Bull Soc Chim Fr (1995) 132, 67-74

Chemoselective synthesis of aliphatic sulfines by direct oxidation of dithioesters

Francesca Cerreta, Anne-Marie Le Nocher, Catherine Leriverend, Patrick Metzner*, Thi Nhàn Pham

Laboratoire de Chimie moléculaire et thio-organique (Unité associée au CNRS), ISMRA et Université, 6, bd du Maréchal-Juin, 14050 Caen, France

(received 11 July 1994, accepted 8 November 1994)

Summary – Oxidation of enethiolizable dithioesters with *m*CPBA affords the corresponding sulfines (thiocarbonyl S-oxides) quantitatively, with a high chemoselectivity. This reaction is (*E*) stereoselective : delivery of the oxygen proceeds from the side opposite the alkylthio group. The thermal stabilities of these new molecules have been evaluated. The competitive oxidation of various thiocarbonyl compounds has been examined.

sulfines / thiocarbonyl oxides / dithioesters / oxidation / heterocumulenes / organic synthesis / sulfur compounds

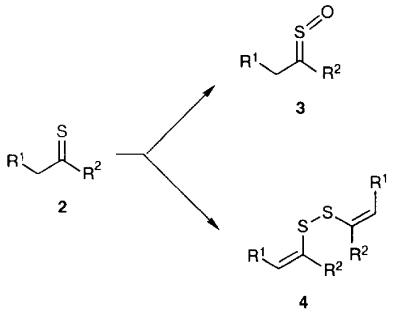
Introduction

With the aim of developing aliphatic sulfines **1** as tools for organic synthesis, we have revisited the oxidation of thiocarbonyl compounds and have met with several surprises. We wish to report a simple and selective access to aliphatic dithioester oxides, their characterization and stabilities. The question of chemoselectivity of the oxidation of various thiocarbonyl derivatives is also addressed.

1

Chemical preparation of these heterocumulenes as well as the isolation of a naturally occurring sulfine (the lachrymatory factor of the onion, $R^1 = H$, $R^2 = Et$) has stimulated a wealth of studies, mainly in the groups of Zwanenburg [1-3], Block [4] and Bonini-Mazzanti [5-8].

Oxidation of thiocarbonyl compounds **2** (thioketones, dithioesters) with peroxycarboxylic acids or hydrogen peroxide offers an attractive entry to sulfines **3** as was reported previously [1, 9, 10]. However, it has long been believed that this reaction is restricted to non-enethiolizable thioketones or dithioesters [1, 2, 11, 12]. Such a limitation might arise from a lack of thermal stability of enethiolizable sulfines, but a few examples of their characterization have been reported [12-14]. Alternatively, the oxidation reaction might follow an unexpected course, such as the formation of divinyl disulfides **4** from the enethiol tautomeric form of thiocarbonyl compounds [12, 15].



2 **3** **4**

Such a reaction is indeed known to occur with specific oxidants such as iodine [16, 17]. We speculated that this one-electron process would not occur with a peroxycarboxylic acid (except in what we believe is a specific case [15]). We actually checked that in the conditions described below (0°C, CH_2Cl_2, some minutes) no oxidation of benzylthiol is observed by reaction of one equivalent of *meta*-chloroperoxybenzoic acid (*m*CPBA). This made us feel confident that re-examination of the oxidation of thiocarbonyl compounds by *m*CPBA could lead to aliphatic sulfines and to the development of their chemistry for synthesis. Following a preliminary communication on dithioesters [18], we now report fully our investigation, further examples and a chemoselectivity study.

It should be noted that aliphatic thioamides can be readily oxidized to the corresponding *S*-oxides [1, 19].

* Correspondence and reprints

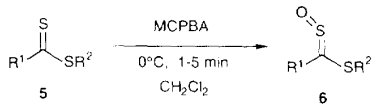
Few examples of other enethiolizable sulfines have been reported [12-14, 20, 21] prior to our contribution [18, 22-24].

Results

Synthesis of sulfines

Thirty-five dithioesters **5** were treated with one equivalent of *m*CPBA in dichloromethane at 0°C. The yellow color of **5** was rapidly discharged. After 1-5 min, a classical work-up was effected. Column chromatography on silica gel could not be performed as substantial decomposition took place; chromatography was therefore avoided.

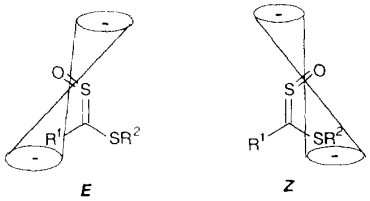
To our delight, NMR spectra of the crude materials revealed signals that were characteristic of sulfines **6**. No other products were formed and the conversion was complete. Yields for the crude products were around 90 % (^{1}H and ^{13}C NMR).



In most cases analysis of the product rapidly after the oxidation of dithioester ($\sim$ 40-60 min) shows that an isomer is very predominant (table I).

The ^{1}H NMR data allow assignment of the (*E*)-(*Z*) stereochemistry of sulfines **6** by considering a deshielding cone along the S=O bond [1, 25]. Compared with the starting dithioesters **5** bearing a SMe group (recorded at δ : 2.6 ppm), an upfield shift is observed for the major isomer (δ : 2.4-2.5 ppm).

We assigned this signal to the (*E*) configuration: the methylthio is located in the external and positive part of the cone. Conversely, the signals for the R^1 group of this major isomer undergo a downfield shift.



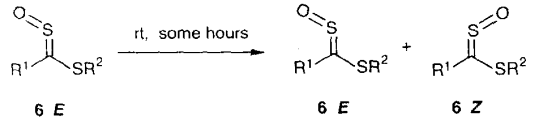
For the minor isomer opposite shifts have been monitored : an SMe group is observed around 2.7 ppm, whereas the R^1 group is shifted upfield.

^{13}C NMR spectra also provide useful information. A highfield shift of 30-40 ppm of the thiocarbonyl carbon is observed from the dithioesters (around 240 ppm) to the sulfines (187-208 ppm). Furthermore we have noticed that the deshielding effects, which were observed for the proton NMR, also apply to the ^{13}C shifts of the sulfine isomers. The above (*E*) and (*Z*) assignments led us to propose that the C=S=O signals for the major (*E*)-isomers are found (table I) at higher field than those of minor (*Z*)-isomers (except when a phenyl group is present).

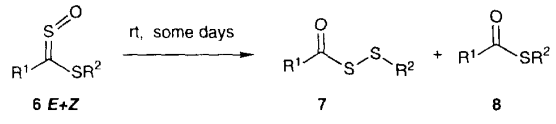
Thus the (*E*)/(*Z*) ratios are easily determined by NMR. In a number of cases the isomers ratio of sulfines exceeds 90:10 (entries 1-3, 5, 6, 11, 12, 14, 16, 22-25, 28, 31).

Stabilities of sulfines

The isomers **6*E*** are not configurationally stable in solution (CCl_4 or $CDCl_3$). Further recording of the NMR spectra of sulfines left at ambient temperature showed isomerization to (*E*) + (*Z*) mixtures. After some hours the isomers ratio remained stable (table I), in the order of 1:1 (except for sulfines **5f** and **5af** which remained unchanged). Thus (*E*) and (*Z*) isomers have close thermodynamic stabilities. This easy isomerization is unprecedented. Its mechanism is not yet clear. It does not appear to be influenced by visible light. We have observed that it is slightly accelerated in acidic medium and thus traces of 4-chlorobenzoic acid could be responsible. It is not observed with sulfines derived from thioketones [23] or thionesters [22].



When the samples were maintained at room temperature a second change surprised us. After a few days, a new species was detected and characterized : dithioperoxyesters **7** were formed [18]. They arise from a rarely precedented rearrangement [26, 27], which is not observed with aromatic sulfines [2]. We suggested that their formation involves an electrocyclization to oxathiirane and migration of the alkylthio with opening of the three-membered ring. This reaction is however not always selective and minor proportions of thiolesters **8** are sometimes formed depending on the nature of the substituents.

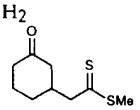


Chemoselectivity of the oxidation of sulfur compounds

Selective oxidation of multifunctional molecules is presently an important challenge and it is considered as difficult when sulfur groups are present. We wished to examine some of aspects of this with thiocarbonyl compounds bearing extra functional groups. Descriptions of such reactions are rare in the literature [28-32].

Our first observations dealt with intramolecular selectivity. A number of examples from table I show that the thiocarbonyl group is oxidized selectively. Carbon-carbon double bonds (entries 12, 14, 24-29) and an amino group (entry 10) were untouched. Baeyer-Villiger

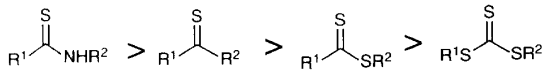
Table I. Synthesis of sulfines.

Entry		Dithioester		Sulfine				
					(*E*)/(*Z*) ratio %		^{13}C NMR of C=SO ppm	
		R^1	R^2		1h after preparation	after equilibration	(*E*)	(*Z*)
1	**5a**	Me	Me	**6a**	95 : 5	55 : 45	191.7	197.3
2	**5b**	Me	i-Pr	**6b**	95 : 5	50 : 50		
3	**5c**	Me	CH_2Ph	**6c**	95 : 5	50 : 50		
4	**5d**	Me	Ph	**6d**	85 : 15	50 : 50		
5	**5e**	Et	Me	**6e**	95 : 5	55 : 45	196.7	204.1
6	**5f**	Et	t-Bu	**6f**	100 : 0	100 : 0	195.5	
7	**5g**	Et	CH_2Ph	**6g**	85 : 15	55 : 45		
8	**5h**	Et	Ph	**6h**	55 : 45	55 : 45	197.4	197.7
9	**5i**	Et	CH_2OMe	**6i**	80 : 20	65 : 35		
10	**5j**	Et	$CH_2CH_2NMe_2$	**6j**	55 : 45	55 : 45		
11	**5k**	i-Pr	Me	**6k**	95 : 5	53 : 47	198.8	208.9
12	**5l**	i-Pr	$CH_2CH{=}CH_2$	**6l**	100 : 0	40 : 60	195.1	204.0
13	**5m**	i-Pr	Bu	**6m**	95 : 5	50 : 50	196.9	208.3
14	**5n**	Me_2CCH_2	Me	**6n**	100 : 0	45 : 55	192.1	201.2
15	**5o**	t-Bu	Me	**6o**	65 : 35	30 : 70	204.6	207.2
16	**5p**	n-C_8H_{17}	Me	**6p**	90 : 10	50 : 50	194.5	202.8
17	**5q**	n-C_8H_{17}	Bu	**6q**	90 : 10	55 : 45	192.2	200.7
18	**5r**	n-C_9H_{19}	Me	**6r**	75 : 25	55 : 45		
19	**5s**	n-$C_{10}H_{21}$	Me	**6s**	80 : 20	50 : 50		
20	**5t**	n-$C_{16}H_{31}$	Me	**6t**	55 : 45			
21	**5u**	cyclo-C_5H_9	Me	**6u**	75 : 25	55 : 45	201.0	208.1
22	**5v**	cyclo-C_6H_{11}	Me	**6v**	90 : 10	50 : 50	198.3	208.5
23	**5w**			**6w**	100 : 0	55 : 45	200.7	203.6
24	**5x**			**6x**	100 : 0	35 : 65	200.3	208.1
25	**5y**	$CH_2{=}CHCHMe$	Me	**6y**	90 : 10			
26	**5z**	$CH_2{=}CMeCH_2$	Me	**6z**	85 : 15			
27	**5aa**	$Me_2C{=}CH$	Me	**6aa**	80 : 20		190.1	192.0
28	**5ab**	$CH_2{=}CHCHMeCH_2$	Me	**6ab**	100 : 0	60 : 40	199.5	
29	**5ac**	$CH_2{=}CHCMe_2CH_2$	Me	**6ac**	75 : 25	65 : 35		
30	**5ad**	$CH_2{=}CHCHMeCHMe$	$CH_2CH{=}CHCH_2$	**6ad**	85 : 15		191.3	201.1
							191.8	201.4
31	**5ae**	$PhOCH_2$	Me	**6ae**	100 : 0	60 : 40	187.2	197.1
32	**5af**	$PhCH_2$	Me	**6af**	70 : 30	70 : 30	192.3	199.7
33	**5ag**	$PhCH_2$	CH_2Ph	**6ag**				
34	**5ah**			**6ah**	100 : 0	60 : 40		
35	**5ai**	Ph	Me	**6ai**	80 : 20	40 : 60		

reaction of a carbonyl group (entries 32-33) was not observed. The reaction time required with *m*CPBA never exceeded 5 min at 0°C and thus is much shorter than the hours necessary for oxidizing a ketone or an alkene.

We then compared the competitive oxidation of different substrate molecules (one equivalent of each) with *m*CPBA (one equivalent). NMR analysis revealed interesting features (table II). An aliphatic sulfide is oxidized selectively in the presence of a thiol (entry 1) or a thioketone (entry 2), but not in the presence of a thioamide (entry 3). A thioketone is attacked much faster than a dithioester (entry 4). Competition between a dithioester and a trithiocarbonate (entry 5) is only slightly in favor of the oxidation of the former (70:30).

These simple experiments suggest the following rough reactivity order :



Among the thiocarbonyl derivatives, thioamides are the most reactive. Towards alkylation reactions they are also known to have a high nucleophilic character. The

Table II. Competitive oxidations.

Entry	Substrates		Expected products		Ratio
	A	B	A oxidized	B oxidized	A_{ox} / B_{ox}
1	$(i\text{-Pr})_2S$	$PhCH_2SH$	$(i\text{-Pr})_2SO$	$(PhCH_2S)_2$	100 : 0
2	$(i\text{-Pr})_2S$	$(i\text{-Pr})_2C{=}S$	$(i\text{-Pr})_2SO$	$(i\text{-Pr})_2C{=}SO$	100 : 0
3	$(i\text{-Pr})_2S$	MeC(=S)NHMe	$(i\text{-Pr})_2SO$	MeC(=O)NHMe	50 : 50
4	t-BuC(=S)Me	t-BuC(=S)SMe	t-BuC(=SO)Me	t-BuC(=SO)SMe	100 : 0
5	i-PrC(=S)Me	$(MeS)_2C{=}S$	i-PrC(=SO)Me	$(MeS)_2C{=}SO$	70 : 30
6	MeC(=S)SMe	i-PrC(=S)SMe	MeC(=SO)SMe	i-PrC(=SO)SMe	60 : 40
7	MeC(=S)SMe	t-BuC(=S)SMe	MeC(=SO)SMe	t-BuC(=SO)SMe	100 : 0
8	MeC(=S)SMe	PhC(=S)SMe	MeC(=SO)SMe	PhC(=SO)SMe	100 : 0
9	t-BuC(=S)SMe	PhC(=S)SMe	t-BuC(=SO)SMe	PhC(=SO)SMe	50 : 50
10	MeC(=S)SMe	MeC(=S)S-i-Pr	MeC(=SO)SMe	MeC(=SO)S-i-Pr	44 : 56
11	EtC(=S)SMe	EtC(=S)S-t-Bu	EtC(=SO)SMe	EtC(=SO)S-t-Bu	40 : 60
12	EtC(=S)SMe	EtC(=S)SPh	EtC(=SO)SMe	EtC(=SO)SPh	40 : 60
13	EtC(=S)S-t-Bu	EtC(=S)SPh	EtC(=SO)S-t-Bu	EtC(=SO)SPh	50 : 50

preceding order parallels this character and relates well to the electrophilic nature of *m*CPBA [33, 34].

We also looked at steric and electronic effects by comparing various dithioesters (entries 6-9 and 10-13). Two selective cases were investigated : the steric bulk of a dithiopivalate (entry 7) hinders the approach of the reagent in favor of the dithioacetate; and conjugation with the phenyl group of a dithiobenzoate decreases the reactivity as compared with a dithioacetate (entry 8). Other examples with smaller or crossed effects were unselective (entries 6 and 9). The variation of the alkylthio group was tested; increasing steric hindrance (S-*i*-Pr, S-*t*-Bu in entries 10 and 11) or adding an aromatic group (SPh, entries 12 and 13) did not lead to any selectivity. Apparently the main effect is repulsion of the sulfur doublets of the alkylthio group.

Discussion

The large number of sulfines that we have reported shows that oxidation of aliphatic dithioesters is a simple and efficient method for their synthesis. The oxidation reaction is fast at 0°C; it needs less than five minutes even with the hindered dithiopivalate **5o** (entry 15). A large variety of sulfines **6** have been prepared, including open-chain or cyclic, unsaturated and heteroatom-substituted compounds.

This easy synthesis stands in contrast with general literature expectations that enethiolizable thiocarbonyl compounds would not lead to sulfines [1, 2, 11, 12]. Utilization of a two-electron oxidizing agent, such as a peroxycarboxylic acid (and not a one-electron reagent such as iodine) led us to a successful formation of sulfines **6**.

A similar synthesis of sulfines **3** (R^2 = alkoxy or alkyl) was achieved by us with thioesters [22] and even more striking with thioketones [23], for which the known and stable tautomeric enethiol [24, 35] form could have provoked the concurrent oxidation to divinyl disulfides **4** proposed in the literature [1, 2, 11, 12]. We believe that synthesis of these disulfides **4** is restricted to the one-electron oxidation (*eg*, with iodine) of thiocarbonyl compounds in base medium.

Aliphatic sulfines **6** are now available for organic synthesis, provided that they are used rapidly and submitted to reactions which are faster than the above rearrangement. We have performed this with no difficulty. We prepared the sulfines immediately before use, isolated through simple work-up (overall it needs 1 h) and treated with nucleophiles to afford thiophilic [36] or carbophilic additions [37]. A rich chemistry of these heterocumulenes is now at hand [1].

Oxidation reactions of multifunctional molecules is an interesting topic. We have shown that thiocarbonyl derivatives (and sulfides) are very rapidly oxidized in the presence of *m*CPBA and that a number of chemoselective transformations may be envisaged.

The (*E*) stereochemistry of the oxidation is noteworthy. The oxygen is kinetically delivered on the side opposite to the alkylthio group. This preference has seldom been reported [38, 39]; with 4-tolyl-4-methoxydithiobenzoate only the (*E*) isomer was obtained [38]. Other cases mention an (*E*) and (*Z*) mixture, probably under thermodynamic control (with methyl dithiobenzoate we observed a 80:20 ratio, whereas a literature report [39] indicated a 50:50 mixture).

Conclusion

Oxidation of aliphatic alkanedithioates with *m*CPBA is achieved in some minutes at 0°C and quantitatively affords corresponding sulfines. The formation of the (*E*) isomers is kinetically preferred.

This simple and overlooked reaction can now be used routinely for the preparation of sulfines.

Experimental section

NMR spectra were recorded in $CDCl_3$ on a Bruker AC 250 spectrometer (250 MHz ^1H), in CCl_4 on a Varian EM 360

spectrometer (60 MHz ^{1}H) and on a Bruker WP 80 spectrometer (20.15 MHz ^{13}C). Chemical shifts are reported relative to TMS (δ 0.00) as an internal standard. Mass spectra were determined at 70 eV on a Nermag spectrometer. The UV-visible absorption spectrum was recorded with a Beckmann Acta M6 spectrometer.

Dithiocarboxylic esters **5** were prepared by : (i) reaction of Grignard reagents with carbon disulfide and reaction of the resulting dithiocarboxylate with alkyl halides (**5a-5c**, **5e**, **5g-5n**, **5p-5v**, **5af**, **5ag**, **5ai**) according to references [40-43]. Modifications of this method were used for specific examples : **5d** according to [44] ; **5o** was prepared according to [45], **5aa** according to [46] ; (ii) reaction of a carboxylic acid with Davy reagent (**5ae**) according to [47, 48] ; (iii) thio-Claisen rearrangement (**5y-z**, **5ab-ad**) according to [49, 50] ; (iv) acid cyclization of an unsaturated dithioacid (**5x**) according to [51] ; (v) thionation of thiolactones with Lawesson reagents (**5w**) according to [52] ; (vi) 1,4-addition of an enethiolate to an enone (**5ah**) according to [53, 54] ; and (vii) reaction of a thiol with a carboxymethyl alkanedithioate (**5f**) according to [55].

General procedure

To a stirred solution of a dithioester **5** (10 mmol) in dichloromethane (50 mL), *m*CPBA (70%, 1 equiv, 2.465 g) was added in one portion at 0°C (the yellow color disappears). After 5 min, the dichloromethane solution was washed successively with saturated aqueous $NaHCO_3$ (3 × 30 mL) and saturated brine (30 mL). The organic layer was dried ($MgSO_4$), filtered and then concentrated under reduced pressure without heating to leave the sulfine **6** as a mixture of *Z* and *E* isomers. NMR analysis was carried out right away, *ie* approximately 1 h after the oxidation step. Kinetic ratios are given in table I.

Yields of crude material (~ 95% purity) were around 90% (^{1}H NMR). At first, the *E* isomer was predominant, and after a period of 3-24 h, an isomerization to an *E* + *Z* mixture was observed (table I). Sulfines were not stable and, after some days, rearranged at room temperature to give dithioperoxyesters with, in some cases, a minor proportion of thiolesters. The thermodynamic ratios given in table I correspond to the equilibrium *E* + *Z* proportion just prior to the observation of dithioperoxyester signals.

• *1-Methylthio-1-sulfinylethane* **6a**

^{1}H NMR ($CDCl_3$) : δ 2.30 (s, C**H**$_3$C=SO, *Z* isomer), 2.49 (s, C**H**$_3$C=SO, *E* isomer), 2.52 (s, SC**H**$_3$, *E* isomer), 2.61 (s, SC**H**$_3$, *Z* isomer).

^{13}C NMR ($CDCl_3$) : δ 14.2, 15.3, 16.0, 18.8, 191.7 (**C**=SO, *E* isomer), 197.3 (**C**=SO, *Z* isomer).

• *1-[(1-Methylethyl)thio]-1-sulfinylethane* **6b**

^{1}H NMR (CCl_4) : δ 1.27 (d, *J* = 7 Hz, (C**H**$_3$)$_2$CH, *E* isomer), 1.32 (d, *J* = 7 Hz, (C**H**$_3$)$_2$CH, *Z* isomer), 2.12 (s, C**H**$_3$C=SO, *Z* isomer), 2.44 (s, C**H**$_3$C=SO, *E* isomer), 3.32 (sept, *J* = 7 Hz, C**H**, *E* isomer). 4.59 (sept, *J* = 7 Hz, C**H**, *Z* isomer).

• *[(1-Sulfinylethylthio)methyl]benzene* **6c**

^{1}H NMR (CCl_4) : δ 2.06 (s, C**H**$_3$, *Z* isomer), 2.33 (s, C**H**$_3$, *E* isomer), 3.86 (s, SC**H**$_2$Ph, *E* isomer), 4.59 (s, SC**H**$_2$Ph, *Z* isomer), 7.20 (s, C$_6$**H**$_5$, *Z* and *E* isomers).

• *[(1-Sulfinylethyl)thio]benzene* **6d**

^{1}H NMR (CCl_4) : δ 1.87 (s, C**H**$_3$, *Z* isomer), 2.38 (s, C**H**$_3$, *E* isomer), 7.42 (s, C$_6$**H**$_5$, *E* isomer), 7.48 (s, C$_6$**H**$_5$, *Z* isomer).

• *1-Methylthio-1-sulfinylpropane* **6e**

^{1}H NMR ($CDCl_3$) : δ 1.26 (t, *J* = 7.5 Hz, C**H**$_3$, *E* isomer), 1.28 (t, *J* = 7.3 Hz, C**H**$_3$, *Z* isomer), 2.47 (s, SC**H**$_3$, *E* isomer), 2.65 (s, SC**H**$_3$, *Z* isomer), 2.67 (q, *J* = 7.3 Hz, C**H**$_2$, *Z* isomer), 3.00 (q, *J* = 7.5 Hz, C**H**$_2$, *E* isomer).

^{13}C NMR ($CDCl_3$) : δ 13.0 (*Z* isomer), 14.2 (*E* isomer), 14.8 (*E* isomer), 15.8 (*Z* isomer), 23.9 (*E* isomer), 25.8 (*Z* isomer), 196.7 (**C**=SO, *E* isomer), 204.1 (**C**=SO, *Z* isomer).

• *1-[(1,1-Dimethylethyl)thio]-1-sulfinylpropane (***E** *isomer)* **6f**

^{1}H NMR (CCl_4) : δ 1.23 (t, *J* = 7 Hz, C**H**$_3$CH$_2$), 1.30 (s, (C**H**$_3$)$_3$CS), 2.93 (q, *J* = 7 Hz, CH$_2$CH$_3$).

^{13}C NMR ($CDCl_3$) : δ 11.9, 27.6, 31.1, 49.2, 195.5 (**C**=SO).

• *[(1-Sulfinylpropylthio)methyl]benzene* **6g**

^{1}H NMR (CCl_4) : δ 1.20 (t, *J* = 7 Hz, C**H**$_3$, *Z* and *E* isomers), 2.35 (q, *J* = 7 Hz, C**H**$_2$CH$_3$, *Z* isomer), 2.98 (q *J* = 7 Hz, C**H**$_2$CH$_3$, *E* isomer), 3.95 (s, SC**H**$_2$Ph, *E* isomer), 4.75 (s, SC**H**$_2$Ph, *Z* isomer), 7.31 (s, C$_6$**H**$_5$, *Z* and *E* isomers).

• *[(1-Sulfinylpropyl)thio]benzene* **6h**

^{1}H NMR (CCl_4) : δ 0.96 (t, *J* = 7 Hz, C**H**$_3$CH$_2$, *Z* isomer), 1.15 (t, *J* = 7 Hz, C**H**$_3$CH$_2$, *E* isomer), 2.36 (q, *J* = 7 Hz, C**H**$_2$, *Z* isomer), 2.83 (q, *J* = 7 Hz, C**H**$_2$, *E* isomer), 7.26 and 7.43 (2s, C$_6$**H**$_5$, *E* and *Z* isomers).

^{13}C NMR ($CDCl_3$) : δ 12.2 (*Z* isomer), 14.3 (*E* isomer), 24.0 (*E* isomer), 25.3 (*Z* isomer), 127.5, 129.1, 129.7, 130.3, 131.8, 135.2, 197.4 (**C**=SO, *E* isomer), 197.7 (**C**=SO, *Z* isomer).

• *1-[(Methoxymethyl)thio]-1-sulfinylpropane* **6i**

^{1}H NMR (CCl_4) : δ 1.21 (t, *J* = 7 Hz, C**H**$_3$CH$_2$, *E* isomer), 1.35 (t, *J* = 7 Hz, C**H**$_3$CH$_2$, *Z* isomer), 2.96 (q, *J* = 7 Hz, C**H**$_2$CH$_3$, *Z* and *E* isomers), 3.32 (s, OC**H**$_3$, *Z* isomer), 3.40 (s, OC**H**$_3$, *E* isomer), 4.69 (s, OC**H**$_2$S, *E* isomer), 5.31 (s, OC**H**$_2$S, *Z* isomer).

• *1-[2-(Dimethylamino)ethylthio]-1-sulfinylpropane* **6j**

^{1}H NMR (CCl_4) : δ 1.16 (t, *J* = 7 Hz, C**H**$_3$CH$_2$, *E* isomer), 1.34 (t, *J* = 7 Hz, C**H**$_3$CH$_2$, *Z* isomer), 2.24 (s, (NC**H**$_3$)$_2$, *Z* and *E* isomers), 2.46 (m, C**H**$_2$CH$_3$, *Z* and *E* isomers), 2.90 (m, SC**H**$_2$), 3.30 (m, C**H**$_2$-N, *Z* and *E* isomers).

• *2-Methyl-1-methylthio-1-sulfinylpropane* **6k**

^{1}H NMR ($CDCl_3$) : δ 1.25 (d, *J* = 6.9 Hz, (C**H**$_3$)$_2$CH, *Z* isomer), 1.29 (d, *J* = 6.8 Hz, (C**H**$_3$)$_2$CH, *E* isomer), 2.48 (s, SC**H**$_3$, *E* isomer), 2.86 (s, SC**H**$_3$, *Z* isomer), 2.94 (sept, *J* = 6.9 Hz, C**H**, *Z* isomer), 4.15 (sept, *J* = 6.8 Hz, C**H**, *E* isomer).

^{13}C NMR ($CDCl_3$) : δ 14.8 (*Z* isomer), 15.8 (*E* isomer), 20.0 (*E* isomer), 22.8 (*Z* isomer), 31.1 (*Z* isomer), 32.1 (*E* isomer), 198.8 (**C**=SO, *Z* isomer), 208.9 (**C**=SO, *E* isomer).

UV-vis (cyclohexane) : λ_{max} = 320 nm (log ε = 3.8).

• *3-[(2-Methyl-1-sulfinylpropyl)thio]prop-1-ene* **6l**

^{1}H NMR ($CDCl_3$) : δ 1.23 (d, *J* = 6.8 Hz, (C**H**$_3$)$_2$CH, *Z* and *E* isomers), 2.51 (d, *J* = 7 Hz, SC**H**$_2$, *E* isomer), 2.92 (sept, *J* = 6.8 Hz, C**H**, *Z* isomer), 4.11 (sept, *J* = 6.8 Hz, C**H**, *E* isomer), 4.16 (d, *J* = 7 Hz, SC**H**$_2$, *Z* isomer), 5.19-5.32 (m, =C**H**$_2$, *Z* and *E* isomers), 5.71-5.89 (m, C**H**=, *Z* and *E* isomers).

^{13}C NMR ($CDCl_3$) : δ 20.6 (*E* isomer), 22.9 (*Z* isomer), 31.3 (*E* isomer), 31.7 (*Z* isomer), 33.4 (*Z* isomer), 36.5 (*E* isomer), 119.5 (*Z* isomer), 120.9 (*E* isomer), 130.5 (*E* isomer), 132.1 (*Z* isomer), 195.1 (**C**=SO, *E* isomer), 204.0 (**C**=SO, *Z* isomer).

• *2-Methyl-1-butylthio-1-sulfinylpropane* **6m**

^{1}H NMR ($CDCl_3$) : δ 0.96 (t, J = 7.3 Hz, CH_3CH_2, *E* isomer), 0.94 (t, J = 7.3 Hz, CH_3CH_2, *Z* isomer), 1.24 (d, J = 6.9 Hz, $(CH_3)_2CH$, *E* isomer), 1.27 (d, J = 6.9 Hz, $(CH_3)_2CH$, *E* isomer), 1.48 (m, CH_2CH_3, *Z* and *E* isomers), 1.72 (m, CH_2CH_2S, *E* and *Z* isomers), 2.85 (t, J = 7.3 Hz, SCH_2, *E* isomer), 2.91 (sept, J = 6.8 Hz, CH, *Z* isomer), 3.53 (t, J = 7.3 Hz, SCH_2, *Z* isomer), 4.15 (sept, J = 6.9 Hz, CH, *E* isomer).

^{13}C NMR ($CDCl_3$) : δ 13.6 (*E* isomer), 13.7 (*Z* isomer), 21.0 (*E* isomer), 21.1 (*Z* isomer), 22.0 (*E* isomer), 23.1 (*Z* isomer), 30.0 (*E* isomer), 30.1 (*Z* isomer), 31.0 (*E* isomer), 32.0 (*Z* isomer), 32.4 (*Z* isomer), 32.5 (*E* isomer), 196.9 (**C**=SO, *Z* isomer), 208.3 (**C**=SO, *E* isomer).

• *3-Methyl-1-methylthio-1-sulfinylbutane* **6n**

^{1}H NMR ($CDCl_3$) : δ 0.90 (d, J = 6.6 Hz, $(CH_3)_2CH$, *Z* isomer), 1.01 (d, J = 6.6 Hz, $(CH_3)_2CH$, *E* isomer), 1.90 (sept, J = 6.8 Hz, CH, *Z* isomer), 2.11 (sept, J = 6.6 Hz, CH, *E* isomer), 2.40 (d, J = 7.0 Hz, CH_2C=SO, *Z* isomer), 2.48 (s, SCH_3, *E* isomer), 2.70 (s, SCH_3, *Z* isomer), 2.87 (d, J = 7.0 Hz, CH_2C=SO, *E* isomer).

^{13}C NMR ($CDCl_3$) : δ 14.5 (*Z* isomer), 15.8 (*E* isomer), 20.2 (*Z* isomer), 21.8 (*E* isomer), 27.6 (*E* isomer), 28.4 (*Z* isomer), 38.4 (*E* isomer), 40.3 (*Z* isomer), 192.1 (**C**=SO, *Z* isomer), 201.2 (**C**=SO, *E* isomer).

• *2,2-Dimethyl-1-methylthio-1-sulfinylpropane* **6o**

^{1}H NMR (CCl_4) : δ 1.30 (s, $(CH_3)_3C$, *Z* isomer), 1.42 (s, $(CH_3)_3C$, *E* isomer), 2.37 (s, SCH_3, *E* isomer), 2.82 (s, SCH_3, *Z* isomer).

^{13}C NMR ($CDCl_3$) : δ 16.9 (*Z* isomer), 18.4 (*E* isomer), 28.0 (*E* isomer), 31.8 (*Z* isomer), 41.0 (*Z* isomer), 44.3 (*E* isomer), 204.6 (**C**=SO, *E* isomer), 207.2 (**C**=SO, *Z* isomer).

MS : (%) 15 (100), 39 (44), 41 (47), 48 (43), 63 (24), 101 (19), 116 (7), 164 (8).

• *1-Methylthio-1-sulfinylnonane* **6p**

^{1}H NMR ($CDCl_3$) : δ 0.89 (t, J = 6.5 Hz, CH_3CH_2, *Z* and *E* isomers), 1.18-1.50 (m, $(CH_2)_5$, *Z* and *E* isomers), 1.63 (m, CH_2CH_2C=SO, *Z* and *E* isomers), 2.47 (s, SCH_3, *E* isomer), 2.56 (t, J = 7.4 Hz, CH_2C=SO, *Z* isomer), 2.67 (s, SCH_3, *Z* isomer), 2.97 (t, J = 7.6 Hz, CH_2C=SO, *E* isomer).

^{13}C NMR ($CDCl_3$) : δ 14.0, 14.3, 15.8, 22.7, 28.6, 28.9, 29.0, 29.1, 29.4, 29.7, 31.8, 31.9, 32.1, 194.5 (**C**=SO, *E* isomer), 202.8 (**C**=SO, *Z* isomer).

• *1-Butylthio-1-sulfinylnonane* **6q**

^{1}H NMR ($CDCl_3$) : δ 0.85-0.98 (m, CH_3, *Z* and *E* isomers), 1.20-1.80 (m, CH_2, *Z* and *E* isomers), 2.51 (t, J = 7.5 Hz, CH_2C=SO, *Z* isomer), 2.84 (t, J = 7.3 Hz, CH_2C=SO, *E* isomer), 2.95 (t, J = 7.5 Hz, SCH_2, *E* isomer), 3.30 (t, J = 7.3 Hz, SCH_2, *Z* isomer).

^{13}C NMR ($CDCl_3$) : δ 13.5, 13.6, 14.1, 21.7, 21.9, 22.7, 28.4, 28.6, 29.1, 29.2, 29.3, 29.7, 30.1, 30.4, 30.8, 31.8, 32.0, 32.4, 192.2 (**C**=SO, *Z* isomer), 200.7 (**C**=SO, *E* isomer).

• *1-Methylthio-1-sulfinyldecane* **6r**

^{1}H NMR (CCl_4) : δ 0.87 (t, J = 7 Hz, CH_3CH_2, *Z* and *E* isomers), 1.3 (m, $(CH_2)_7$, *Z* and *E* isomers), 2.43 (s, SCH_3, *E* isomer), 2.84 (s, SCH_3, *Z* isomer), 2.90 (t, J = 7 Hz, CH_2C=SO, *Z* isomer).

• *1-Methylthio-1-sulfinylundecane* **6s**

^{1}H NMR ($CDCl_3$) : δ 0.81 (t, J = 6.6 Hz, CH_3CH_2, *Z* and *E* isomers), 1.18-1.40 (m, $(CH_2)_7$, *Z* and *E* isomers), 1.72 (m, CH_2CH_2C=SO, *Z* and *E* isomers), 2.40 (s, SCH_3, *E* isomer), 2.50 (t, J = 7.4 Hz, CH_2C=SO, *Z* isomer), 2.61 (s, SCH_3, *Z* isomer), 2.90 (t, J = 7.6 Hz, CH_2C=SO, *E* isomer).

• *1-Methylthio-1-sulfinylhexadecane* **6t**

^{1}H NMR ($CDCl_3$) : δ 0.88 (t, J = 6.7 Hz, CH_3CH_2, *Z* and *E* isomers), 1.20-1.50 (m, $(CH_2)_{13}$, *Z* and *E* isomers), 1.63 (m, CH_2CH_2C=S, *Z* and *E* isomers), 2.47 (s, SCH_3, *E* isomer), 2.56 (t, J = 7.4 Hz, CH_2C=SO, *Z* isomer), 2.67 (s, SCH_3, *Z* isomer), 2.97 (t, J = 7.6 Hz, CH_2C=SO, *E* isomer).

• *1-[Methylthio(sulfinyl)methyl]cyclopentane* **6u**

^{1}H NMR ($CDCl_3$) : δ 1.73 (m, CH and CH_2, *Z* and *E* isomers), 2.49 (s, SCH_3, *E* isomer), 2.63 (s, SCH_3, *Z* isomer), 4.12-4.26 (m, CHC=SO, *Z* and *E* isomers).

^{13}C NMR ($CDCl_3$) : δ 15.1, 15.8, 25.6, 26.8, 32.3, 33.0, 41.6, 42.5, 201.0 (**C**=SO, *E* isomer), 208.1 (**C**=SO, *Z* isomer).

• *1-[Methylthio(sulfinyl)methyl]cyclohexane* **6v**

^{1}H NMR ($CDCl_3$) : δ 1.12-1.91 (m, CH_2, *E* and *Z* isomers), 2.45 (s, SCH_3, *E* isomer), 2.83 (s, SCH_3, *Z* isomer), 3.78-3.93 (m, CHC=SO, *Z* and *E* isomers).

^{13}C NMR ($CDCl_3$) : δ 15.1 (*Z* isomer), 15.9 (*E* isomer), 25.6 (*Z* isomer), 25.7 (*E* isomer), 26.2 (*E* and *Z* isomers), 26.4 (*E* and *Z* isomers), 27.0 (*E* isomer), 30.3 (*Z* isomer), 31.5 (*E* isomer), 33.7 (*Z* isomer), 40.8 (*E* isomer), 42.1 (*Z* isomer), 198.3 (**C**=SO, *E* isomer), 208.5 (**C**=SO, *Z* isomer).

• *2-Sulfinylthiolane* **6w**

^{1}H NMR (CCl_4) : δ 2.39 (m, J = 6 Hz, CH_2CH_2-S, *Z* and *E* isomers), 3.01 (t, J = 6 Hz, CH_2C=SO, *Z* and *E* isomers), 3.35 (t, J = 6 Hz, SCH_2, *Z* and *E* isomers).

^{13}C NMR ($CDCl_3$) : δ 24.7 (isomer), 29.9 (*Z* isomer), 30.9 (*E* isomer), 33.8 (*E* isomer), 36.5 (*E* isomer), 39.0 (*Z* isomer), 200.7 (C=SO, *E* isomer), 203.6 (**C**=SO, *Z* isomer).

MS : (%) 45 (49), 48 (100), 58 (81), 71 (17), 85 (26), 134 (9).

• *5-Methyl-2-sulfinylthiolane* **6x**

^{1}H NMR (CCl_4) : δ 1.53 (d, J = 7 Hz, CH_3, *Z* and *E* isomers), 2.23 (m, CH_2CH_2C=SO, *Z* and *E* isomers), 3.03 (dt, J = 6 and 7 Hz, CH_2CH_2C=SO, *Z* and *E* isomers), 3.86 (m, J = 7 Hz, HCS, *Z* and *E* isomers).

^{13}C NMR ($CDCl_3$) : δ 20.2 (*E* isomer), 21.6 (*Z* isomer), 33.2 (*Z* isomer), 34.2 (*E* isomer), 39.3 (*Z* isomer), 45.4 (*Z* isomer), 49.1 (*E* isomer), 200.3 (**C**=SO, *E* isomer), 208.1 (**C**=SO, *Z* isomer).

• *3-Methyl-4-methylthio-4-sulfinylbut-1-ene* **6y**

^{1}H NMR ($CDCl_3$) : δ 1.38 (d, J = 7 Hz, CH_3CH, *E* isomer), 1.45 (d, J = 7 Hz, CH_3CH, *Z* isomer), 2.48 (s, SCH_3, *E* isomer), 2.80 (s, SCH_3, *Z* isomer), 3.37-4.68 (quint, J = 7 Hz (CH_3)CH, *Z* and *E* isomers), 5.0-5.4 (m, $=CH_2$, *Z* and *E* isomers), 5.6-6.2 (m, HC=, *Z* and *E* isomers).

• *2-Methyl-4-methylthio-4-sulfinylbut-1-ene* **6z**

^{1}H NMR ($CDCl_3$) : δ 1.82 (s, CH_3C, *Z* and *E* isomers), 2.50 (s, SCH_3, *E* isomer), 2.61 (s, SCH_3, *Z* isomer), 3.27 (s, 2H, CH_2, *Z* isomer), 3.70 (s, CH_2, *E* isomer), 4.92-4.98 (m, $=CH_2$, *Z* and *E* isomers), 5.6-6.2 (m, HC=, *Z* and *E* isomers).

• *3-Methyl-1-methylthio-1-sulfinylbut-2-ene* **6aa**

^{1}H NMR ($CDCl_3$) : δ 1.90 (s, CH_3 *trans*, *Z* isomer), 1.95 (s, CH_3 *cis*, *Z* isomer), 2.00 (s, CH_3 *trans*, *E* isomer), 2.05 (s, CH_3 *cis*, *E* isomer), 2.35 (s, SCH_3, *E* isomer), 2.45 (s, SCH_3, *Z* isomer), 5.65 (s, =CH, *Z* isomer), 6.50 (s, =CH, *E* isomer).

^{13}C NMR ($CDCl_3$) : δ 14.7 (*Z* isomer), 18.2 (*E* isomer), 20.5 (*Z* isomer), 21.8 (*E* isomer), 26.6 (*Z* isomer), 28.1 (*E* isomer), 112.2 (*Z* isomer), 117.7 (*E* isomer), 147.0 (*Z* isomer), 148.7 (*E* isomer), 190.1 (C=SO, *E* isomer), 192.0 (C=SO, *Z* isomer).

• *3-Methyl-5-methylthio-5-sulfinylpent-1-ene* **6ab**

^{1}H NMR ($CDCl_3$) : δ 1.12 (d, J = 6.7 Hz, CH_3, *E* isomer), 1.18 (d, J = 6.2 Hz, CH_3, *Z* isomer), 2.47 (s, SCH_3, *E* isomer), 2.67 (m, CH_2C=SO, *Z* isomer), 2.88 (s, SCH_3, *Z* isomer), 3.00 (m, CH_2C=SO, *E* isomer), 4.98-5.13 (m, $=CH_2$, *Z* and *E* isomers), 5.68-5.82 (m, CH=, *Z* and *E* isomers).

^{13}C NMR ($CDCl_3$) : δ 16.1, 19.7, 37.4, 38.3, 114.2, 141.8, 199.5 (C=SO).

MS : (%) 55 (100), 69 (65), 79 (11), 91 (7), 97 (51), 109 (13), 131 (5), 145 (10), 161 (9), 176 (4).

• *3,3-Dimethyl-5-methylthio-5-sulfinylpent-1-ene* **6ac**

^{1}H NMR (CCl_4) : δ 1.14 (s, $(CH_3)_2$, *Z* and *E* isomers), 2.42 (s, SCH_3, *E* isomer), 2.77 (s, SCH_3, *Z* isomer), 2.90 (s, CH_2, *Z* and *E* isomers), 4.8-5.4 (m, $=CH_2$, *Z* and *E* isomers), 5.7-6.2 (m, CH=, *Z* and *E* isomers).

• *5-(But-2-enylthio)-3,4-dimethyl-5-sulfinylpent-1-ene* **6ad**

^{1}H NMR (CCl_4) : δ 0.9-1.3 (m, CH_3CH, *Z* and *E* isomers), 1.75 (d, CH_3CH=, *Z* and *E* isomers), 2.0-2.8 and 3.2-4.3 (2m, CHCSO, SCH_2 and CHC=, *Z* and *E* isomers), 4.7-6.0 (m, $=CH_2$ and CH=, *Z* and *E* isomers).

^{13}C NMR ($CDCl_3$) : δ 17.4, 18.7, 32.9, 33.2, 36.1, 36.4, 41.0, 41.6, 42.2, 42.5, 114.6, 114.8, 123.6, 123.7, 125.5, 131.7, 132.0, 132.2, 141.0, 141.2, 191.3 and 191.8 (C=SO, 2 diastereoisomers of the *E* isomer), 201.1 and 201.4 (C=SO, 2 diastereoisomers of the *Z* isomer).

• *(2-Methylthio-2-sulfinylethoxy)benzene* **6ae**

^{1}H NMR (CCl_4) : δ 2.53 (s, SCH_3, *E* isomer), 2.60 (s, SCH_3, *Z* isomer), 4.70 (s, CH_2C=SO, *Z* isomer), 5.23 (s, CH_2C=SO, *E* isomer), 7.00 (m, C_6H_5O, *Z* and *E* isomers).

^{13}C NMR ($CDCl_3$) : δ 14.3 (*E* isomer), 16.2 (*Z* isomer), 63.2 (*E* isomer), 64.2 (*Z* isomer), 122.1 and 122.7 (*Z* isomer), 129.8 (*E* isomer), 187.2 (C=SO, *E* isomer), 197.1 (C=SO, *Z* isomer).

• *(2-Methylthio-2-sulfinylethyl)benzene* **6af**

^{1}H NMR (CCl_4) : δ 2.26 (s, SCH_3, *E* isomer), 2.43 (s, SCH_3, *Z* isomer), 3.73 (s, CH_2C=SO, *Z* isomer), 4.13 (s, CH_2C=SO, *E* isomer), 7.20 (m, C_6H_5, *Z* and *E* isomers).

^{13}C NMR ($CDCl_3$) : δ 14.3 (*Z* isomer), 16.1 (*E* isomer), 35.1 (*Z* isomer), 37.3 (*E* isomer), 127.7 and 128.6 (*Z* isomer), 129.0 and 129.2 (*E* isomer), 192.3 (C=SO, *Z* isomer), 199.7 (C=SO, *E* isomer).

• *(2-Benzylthio-2-sulfinylethyl)benzene* **6ag**

^{1}H NMR (CCl_4) : δ 3.55 (s, $PhCH_2C$=SO, *Z* isomer), 3.70 (s, $PhCH_2C$=SO, *E* isomer), 4.08 (s, SCH_2Ph, *E* isomer), 4.50 (s, SCH_2Ph, *Z* isomer), 7.20 (m, C_6H_5, *Z* and *E* isomers).

• *3-(2-Methylthio-2-sulfinylethyl)cyclohexanone* **6ah**

^{1}H NMR (CCl_4) : δ 1.0-2.4 (m, CH_2 and CH, *Z* and *E* isomers), 2.47 (s, SCH_3, *E* isomer), 2.79 (s, SCH_3, *Z* isomer).

^{13}C NMR ($CDCl_3$) : δ 14.7, 16.0, 22.7, 24.7, 30.7, 36.1, 37.5, 37.9, 38.3, 41.1, 47.1, 189.8 and 198.9 (C=SO, *Z* and *E* isomers), 209.6 and 209.9 (2s, C=O, *Z* and *E* isomers).

• *[Methylthio(sulfinyl)methyl]benzene* **6ai**

Previously reported [39] as a 1:1 mixture of *E*/*Z* isomers. We have observed a kinetic ratio of 80:20.

^{1}H NMR (CCl_4) : δ 2.27 (s, SCH_3, *E* isomer), 2.66 (s, SCH_3, *Z* isomer), 7.4-7.6 (m, C_6H_5, *Z* and *E* isomers), 8.10-8.4 (m, aromatic H-*ortho*-, *E* isomer).

Competitive oxidations

To a stirred solution of two different thiocarbonyl or sulfur compounds (1 equiv of each) in dichloromethane, *m*CPBA (1 equiv) was added in one portion at 0°C. After 5-20 min, the dichloromethane solution was washed successively with saturated aqueous $NaHCO_3$ and saturated brine. The organic layer was dried ($MgSO_4$), filtered and then concentrated under reduced pressure. The crude material was analyzed by NMR, compared with the known oxidation products leading to data reported in table II. Dithioester *S*-oxide spectra are reported above, thioketone *S*-oxides in a preceding paper [23] and the trithiocarbonate *S*-oxide will be described forthcoming [56]. Diisopropyl sulfoxide had NMR signals at 1.26 (d, J = 7, Me) and 2.63 (hept, J = 7, CH).

References

1 Zwanenburg B, *Recl Trav Chim Pays-Bas* (1982) 101, 1-27

2 Zwanenburg B, *Phosphorus, Sulfur Silicon Relat Elem* (1989) 43, 1-24

3 Zwanenburg B, Lenz BG, dans *Houben-Weyl Methoden der Organischen Chemie*, Band E11, Teil 1, Klamann D, Thieme, Stuttgart (1985) p 911-949

4 Block E, *Angew Chem, Int Ed Engl* (1992) 31, 1135-1178

5 Bonini BF, Maccagnani G, Mazzanti G, Rosini G, Foresti E, *J Chem Soc, Perkin Trans I* (1981) 2322-2327

6 Bonini BF, Busi F, de Laet RC, Mazzanti G, Thuring JWJF, Zani P, Zwanenburg B, *J Chem Soc, Perkin Trans I* (1993) 1011-1018

7 Mazzanti G, Ruinaard R, Van Vliet LA, Zani P, Bonini BF, Zwanenburg B, *Tetrahedron Lett* (1992) 33, 6383-6386

8 Barbaro G, Battaglia A, Giorgianni P, Bonini BF, Maccagnani G, Zani P, *J Org Chem* (1990) 55, 3744-3748

9 Strating J, Thijs L, Zwanenburg B, *Tetrahedron Lett* (1966) 65-67

10 Zwanenburg B, Thijs L, Strating J, *Tetrahedron Lett* (1967) 3453-3456

11 Van der Leij M, Zwanenburg B, *Tetrahedron Lett* (1978) 3383-3386

12 Porskamp PATW, van der Leij M, Lammerink BHM, Zwanenburg B, *Recl Trav Chim Pays-Bas* (1983) 102, 400-404

13 Zwanenburg B, Wagenaar A, Thijs L, Strating J, *J Chem Soc, Perkin Trans I* (1973) 73-75

14 Bonini BF, Maccagnani G, Mazzanti G, Thijs L, Veenstra GE, Zwanenburg B, *J Chem Soc, Perkin Trans I* (1978) 1218-1224

15 Carlsen L, Duus F, *Synthesis* (1977) 256-258

16 Mayer R, Scheithauer S, dans *Houben-Weyl Methoden der Organischen Chemie*, Band E5, Teil 2, Falbe J, Thieme, Stuttgart (1985) p 891-930

17 Metzner P, *Synthesis* (1992) 1185-1199

18 Metzner P, Pham TN, *J Chem Soc, Chem Commun* (1988), 390-391

19 Walter W, Curts J, *Chem Ber* (1960) 93, 1511-1517

20 Veenstra GE, Zwanenburg B, *Recl Trav Chim Pays-Bas* (1976) 95, 37-39

21 Pushkara Rao V, Ramamurthy V, *Synthesis* (1985) 526-527

22 Lemarié M, Metzner P, Pham TN, *Tetrahedron Lett* (1991) 32, 7411-7414

23 Le Nocher AM, Metzner P, *Tetrahedron Lett* (1991) 32, 747-750

24 Metzner P, *Phosphorus, Sulfur Silicon Relat Elem* (1991) 59, 1-16

25 Tangerman A, Zwanenburg B, *J Chem Soc, Perkin Trans II* (1975) 352-361

26 Nilsson NH, Senning A, *Angew Chem Int Ed Engl* (1972) 11, 295

27 Karlstrom G, Roos BO, Carlsen L, *J Am Chem Soc* (1984) 106, 1557-1561

28 Schaumann E, Lange B, Reinholdt K, *J Chem Soc, Chem Commun* (1983) 797-798

29 Cooke MD, Moore KW, Ross BC, Turner SE, *Tetrahedron Lett* (1983) 24, 3373-3376

30 Aloup JC, Bouchaudon J, Farge D, James C (Rhône-Poulenc Santé), *Eur Pat* 97 584

31 Zwanenburg B, Thijs L, Strating J, *Recl Trav Chim Pays-Bas* (1967) 86, 577-588

32 Battaglia A, Dondoni A, Giorgianni P, Maccagnani G, Mazzanti G, *J Chem Soc B* (1971) 1547-1550

33 Haines AH, *Method for the Oxidation of Organic Compounds, Alkanes, Alkenes, Alkynes, and Arenes*, Academic, London (1985)

34 Adam W, Haas W, Lohray BB, *J Am Chem Soc* (1991) 113, 6202-6208

35 Le Nocher AM, Metzner P, *Tetrahedron Lett* (1992) 33, 6151-6154

36 Cerreta F, Chapron I, Metzner P, to be published

37 Cerreta F, Leriverend C, Metzner P, *Tetrahedron Lett* (1993) 34, 6741-6742

38 Veenstra GE, Zwanenburg B, *Recl Trav Chim Pays-Bas* (1976) 95, 195-224

39 Perez MA, Kresze G, *Liebigs Ann Chem* (1981) 1505-1509

40 Beiner JM, Thuillier A, *CR Acad Sci, Ser C* (1972) 274, 642-645

41 Meijer J, Vermeer P, Brandsma L, *Recl Trav Chim Pays-Bas* (1973) 92, 601-604

42 Metzner P, Thuillier A, *Sulfur Reagents in Organic Synthesis*, Academic, Londres (1994)

43 Kpegba K, Metzner P, Rakotonirina R, *Tetrahedron* (1989) 45, 2041-2056

44 Beslin P, Dlubala A, Levesque G, *Synthesis* (1987) 835-837

45 Westmijze H, Kleijn H, Meijer J, Vermeer P, *Synthesis* (1979) 432-434

46 Gosselin P, Masson S, Thuillier A, *Tetrahedron Lett* (1978) 2715-2716

47 Davy H, *J Chem Soc, Chem Commun* (1982) 457-458

48 Davy H, Metzner P, *J Chem Res* (1985), (S) 272; (M) 2701-2712

49 Schuijl PJW, Brandsma L, *Recl Trav Chim Pays-Bas* (1968) 87, 929-939

50 Désert S, Metzner P, Ramdani M, *Tetrahedron* (1992) 48, 10315-10326

51 Schoufs M, Meijer J, Vermeer P, Brandsma L, *Synthesis* (1978) 439-440

52 Scheibye S, Kristensen J, Lawesson SO, *Tetrahedron* (1979) 35, 1339-1343

53 Berrada S, Metzner P, Rakotonirina R, *Bull Soc Chim Fr* (1985) 881-890

54 Metzner P, *J Chem Soc, Chem Commun* (1982) 335-336

55 Leon NH, Asquith RS, *Tetrahedron* (1970) 26, 1719-1725

56 Le Nocher AM, Leriverend C, Metzner P, manuscript in preparation