	R¹	catalyst	Temp/hrs	Yield (%)
Me	H	-	0°C / 18	70
Me	H	$SnCl_4$	-25°C /1	96
Ph	H	-	0°C / 18	76
Ph	H	$SnCl_4$	-25°C / 1	88
Me	OAc	-	20°C /72	trace
Me	OAc	$SnCl_4$	-25°C /1	82
Ph	OAc	-	20°C /72	trace
Ph	OAc	$SnCl_4$	-25°C /1	80

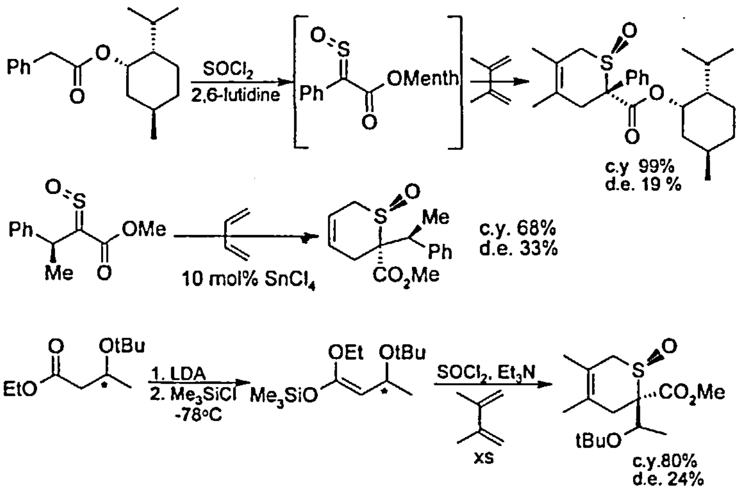
SCHEME 14

For an alternative approach to accomplish an asymmetric Diels-Alder reaction, either a chiral diene or a chiral sulfine can be considered. As a chiral diene the so called Trost diene[43,44], essentially derived from mandelic acid, was used (Scheme 15). A mixture of expected regioisomeric cycloadducts was obtained upon reaction with bis-(methoxycarbonyl)-sulfine. The diastereomers of the separated regioisomers could be detected in the ^{1}H-NMR spectrum but unfortunately their ratio could not be determined. Currently, other chiral dienes are considered for the asymmetric Diels-Alder reaction of sulfines.



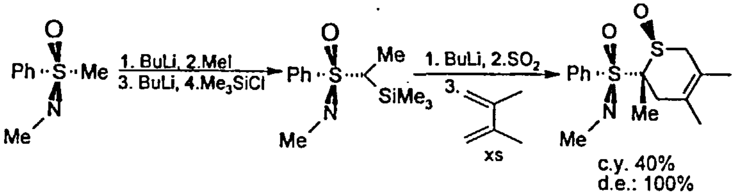
SCHEME 15

Three alkoxycarbonyl substituted sulfines having a chiral center at different positions were next investigated (Scheme 16). Reaction of menthyl phenylacetate with thionylchloride in the presence of 2,6-lutidine and 2,3-dimethyl-1,3-butadiene gave the cycloadduct in good yield, but in a rather poor diastereoselectivity (d.e. 19%)[45]. Clearly the stereogenic centers are too remote to be effective in the asymmetric cycloaddition reaction. The second sulfine (see also Scheme 13) contains the stereogenic center at the carbon atom adjacent to the sulfine unit. Cycloaddition with 2,3-dimethyl-1,3-butadiene in the presence of 10 mol% of $SnCl_4$ resulted in a cycloadduct with a d.e. of 33%. The third sulfine was derived from 3-hydroxybutanoate (third line, Scheme 16). This sulfine was conveniently generated by reaction with thionyl chloride in the presence of triethylamine and excess of the trapping diene. The cycloadduct was obtained in a high chemical yield but with a rather low d.e. of 24%. The latter two examples show that in spite of the adjacency of the stereogenic center to the sulfine moiety, the asymmetric induction is disappointing. This result sharply contrasts the



SCHEME 16

complete asymmetric induction obtained previously with sulfoximino substituted sulfines (Scheme 17). [46,14,27,28] Apparently, the nature of the chiral center plays a decisive role in the asymmetric Diels-Alder reaction of sulfines.



SCHEME 17

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