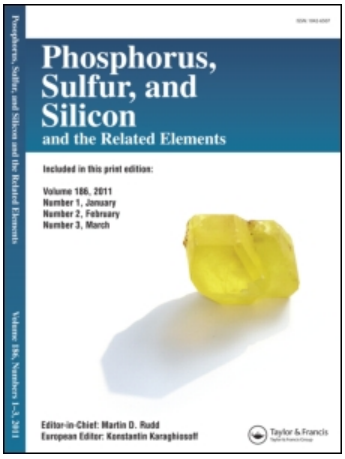

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Recent Synthetic Developments in Thiocarbonyl Chemistry

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Recent Synthetic Developments in Thiocarbonyl Chemistry

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Abstract

Direct oxidation of enethiolizable thioketones and dithioesters with a peroxycarboxylic acid affords the corresponding sulfines quantitatively. This observation stands in contrast with literature expectations, stating that this reaction would lead to divinyl disulfides. The oxidation shows a high stereoselectivity: delivery of the oxygen proceeds from the side opposite to the alkylthio group of dithioesters and from the side opposite to the more hindered substituent in the case of thioketones. The thermal stability of these sulfines was studied and a novel rearrangement was observed.
The second part of this report deals with the thio-Claisen rearrangement of precursors bearing a chiral centre adjacent to the pericyclic nucleus and its use for stereocontrol in the acyclic series. This thermally facile transposition leads to allylated dithioesters with good to excellent yields. A high diastereomeric selectivity was obtained in a number of cases involving either a steric effect with alkyl groups on the chiral centre or a noteworthy electronic effect when this centre bears a heteroatomic group. It was also carried out in the homochiral series. A favoured conformation and approach model is proposed to explain the formation of syn isomers.

INTRODUCTION

Thiocarbonyl compounds are getting more widespread use in organic synthesis (1-4). Their specific behaviour has been put in evidence for a number of reactions, including thiophilic addition (1, 5-7), S-alkylation (4)

and Michael addition reaction of enethiolates (8-11), dipolar cycloadditions (12), the Eschenmoser reaction (13), and the Barton radical addition (14).

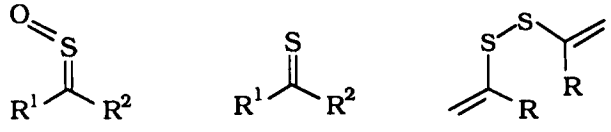
We would like to report on two aspects of thiocarbonyl chemistry that we have revisited or explored recently:

• oxidation of enethiolizable thioketones and dithioesters and direct synthesis of aliphatic sulfines.

• acyclic diastereocontrol with the aid of the thio-Claisen rearrangement.

DIRECT SYNTHESIS OF SULFINES BY OXIDATION OF ENETHIOLIZABLE THIOCARBONYL COMPOUNDS

Sulfines **1** are reactive cumulenes, which have been extensively studied by Zwanenburg *et al*, and by other groups (15-17). A variety of synthetic routes has been developped. Direct oxidation of thiocarbonyl compounds **2** has been successfully achieved in a number of cases. Many sulfines have been prepared from thioamides by this way (15, 17-19). For dithioesters and thioketones this reaction appears limited to aromatic, non enethiolizable or α-unsaturated cases. Literature reports (15-17, 20, 21) assume that sulfines **1** are not accessible through oxidation of enethiolizable thiocarbonyl compounds **2** and predicts the formation of divinyl disulfides **3** (scheme 1).



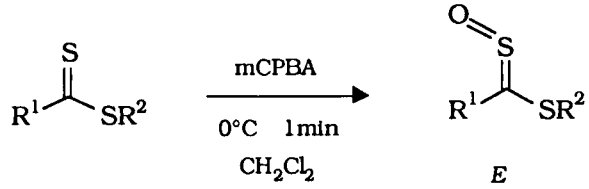
1 **2** **3**

Scheme 1

Needing aliphatic sulfines for synthetic purposes we were puzzled by this situation and wondered whether it arises from poor thermal stability of these species or from the lack of an adequate method for their synthesis. It led us to investigate the reaction of aliphatic dithioesters and thioketones with a type of oxydizing reagent which is classical in this field: peroxycarboxylic acids.

Sulfines from aliphatic dithioesters

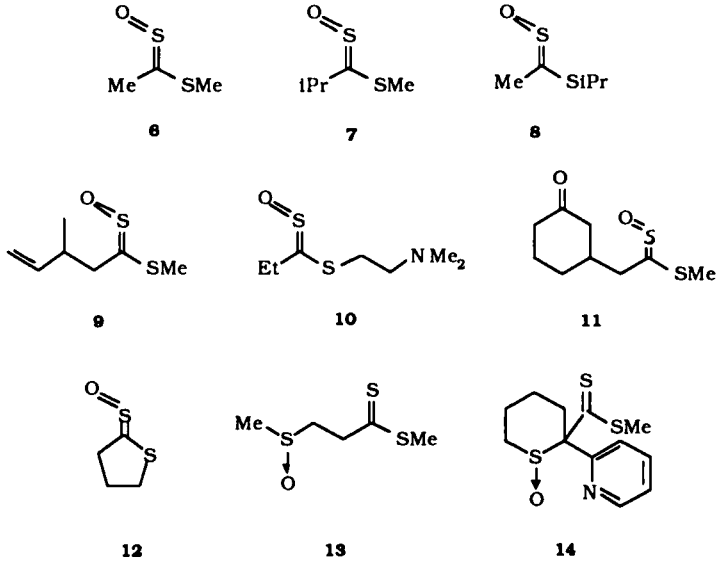
We examined (22) the behaviour of a variety of dithioesters **4**, bearing a hydrogen on the α position, with *meta*-chloroperoxybenzoic acid (MCPBA) and dichloromethane as solvent. At 0°C we observed an immediate loss of the yellow colour of the dithioester. To our surprise the products exhibit NMR signals that are characteristic of sulfines **5** (scheme 2). The proton NMR signal for the methylthio is observed at 2.45 ppm. This upfield shift reveals that the formation of the *E* isomer is kinetically favoured. Oxidation occurs on the opposite side of the alkylthio group. The *E*/*Z* ratios are usually around 90 : 10. ^{13}C NMR signals for the sulfinyl carbon are observed around 190 and 210 ppm for the *E* and *Z* isomers.



4 **5**

Scheme 2

On scheme 3 are depicted some examples of products formed by oxidation.



Scheme 3

This reaction exhibits an interesting chemoselectivity (scheme 3). Attack at the π system of the thiocarbonyl site is so fast that other functions remain unaffected (C=C, C=O, NR_2) and thus sulfines **6-12** were formed.

We could find only one exception for a dithioester bearing a chain with a dialkylsulfide group: the latter moiety was oxidized to a sulfoxide **13** and no sulfine was formed. An analogous result (compound **14**) was observed independently by Aloup *et al* from a Rhône-Poulenc group (23) during the course of an antiulcer and antihypertensive drug synthesis (24).

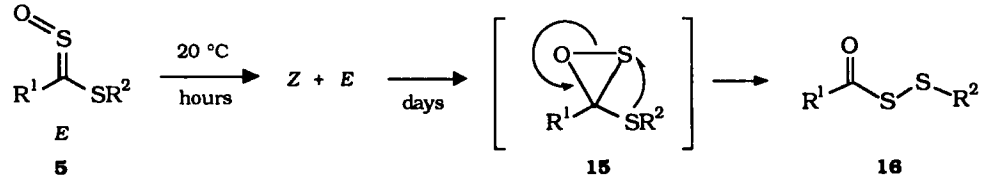
At this stage we were still wondering why sulfines were not observed previously in these cases.

We then examined the thermal stability of sulfines at room temperature. After a few hours isomerization to *Z* and *E* mixtures was monitored by NMR (scheme 4). Equilibrium ratios are of the order of 1 : 1.

A second surprise came after some days when a new species was detected by NMR and a carbonyl group was demonstrated by IR. The presence of thiolesters, resulting from an eventual loss of sulfur, was ruled out from IR and mass spectra. Data revealed that dithioperoxyesters **16** had actually been formed. This structure was confirmed by independent synthesis of methyl dithioperoxyacetate, through reaction of thioacetic acid with methyl methanethiosulfonate. One promising feature of compounds **16** is their sulfur-sulfur bond.

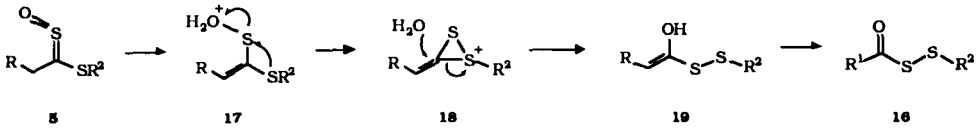
To our knowledge the rearrangement of sulfines **5** to dithioperoxyesters **16** was unprecedented. It was not observed for aromatic sulfines, apparently because of their greater thermal stability.

We suggest the following mechanism (scheme 4). The first step involves a thermally allowed electrocyclization (25) to give an oxathiirane **15**. Analogous intermediates have been detected spectroscopically by Carlsen (26). The alkylthio group then migrates to the sulfur centre of the heterocycle with concomitant opening of the three membered ring.



Scheme 4

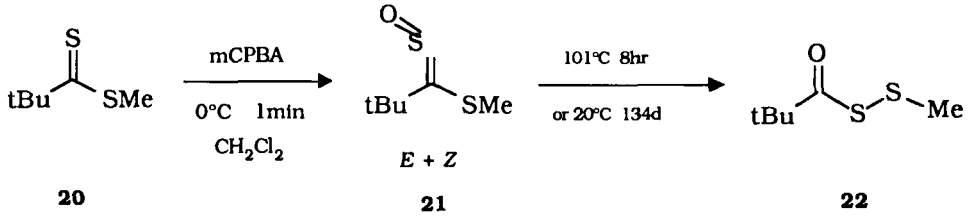
At the preceding Sulfur Symposium at Odense, Zwanenburg reported that he was surprised by our results. For the rearrangement he proposed (16) an alternative mechanism involving a vinylsulfenic acid, arising from enolization of the sulfine (scheme 5).



5 **17** **18** **19** **16**

Scheme 5

In order to shed some light on this point we achieved (27) the oxidation of the aliphatic dithioester **20** which does not bear an hydrogen α to the thiocarbonyl group. Reaction of MCPBA furnished the awaited sulfine **21** (scheme 6). This compound is thermally more stable than previous sulfines, such as **6-11**, but letting it stand room temperature or heating it at 101°C for some hours led to dithioperoxyester **22**.

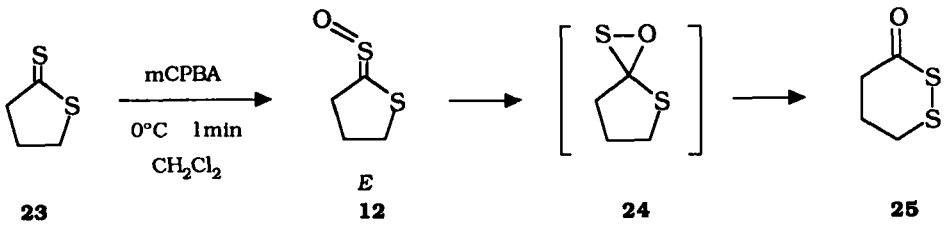


20 **21** **22**

Scheme 6

The rearrangement has indeed occured in the absence of an α-hydrogen. This means that the intermediate oxathiirane **15** (scheme 4) is still compatible with the experimental results whereas an α-vinylsulfenic acid (scheme 5) can be ruled out. We can also conclude that the requisite for this rearrangement is the aliphatic nature of R^1. When R^1 is an aromatic substituent Zwanenburg and co-workers have not observed this reaction.

We also wished to examine the behaviour of a cyclic dithioester **23** (scheme 7). Treatment with MCPBA leads to the *E* sulfine **12**, which slowly yields compound **25** bearing an interesting cyclic S-S bond. The rearrangement has taken place even when the migrating group is part of a ring, possibly through the spirobicyclic intermediate **24**.



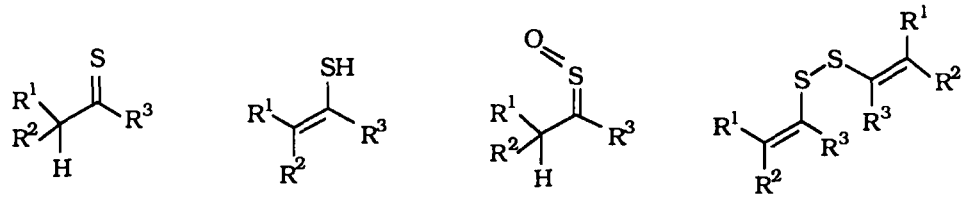
23 **12** **24** **25**

Scheme 7

These observations with sulfines obtained from dithioesters led us to revisit the oxidation reaction of thioketones.

Sulfines from thioketones

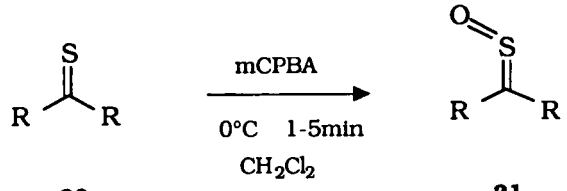
Aliphatic thioketones **26** are highy enethiolizable (scheme 8). Their enethiols **27**, which can be isolated, are isomerically stable (28, 29). Therefore we were especially eager to know the oxidation course for **26**: sulfines **28** or divinyl disulfides **29**. Only one case was reported so far: Duus and Carlsen (30) oxidized a β-thioxoketone and obtained a divinyldisulfide.



26 **27** **28** **29**

Scheme 8

We first examined (31) the oxidation of symmetric aliphatic thioketones **30**. We carefully checked that our starting materials were devoid of isomeric enethiols. Immediate loss of the red colour was observed after addition of one equivalent of MCPBA at 0°C. The products exhibit NMR signals which are characteristic of sulfines **31** (scheme 9). The reaction is quantitative. We did not observe any divinyl disulfide **29**.



30

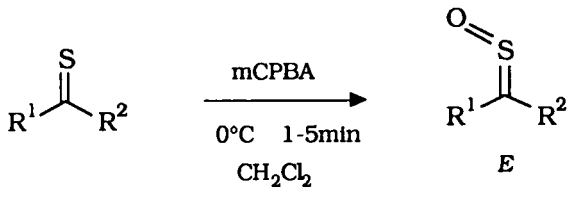
R = iPr

R = nC_6H_{13}

31

Scheme 9

We then looked to the case of unsymmetric thioketones **32**. Sulfines **33** were obtained quantitatively (scheme 10). The oxidation reaction is highly regioselective in the case of two compounds bearing a methyl group and an alkyl group, for which sulfines E were formed. Delivery of oxygen thus occurs on the side of this methyl substituent and opposite to the bulky tertiobutyl group. More surprising is the selectivity observed with R^1 = Me and R^2 = nPentyl. Other thiones, bearing various groups, led to mixtures of *E* and *Z* isomers. We have detected no variation in these ratios. We believe that these compounds result from kinetic control and that these sulfines are configurationally stable, in contrast with those sulfines obtained from dithioesters that isomerize rapidly. Stereochemical assignments have been achieved by complexation with a lanthanide shift reagent.



32

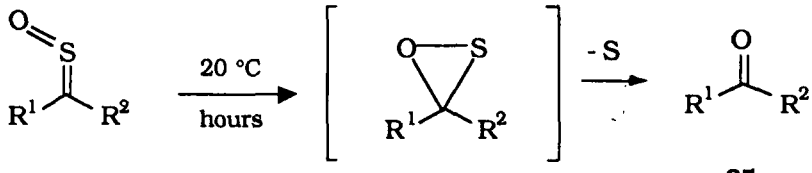
E

33

R^1	**R^2**	***E / Z***
Me	nC_5H_{11}	100 : 0
Me	tBu	100 : 0
Me	sBu	80 : 20
nC_5H_{11}	iPr	67 : 33
Et	Pr	50 : 50
Et	2-Me Bu	50 : 50

Scheme 10

The thermal stabilities of sulfines **31** and **33**, derived from thioketones, were examined. After some days at room temperature, atomic sulfur is formed and the corresponding ketones **35** are produced quantitatively (scheme 11). The preceding rearrangement (scheme 4) has not been observed. The formation of the ketones **35** can be explained by electrocyclization of sulfines **33**, formation of an intermediate oxathiirane **34** and sulfur extrusion (15)



33 **34** **35**

Scheme 11

Our results (22, 27, 31) stand in contrast with literature expectations (15, 20, 16, 21). We have achieved for the first time the direct oxidation of enethiolizable thioketones and dithioesters. It occurs with a noteworthy selectivity in favour of the *E* isomer.

These reactions provide an easy entry to aliphatic sulfines. They can now be used for organic synthesis within the limit of their thermal stability. We are presently looking at their behaviour.

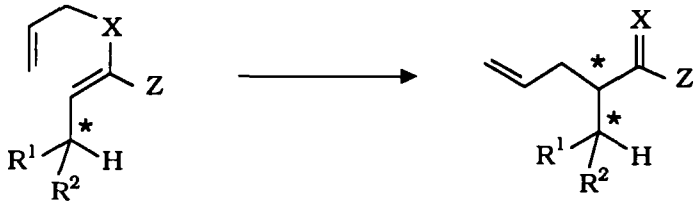
They also provide access to dithioperoxyesters, compounds of chemical (32) and therapeutical interest (33).

ACYCLIC STEREOCONTROL WITH THE AID OF THE THIO-CLAISEN REARRANGEMENT.

A very large number of stereochemical studies of the Claisen-rearrangement have appeared (34, 35). Impressive applications have been achieved in the field of natural products synthesis. However certain aspects of this reaction have not yet been examined or have been overlooked. We have wished to study cases for which the introduction of sulfur could offer advantages.

Most of the examples known in the oxygen series involve stereochemical elements present on the pericyclic nucleus. We wished to study the introduction of a chiral center adjacent to this nucleus (scheme

12), in order to provide a new means of control of the relative configuration of vicinal carbons in the challenging acyclic series. No general study of this question is available so far with neutral species (36-43).



Scheme 12

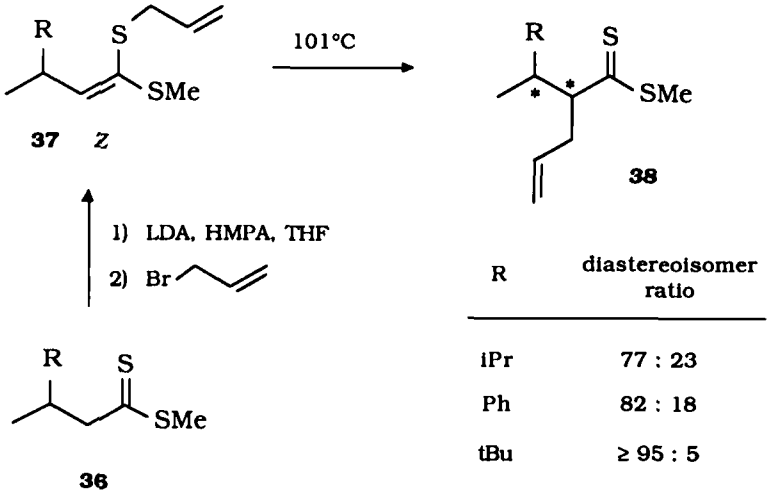
We undertook such a study with sulfur because, from the initial work of Brandsma and his group, we know (44-46) that:

• neutral precursors, such as S-allyl ketenedithioacetals, are easy to prepare from dithioesters

• the thio-Claisen transposition is thermally facile: it occurs at room temperature or by heating at most to 100°C. It is often a high yielding reaction.

We now wish to report our first results with precursors having a chiral carbon centre adjacent to carbon 1 of the pericyclic nucleus.

Our study started (47) with the effect of alkyl groups on the asymmetric center. We introduced a methyl group and various alkyl substituents to determine is a favoured conformation will lead to diastereocontrol (scheme 13).



37 *Z*

38

R	diastereoisomer ratio
iPr	77 : 23
Ph	82 : 18
tBu	≥ 95 : 5

36

Scheme 13

The starting materials are racemic methyl β-substituted butanedithioates **36**. Deprotonation by LDA required the addition of HMPA and temperatures around 0°C because of the steric hindrance on the adjacent carbon. Quenching with allyl bromide afforded quantitatively S-allyl ketenedithioacetals **37** arising from the awaited S-allylation of the enethiolates. Though it is not relevant for the following discussion, it can be noted that only the Z isomer is formed in this step. The formation of *cis* enethiolates is general for the deprotonation of thiocarbonyl compounds (8, 48, 10).

The thio-Claisen rearrangement could be performed at 101°C. Heating was necessary, in contrast to many examples performed at room temperature, because of the relatively strong steric hindrance α to the created C-C bond. Chemical yields for allylated dithioesters **38** are in the order of 90 %.

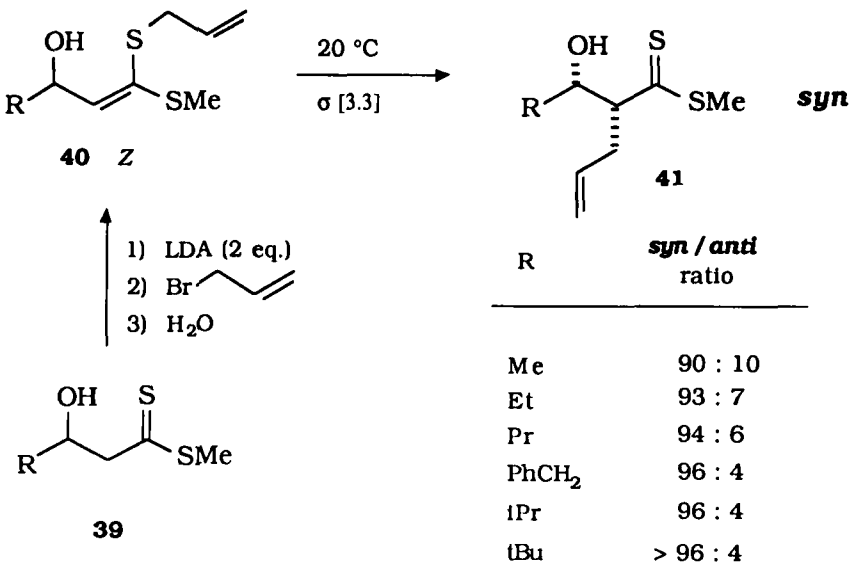
Ratios of diastereoisomers, determined by NMR, were compared to the nature of the R group (scheme 13). With an isopropyl group one gets a modest selectivity, 77 : 23. The phenyl group causes an increase. The t-butyl group affords the highest selectivity, with a record higher than 95 : 5.

The assignement of relative configuration of the major diastereoisomer is under investigation.

The order iPr, Ph, tBu follows the degree of steric hindrance of these substituents. We have here a steric effect which drives the transition state towards a preferred conformation.

For the second set of experiments (49) we introduced an electronegative heteroatomic group on the chiral center. We placed an hydroxy group and various alkyl groups (scheme 14). Double deprotonation of racemic aldols **39** is carried out easily with 2 equivalents of LDA at -78°C. Quenching with allyl bromide and water yields the allyl ketene dithioacetals **40**. A single Z isomer is observed arising again from a selective *cis* deprotonation.

The transposition of compounds **40** occurs at room temperature after a couple of days. This example shows how easy the thio-rearrangement is from the thermodynamic point of view, when no severe steric hindrance is present. We obtained allylhydroxydithioesters **41**. This reaction affords mainly the ***syn*** diastereomer. The configuration has been assigned by chemical correlation with known molecules in the oxygen series.



R	*syn / anti* ratio
Me	90 : 10
Et	93 : 7
Pr	94 : 6
$PhCH_2$	96 : 4
iPr	96 : 4
tBu	> 96 : 4
Ph	86 : 14

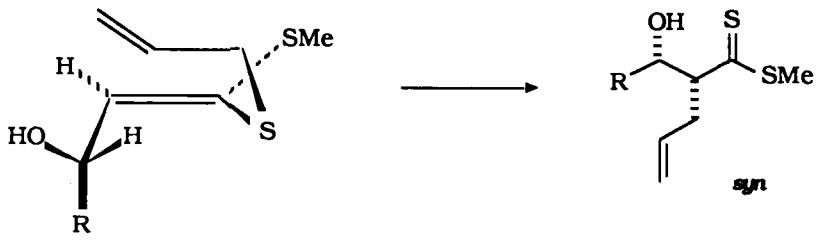
Scheme 14

Let us examine the ratios of isomers *versus* the nature of the substituent R. Except for the phenyl group ratios are all equal or higher than 90 : 10. There is only a slight variation of selectivity when the size of R increases. It is noterworthy that even with a methyl group the selectivity is high, *i. e.* 90 : 10. With a t-butyl group it is in excess of 96 : 4.

These differences are obviously too small to be explained only by steric effects. If one uses A-strain values the variations should be much higher, though of the same order. The selectivity effect has here mainly an electronic origin.

We propose model **42** for the preferred approach. It involves a chair pseudo-cyclic transition state (scheme 15).

The smallest group, hydrogen, is placed in a staggered position to the double bond. The hydroxy group is located on the outside allylic staggered position. The alkyl group R is perpendicular to the double bond. This position is analogous to proposals by Houk and co-workers (50, 51) to explain the outcome of reactions with allylic systems.

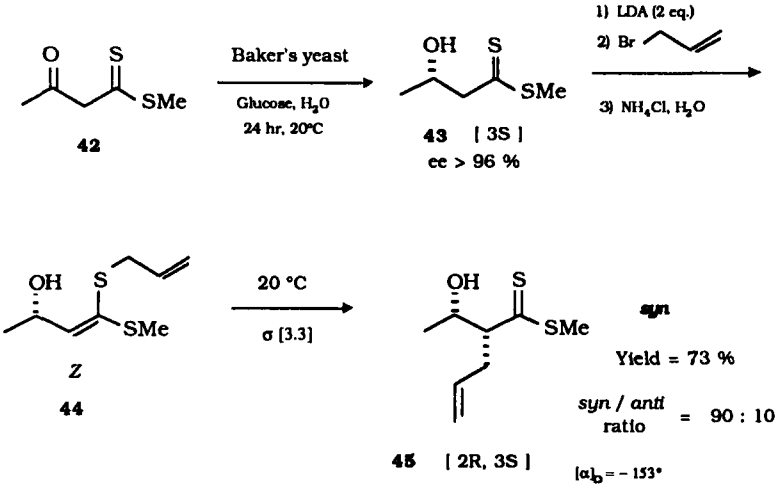


42 41

Scheme 15

If we consider the electrostatic model of Kahn and Hehre (36) and that the ketene dithioacetal is the nucleophilic part, attack will occur on the electron rich face of this part. The allyl group will approach on the side of the hydroxyl group and thus in an antiperiplanar position to the R group, above the ketene dithioacetal double bond plane. This model leads to a *syn* configuration **41** as we have observed experimentally.

The thio-rearrangement has also been carried out in the homochiral series (scheme 16). Aldol **43** has been prepared by an enzymatic way. Reduction of the the prochiral oxodithioester **42** has been performed with baker's yeast under conditions reported by Fujisawa (52). One gets the 3S isomer with an enantiomeric excess superior to 96 %. This homochiral compound was then submitted to the same sequence as previously: formation of the ketenedithioacetal **44** through deprotonation and allylation on the sulfur. The sigmatropic shift affords the 2R,3S enantiomer of dithioester **45** with *syn* relative configuration in high e. e.

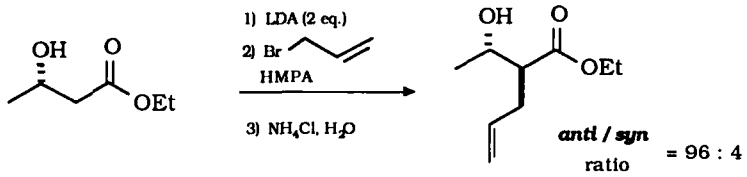


42 43 [3S] ee > 96 %

Z 44 45 [2R, 3S] $[\alpha]_D = -153°$

Scheme 16

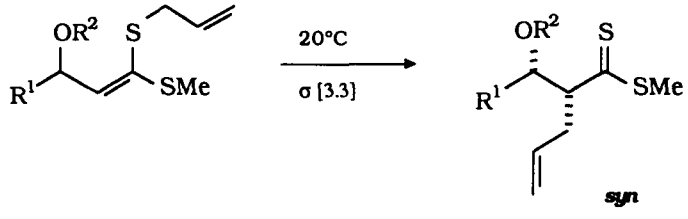
This remarkable stereocontrol complements the synthesis of analogous oxygen compounds reported (53) by Frater (scheme 17). He described the direct allylation of 3S-hydroxybutanoate **46** and uncovered that it selectively affords the ***anti*** 2S,3S products **47.** Our method yields the ***syn*** isomer and is thus complementary. We also noted that it allows more variations than with the direct alkylation, *e. g.* use of a crotyl chain for the creation of 3 chiral centers (54).



46 [3S] **47** [2S, 3S]

Scheme 17

This way of controlling acyclic stereochemistry led us to investigate further the scope of this reaction (54). We wondered what would occur on changing the hydroxyl group for an ether group. According to our model it should not much change the stereoselection. We silylated our starting materials and examined their sigmatropic shift, in the racemic series (Scheme 18). The reaction course is similar: we obtained the *syn* diastereomer with only a slightly lower selectivity.



R^1	R^2	***syn / anti*** ratio
Me	H	90 : 10
	Si^tBuMe_2	88 : 12
iPr	H	96 : 4
	$SiMe_3$	86 : 14
	Si^tBuMe_2	75 : 25

Scheme 18

So, we have been able to use either steric or electronic effects to drive a transition state towards a favoured conformation and attain good to excellent stereocontrol in the acyclic series.

CONCLUSION

By revisiting the oxidation of thiocarbonyl compounds we obtained results opposed to literature expectations. Synthesis of sulfines is feasible from enethiolizable thioketones and dithioesters. Their chemistry and uses can now be studied.

In a second part we have made profit of the thermal easiness of the thio-Claisen rearrangement to examine a novel way of stereocontrol. Steric or electronic effects on an asymmetric carbon adjacent to the pericyclic nucleus leads to the favoured formation of a diastereoisomer. This is useful for the synthesis of allylated dithioesters with two vicinal chiral centres and for enantiomerically pure compounds. Further studies are in due course to extend the scope of this transposition to systems bearing various substituents.

Thiocarbonyl chemistry has still a number of aspects to explore and we believe that its role in organic synthesis will be further developped.

Acknowledgment

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