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Thiophilic Addition of Organolithiums to Trithiocarbonate Oxides (Sulfines)

Synthesis of β-Oxoketene Dithioacetals, 1,4-Dicarbonyl Compounds, and Allyl Sulfoxides

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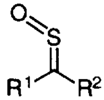
Abstract. *Reaction of trithiocarbonates with meta-chloroperoxybenzoic acid in CH_2Cl_2 at 0°C affords the corresponding S-oxides. These sulfines are relatively stable compounds which can be purified by chromatography. They react readily with organolithiums in THF at -78°C in a thiophilic manner to give carbanions which are stabilized by three sulfur groups. Hydrolysis affords trithioorthoester oxides. The thermal behaviour of these hindered products has been investigated and new rearrangement processes have been evidenced. The former carbanions are soft nucleophiles: 1,4-addition of these intermediates to α-enones was achieved selectively to lead to β-oxo ketenedithioacetals, which are easily transformed into 4-oxoalkanethioates. This "Umpolung" route allows the formal use of the (alkylthio)carbonyl anion. A thiophilic addition was also observed with allylsilanes in the presence of n-Bu_4NF furnishing allyl sulfoxides.*

Sulfines **1** are attractive heterocumulenes with a C=S=O moiety. A great deal of studies on these thiocarbonyl oxides was carried out by the group of B. Zwanenburg[1-4] in the 70's. Despite some recent work from this group and those of Bonini and Mazzanti,[5-8] Julia[9-11] and Bravermann,[12] their chemistry and especially the synthetic applications of sulfines are underexploited. We have recently described investigations[13,14] leading to the first preparation of aliphatic sulfines **1** by oxidation of dithioesters,[15,16] thionesters[17] and thioketones[18] and to their thiophilic *versus* carbophilic behaviour towards nucleophiles.[13,19,20]



R^1 = Alkyl, R^2 = Alkyl, SR, OR

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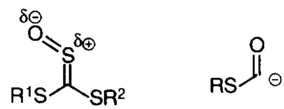
We wish to report the use of trithiocarbonate S-oxides **2** as new examples of (alkylthio)carbonyl anions **3** in *"Umpolung"* type reactions through thiophilic addition of alkylithiums to the electrophilic sulfur atom of the C=S=O group.

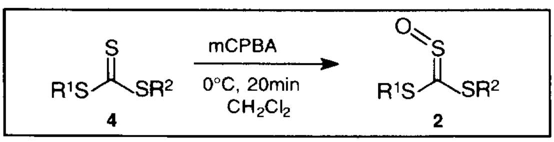


2 **3**

Synthesis of Trithiocarbonate Oxides

Only few examples of sulfines **2** have appeared in the literature. Oxidation of trithiocarbonates (bearing aromatic groups) was used with a peroxycarboxylic acid[21-24] or with lead tetracetate[24,25]. A Peterson type reaction involving the addition of an α-silylcarbanion with sulfur dioxide also led[26] to two examples of **2**. We report on the preparation of new examples and especially sulfines from trithiocarbonates bearing aliphatic groups.

Our satisfactory experience in the oxidation of a variety of thiocarbonyl compounds[16-18,27] led us to choose mCPBA as reagent. Trithiocarbonates **4** were prepared by usual techniques.[28-30] We achieved their oxidation with one equivalent of mCPBA in dichloromethane at 0°C. It requires a reaction time of 15 to 20 min, revealing a slower reaction than for other thiocarbonyl compounds,[16] such as dithioesters or thioketones (1 min). After aqueous work-up and base elimination of *meta*-chlorobenzoic acid, the quantitative formation of the yellow sulfines **2** was analysed by NMR of the crude material. No evidence for the oxidation of one of the other sulfur atoms was detected.



Having so far worked with thermally unstable sulfines, produced from dithioesters[15] or thioketones,[18] we were pleased to observe that trithiocarbonate oxides **2** can be purified by column chromatography on silica gel or by crystallisation (Tables 1 and 2). Yields of isolated materials range from 73 to 94 %. They are relatively stable and can be kept for months at -18°C. One exception is sulfine **2e** (5 membered ring) which, in the solid state, decomposes in few hours but can be kept in solution ($CDCl_3$) for weeks.

The sulfine structure was assigned by NMR, mass spectroscopy and elemental analysis. The carbon 13 signal of the C=S=O group of symmetrical sulfines **2a-f** resonates at 182-200 ppm. Thus an upfield shift of 22 to 40 ppm is observed relative to the starting thiocarbonyl compound **4**.

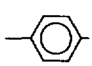
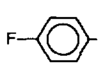
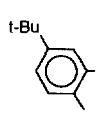
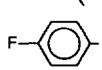
For unsymmetrical sulfines **2g-l** *E/Z* isomerism[31-34] is expected. Two cases have been observed depending on the nature of the R^1 and R^2 substituents.

i) With R^1 being **aromatic** (entries 8-11), NMR spectra, recorded just immediately after work-up, reveal a major isomer to which can be assigned a *Z* structure according[4] to the sulfinyl group strong anisotropic effect (see discussion). The *Z/E* ratio of **5h-k** ranges from 70 : 30 to 90 : 10. The kinetic isomer is not the one which has the oxygen atom on the less hindered side of the C=S double bond, namely that of

Table 1. Symmetrical Trithiocarbonate Oxides (2)

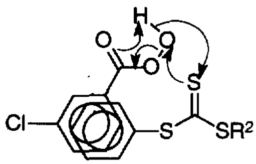
Entry	Trithiocarbonates 4			Sulfines 2		
		R^1	R^2		Yield (%)	^{13}C NMR: CSO (ppm)
1	**4a**	Me	Me	**2a**	73	192.2
2	**4b**	Et	Et	**2b**	75	186.2
3	**4c**	i-Bu	i-Bu	**2c**	85	188.8
4	**4d**	CH_2Ph	CH_2Ph	**2d**	78	182.4
5	**4e**	$-CH_2-CH_2-$		**2e**	82	199.8
6	**4f**	$-CH_2-CH_2-CH_2-$		**2f**	94	193.5

Table 2. Unsymmetrical Trithiocarbonate Oxides (2)

Entry	Trithiocarbonates 4			Sulfines 2					
						Ratio $Z:E$		NMR (ppm)	
		R^1	R^2	Yield (%)		1h after preparation	at equilibrium	^1H SCH_3 or SCH_2	^{13}C CSO
7	**4g**	t-Bu	Me	78	**2g**	0 : 100	0 : 100	E : 2.66	E : 185.2
8	**4h**	Ph	Me	94	**2h**	70 : 30	20 : 80	Z : 2.27 E : 2.56	Z : 194.5 E : 186.4
9	**4i**		Me	93	**2i**	80 : 20	25 : 75	Z : 2.27 E : 2.55	Z : 196.5 E : 187.5
10	**4j**		Me	88	**2j**	90 : 10	25 : 75	Z : 2.29 E : 2.59	Z : 194.6 E : 186.8
11	**4k**		Me	88	**2k**	85 : 15	35 : 65	Z : 2.26 E : 2.54	Z : 196.3 E : 188.5
12	**4l**		Allyl	100[a]	**2l**	na[b]	30 : 70	Z : 3.06 E : 3.93	Z : 186.3 E : 183.6

na: not available
a: crude yield
b: 3h after preparation: 45 : 55.

alkylthio SR^2, but on the side of the arylthio group. This might be a new example of π stacking, taking place between the aromatic nuclei of the trithiocarbonate and the electrophilic mCPBA.



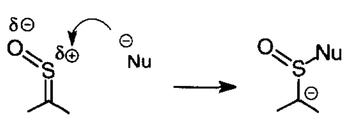
When sulfines **2 h-k** are left at ambient temperature the *Z/E* ratio changes. After some days the *E* isomer is predominant: equilibrium ratios are 20 : 80 to 35 : 65. The configuration with the oxygen atom opposite to the aromatic group is thus thermodynamically favoured. The separation of *E* and *Z* isomers by column chromatography was not successful.

ii) With two **aliphatic** groups (R^1 = t-Bu and R^2 = Me, entry 12) we have detected a single isomer to which we have assigned the *E* structure. Expectedly the kinetic oxidation has taken place on the less hindered doublet of the thiocarbonyl sulfur. No subsequent isomerization was observed. The *E* configuration is also probably the more stable.

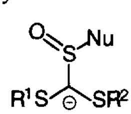
Ratios of isomers were determined by proton NMR (table 2). The sulfinyl group exerts a strong anisotropic effect.[33] A methylthio group is shifted downfield when it is *cis* to the oxygen atom (inside the negative zone) and upfield when it is *trans* (positive zone). Applied for instance to sulfine **2h** (R^1 = Ph, R^2 = Me) it allows to assign the *E* structure to the compound bearing a downfield methyl (2.56 ppm) and the *Z* structure to the isomer with an upfield methyl shift (2.27 ppm). ^{13}C NMR signals also permit[16] differentiation of the isomers with the same variations of shifts for the α and β carbons. Moreover for the sulfinyl group we have shown that the carbon signals of the *Z* isomers are deshielded relatively to the *E* isomers generally by 8-9 ppm.

Thiophilic Addition of Organolithiums to Sulfines

The first evidence of the electrophilic character of the sulfur atom of sulfines in the reaction with organolithium was reported by Schlessinger and Schulz.[35] This original access to sulfoxides initiated further studies with thioketones[7,36] and dithioester oxides.[20,37-39] Only one report dealt briefly with a trithiocarbonate oxide.[37]



We decided to reconsider this reaction with a variety of sulfines with the aim of synthetic applications. We expect a high electrophilic character for sulfines (*"super electrophiles"?*) and prospects of chemoselectivity (especially *versus* carbonyl groups). Assuming a thiophilic course to the addition of nucleophiles to trithiocarbonate oxides **2** we may have access to carbanions **5**.



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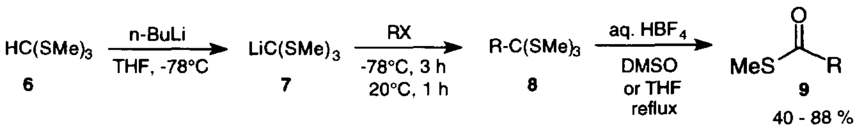
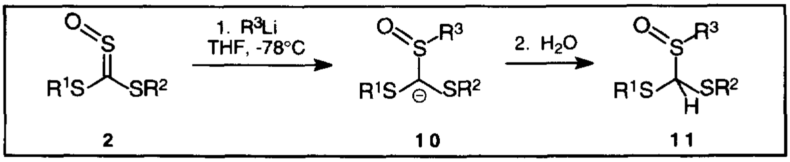
Strangely enough, these intermediates, which are stabilized by three sulfur groups are almost unknown.[37,40] The nearest related chemistry involves[41-46] alkyl trithioorthoformates **6** which have been deprotonated, then treated with alkyl halides to afford trithioorthoesters **8**. Acid treatment of **8** with heating led[41] to thiolesters **9**.



We have performed the reaction of sulfines **2a-h** with methyllithium at -78°C for 10 min in THF. The yellow colour of **2** was rapidly discharged. After quenching with water and work-up we observed the quantitative formation of trithioorthoesters oxides **11** (Table 3). Thus a thiophilic addition is proved. The low temperature conditions indicate that sulfines **2** are highly reactive towards methyllithium.



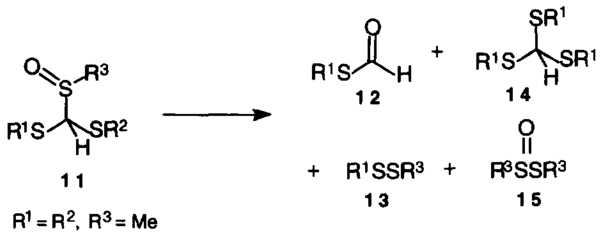
Similar results were obtained with other alkyllithiums: n-butyl- and phenyllithium led to adducts **11ab** and **11ac** (entries 8 and 9).

Table 3. Thiophilic Addition to Sulfines (2) and Synthesis of Trithioorthoester Oxides (11)

Entry	Sulfine **2**			R^3Li	Trithioorthoester oxide **11**
		R^1	R^2		
1	**2a**	Me	Me	MeLi	**11aa**
2	**2b**	Et	Et	MeLi	**11ba**
3	**2c**	i-Bu	i-Bu	MeLi	**11ca**
4	**2d**	CH_2Ph	CH_2Ph	MeLi	**11da**
5	**2f**	$-CH_2-CH_2-CH_2-$		MeLi	**11fa**
6	**2g**	t-Bu	Me	MeLi	**11ga**
7	**2h**	Ph	Me	MeLi	**11ha**
8	**2a**	Me	Me	BuLi	**11ab**
9	**2a**	Me	Me	PhLi	**11ac**

For unsymmetrical sulfines **2g** and **2h** (entries 6 and 7) a mixture of diastereomers **11ga** and **11ha** is obtained approximately in a 1 : 1 ratio.

Trithioorthoester oxides **11** are unstable at ambient temperature. After a period of 10 days their transformation was complete. To simplify enough we will present the behaviour of products **11** derived from symmetrical sulfines ($R^1 = R^2$). The major product was thiolester **12**. It was accompanied by a disulfide **13**, a trithioorthoester **14** and methyl methanethiosulfinate **15**.



The formation of thiolester **12** and disulfide **13** can be explained but their proportion was not 1 : 1. Two concurrent rearrangements actually took place and they both produced thiolester **12**. We assume that after a common first step two processes are possible: intramolecular (A) or intermolecular (B).

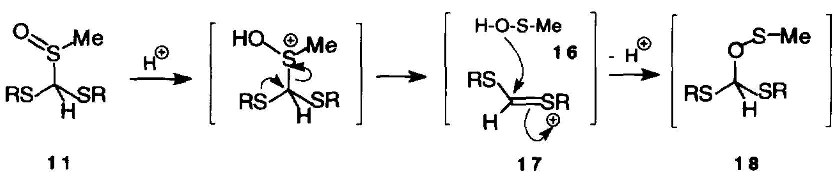
We have experimentally noticed that these rearrangements are efficiently inhibited by the addition of a small amount of a tertiary amine: oxides **11** were not transformed after months at room temperature under these conditions. This suggests that the rearrangements are acid catalysed and that they are inhibited by neutralization of a trace of acid (present in CH_2Cl_2 used for extraction) by the amine. The transformation of dithioacetal or trithioester oxides in acidic conditions has been observed by Zwanenburg and his group.[37,39]

Table 4. Transformation of Symmetrical Trithioorthoester Oxides (11)

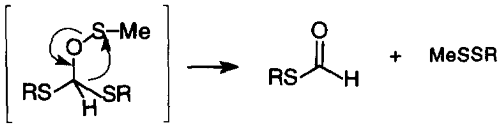
Entry	Trithioorthoester oxide 11				Products (determined by NMR)		
		R^1	R^2	R^3	R^1SCHO **12** Routes A and B	$(R^1S)_3CH$ **14** Route B	Ratio A / B
1	**11aa**	Me	Me	Me	70 %	30 %	40 : 60
2	**11ba**	Et	Et	Me	80 %	20 %	60 : 40
3	**11ca**	i-Bu	i-Bu	Me	70 %	30 %	40 : 60
4	**11da**	CH_2Ph	CH_2Ph	Me	70 %	30 %	40 : 60
5	**11fa**	$-CH_2-CH_2-CH_2-$		Me	56 % [a]	na	na
6	**11ab**	Me	Me	Bu	60 %	40 %	60 : 40
7	**11ac**	Me	Me	Ph	75 %	25 %	50 : 50

a yield of product isolated by chromatography.
na: not available

The series of events would start by the elimination of methanesulfenic acid **16** from the protonated oxyde **11**, generating a stabilized thionium ion **17**. Recombination of **17** with **16** would lead to compound **18** with a sulfenate moiety. A concerted pathway (sulfoxide to sulfenate) cannot be ruled out at this stage.

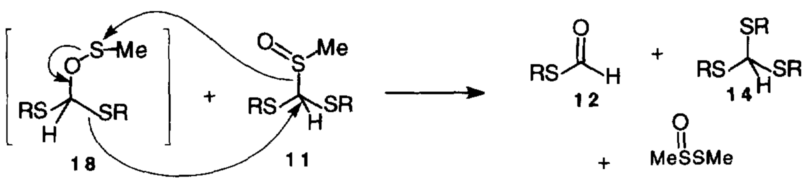


Intramolecular rearrangement of **18** (route A) leads to thioformate **12** and disulfide **13**.



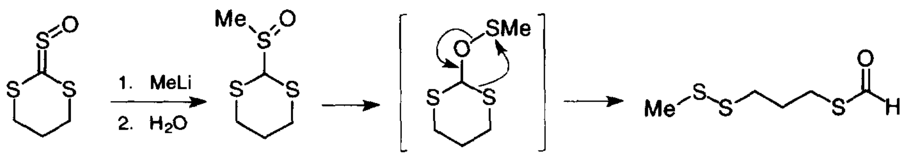
18 12 13

Alternatively intermolecular reaction (B) of the sulfoxide **11** with the weak O-S bond of sulfenate **18**, followed by cleavage of a C-SR bond, could explain the formation of thioformate **12**, trithioorthoester **14** and methyl methanethiosulfinate **15**. The ratio of pathways A and B was estimated by NMR. It depends on the substituents and varies from 40 : 60 to 60 : 40 (Table 4). The reactions carried out with n-BuLi and PhLi (instead of MeLi) supports the preceding mechanisms.



18 11 12 14 15

In the specific example of an acyclic sulfine **2f**, the intramolecular pathway is favoured. A molecule bearing both the disulfide and thiolester groups was isolated in a 56 % yield.



2f 11fa 18fa 19 Yield: 56 %

Similar rearrangements were observed from unsymmetrical sulfines **4g** and **4h**. Each trithioorthoester oxide, **11ga** or **11ha**, was converted into two thiolesters.

Thiophilic Addition and Electrophilic Attack of Enones

We have wished to use the intermediates formed by the thiophilic addition by treating them with electrophiles other than water. Assuming a soft character for trithioorthoester oxide carbanions we have studied their behaviour towards enones, with the aim of achieving a conjugate addition. Analogous dithioacetal oxides have indeed been successfully used in this reaction by Ogura,[47] Schlessinger[48,49] and Zwanenburg.[37]

We have submitted to each four sulfines **2a-d** one equivalent of methyllithium in THF at -78°C. Enones **20a-c** were added at -78°C and the mixture kept at this temperature (Table 5, entries 1-2) or allowed to rise to 20°C (entries 3-7). The crude materials consist of adducts **21**, whose characteristic features were shown by NMR: C=O (^{13}C at 207-209 ppm), MeSO (^{1}H at 2.8 and ^{13}C at 35-36 ppm). It is worthy of note that 3-buten-2-one gives good conversion in contrast to its usual propensity to side reactions.

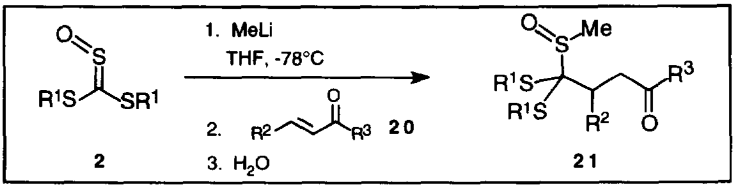
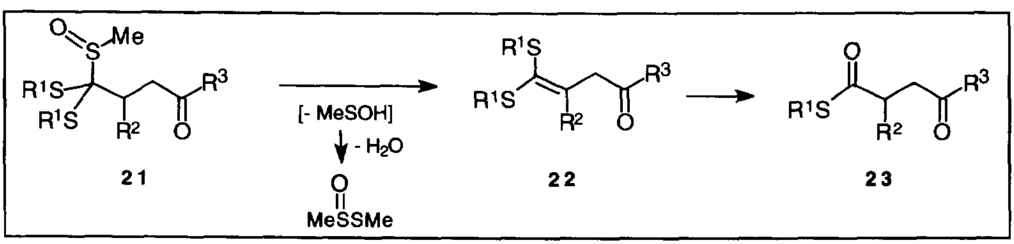


Table 5. Addition of Methyl Lithium to Sulfines (1) and Electrophilic Attack of Enones (4). Initial Products and their Transformation

Entry	Sulfine **2**		Enone **20**			Conditions		Trithioortho-ester oxide **21**		Ketene dithioacetal **22**		Thiolester **23**	
		R^1		R^2	R^3	Temperature °C	Time		Yield[a] %		Observed[c]		Isolated yield %
1	**2a**	Me	**20a**	Me	H	-78	10 min	**21aa**	80	**22aa**	yes	**23aa**	52
2	**2a**	Me	**20b**	Et	H	-78	10 min	**21ab**	70	**22ab**	yes	**23ab**	41
3	**2a**	Me	**20c**	Me	Me	-78 to 20	3 h	**21ac**	b	**22ac**	no	**23ac**	55
4	**2b**	Et	**20a**	Me	H	-78 to 20	6 h	**21ba**	50	**22ba**	yes	**23ba**	37
5	**2c**	i-Bu	**20a**	Me	H	-78 to 20	4 h	**21ca**	b	**22ca**	80%	**23ca**	56
6	**2c**	i-Bu	**20c**	Me	Me	-78 to 20	7 h	**21cc**	b	**22cc**	no	**23cc**	55
7	**2d**	$PhCH_2$	**20a**	Me	H	-78 to 20	6 h	**21da**	na	**22da**	yes	**23da**	54

na: not available.
a: from the NMR of the crude material.
b: not observed.
c: detection by NMR after a few days at r.t.

Compounds **21** are unstable. They readily rearrange into β-ketene dithioacetals **22** in a few hours. The elimination of methanesulfenic acid is supported by the detection of methyl methanesulfinate (2.68 and 2.99 singlets in the ^{1}H NMR spectra). For some cases (entries 3, 5, 6) the compounds **22** were obtained directly and products **21** could not be detected. A similar elimination has been reported with dithioacetal oxides.[37]

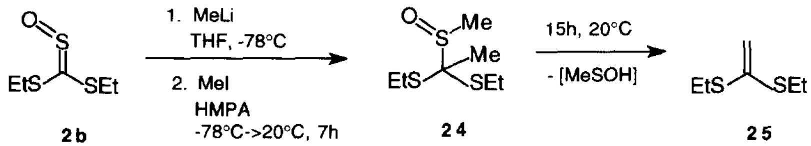


In contrast to α-oxoketene dithioacetals, the chemistry of their non conjugated analogues **22** have not been much developed. Among the few reports[50,51] only one method[51] offers a general entry to compounds **22**, involving an acid catalyzed opening of *gem*(diphenylthio)cyclopropyl ketones.

The ketenedithioacetals **22** that we have formed are sensitive to water. When left to ambient temperature and submitted to liquid chromatography on silica gel they were transformed into 4-oxothiolesters **23** yielded at 37-55 %.

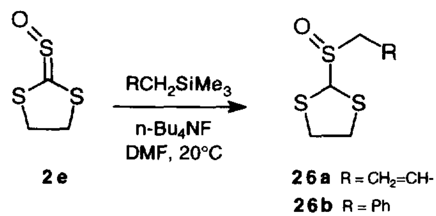
The overall transformation provides a new means for the synthesis of 1,4-dicarbonyl compounds. It involves the formal use of an (alkylthio)carbonyl anion for Michael addition to enones. It adds a new synthon to the available catalogue for *"Umpolung"* type reactions.[52-55]

We have also briefly examined the reactivity of an intermediate carbanion towards alkyl halides. We could achieve the following example involving iodomethane only with the addition of HMPA to enhance the nucleophilicity of the intermediate. Adduct **24** was obtained. It rapidly underwent the above elimination reaction ending to unsubstituted ketenedithioacetal **25**. Though the alkylation reaction is sluggish a new access to ketenedithioacetals has been provided by creating the carbon-carbon double bond.



Addition of Silanes

Silanes have also been successfully employed as alternative nucleophiles for thiophilic addition. Sulfine **2e** was submitted to allyl and benzylsilanes in the presence of tetra-n-butylammonium fluoride in a DMF solution. After some hours of reaction we could isolate sulfoxides **26a-b** yield at 38-41% after chromatography.

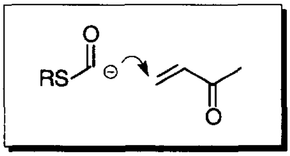


The products also arise from thiophilic addition. These new examples of this reaction with silanes[56] bring us a further access to allyl and benzyl sulfoxides. No evidence for the [2.3] sigmatropic shift of an intermediate allyl sulfinyl carbanionic species was detected.

Conclusion

Addition of alkyllithiums to a variety of new and stable trithiocarbonate oxides occurs readily at low temperature and exclusively in a thiophilic manner, as a result of the electrophilic character of the sulfur atom of sulfines. The intermediate carbanion, stabilized by three sulfur groups, was quenched with water to quantitatively afford trithioorthoester oxides. The latter molecules had almost not been reported previously. Their thermal behaviour was explored and new rearrangement pathways were observed.

Trithioorthoester oxide carbanions exhibit a soft character and react in a conjugate fashion with α-enones. The primary products were detected but they are not stable. Elimination of methanesulfenic acid gives interesting β-oxo ketenedithioacetals, non conjugated isomers of the classical α-analogues. The ketene dithioacetal moiety is easily converted to a thiolester group, thus affording new 1,4-dicarbonyl compounds. The overall sequence allows the use of an (alkylthio)carbonyl anion for Michael addition in polarity reversal reactions.



We have also shown that a benzyl or an allylsilane can react with sulfines to lead, with a thiophilic course, to allyl and benzyl trithioester oxides.

Experimental Section

General

All reactions were run under a positive pressure of nitrogen. THF was distilled over sodium benzophenone ketyl. Methyllithium had a low chloride content (Janssen - Acros) and was titrated before use. Preparative flash liquid chromatography was performed with Merck 60 silica gel (63-200 microns) in the eluting solvents indicated below. ^{1}H NMR 250 MHz spectra were recorded on a Bruker AC 250 spectrometer. Data appear in order: chemical shift in ppm, multiplicity (s, singlet ; d, doublet ; t, triplet ; q, quartet; hept, heptuplet ; m, multiplet), coupling constant in hertz, number of protons, assignment. ^{13}C NMR spectra were determined at 62.9 MHz with the same spectrometer, operating with broad band ^{1}H decoupling. The solvent used is $CDCl_3$ and TMS is the internal standard. ^{19}F NMR spectra were executed at 75.4 MHz with a Bruker WP 80 SY apparatus. IR absorption spectra were run on Perkin-Elmer 684 and 16 PC FT-IR. Mass spectra were obtained at 70 eV with a Nermag R10 RH spectrometer and the data tabulated as m/e and relative intensities expressed as percentages. Elemental analyses were performed by Service Central d'Analyse of CNRS at Vernaison for C and H and by LCMT for S. The results are described as percentages.

Starting Materials

Symmetrical Trithiocarbonates

Trithiocarbonates **4a-f** were prepared according to Lee *et al*[28] by formation of the dianion CS_3^{2-} and alkylation. They were purified by chromatography on silica gel or by cristallisation.

Dimethyl trithiocarbonate (4a). Reaction on a 40 mmol scale with iodomethane. Yield: 95% after chromatography (petroleum ether / ethyl acetate 80:20). Yellow oil. ^{1}H NMR: lit[28]. ^{13}C NMR: 20.2 [SCH_3], 225.8 [C=S].

Diethyl trithiocarbonate (4b). Reaction on a 40 mmol scale with bromoethane. Yield: 90% after chromatography (petroleum ether / ethyl acetate 95:5). Yellow oil. ^{1}H NMR: lit[28]. ^{13}C NMR: 13.2 [CH_3], 32.2 [SCH_2], 224.4 [C=S].

Bis(2-methylpropyl) trithiocarbonate (4c). Reaction on a 40 mmol scale with 1-bromo-2-methylpropane. Yield: 77% after chromatography (dichloromethane). Yellow oil. ^{1}H NMR: 1.02 [d, J = 6.7 Hz, 12H, CH_3], 2.00 [m, 2H, CH], 3.29 [d, J = 6.8 Hz, 4H, CH_2S]. ^{13}C NMR: 13.2 [CH_3], 32.2 [SCH_2], 224.4 [C=S]. MS: 222 (M^+, 1), 165 (i-BuSCS_2^+, 5), 133 (i-BuS_2C^+, 1), 110 (8), 90 (1), 55 (i-Bu^+, 100). Anal. calcd.: C, 48.60; H, 8.16; S, 43.24. Found: C, 48.62; H, 8.14; S, 43.74.

Bis(phenylmethyl) trithiocarbonate (4d). Reaction on a 40 mmol scale with benzyl bromide. Yield: 96% after chromatography (petroleum ether / dichloromethane 80:20). Yellow crystals, mp 27-28°C. ^{1}H NMR: lit[28]. ^{13}C NMR: 41.6 [CH_2S], 127.9, 128.8 and 129.4 [aromatic CH], 135.1 [CCH_2S], 222.9 [C=S].

2-Thioxo-1,3-dithiane (4f). Reaction on a 20 mmol scale with 1,3-dichloropropane. Yield: 25% after cristallisation (methanol). Yellow crystals, mp 85°C. ^{1}H NMR: lit[28]. ^{13}C NMR: 20.7 [CH_2], 34.5 [CH_2S], 221.4 [C=S].

Unsymmetrical Dialkyl Trithiocarbonate

Trithiocarbonate **4g** was prepared according to Degani *et al*,[29] using the following procedure. To a mixture of tertiobutylthiol (1.127 mL, 10 mmol), aqueous sodium hydroxide (10 mL of H_2O, 0.4g of NaOH) and carbon disulfide (1.2 mL, 20 mmol) was added one phase transfer agent, trioctylmethyl ammonium chloride, also called TOMAC or ALIQUAT 336 (0.137 mL, 0.3 mmol). The mixture, which became orange over the course of the reaction, was stirred vigorously at ambient temperature for 1 h 15 min. Iodomethane (0.625 mL, 10 mmol) was added and stirring maintained until the colour of the aqueous phase was discharged (45 min). The mixture was extracted with petroleum ether (150-200 mL) and the organic phase was dried on $MgSO_4$ and filtered on a small pad of silica gel (elution with petroleum ether). After concentration the crude trithiocarbonate was obtained in a satisfactory purity to be used without further purification. Yellow oil. Yield: 57%.

Methyl 1,1-dimethylpropyl trithiocarbonate (4g). ^{1}H NMR: 1.64 [s, 9H, t-Bu], 2.66 [s, 3H, CH_3S]. ^{13}C NMR: 19.7 [SCH_3], 29.5 [$C(CH_3)_3$], 54.2 [$C(CH_3)_3$], 224.6 [C=S]. MS: 180 (M^+, 33), 165 (t-BuSCS_2^+, 12), 124 (MeSCS_2^+, 17), 91 (MeS_2C^+, 30), 59 (t-BuSC^+, 9), 57 (t-Bu^+, 100), 47 (MeS^+, 29), 41 (83).

Aryl Alkyl Trithiocarbonates

Trithiocarbonates **4h-l** were prepared according to Sugawara *et al*[30] using the following procedure. To a solution of aromatic thiol (0.1 mol) in 20% aqueous sodium hydroxyde (20 mL of H_2O, 0.4g of NaOH, 0.1mmol) were added carbon disulfide (12 mL, 0.2 mol) and a phase transfert agent, trioctylmethyl ammonium chloride (5 mL, 10 mmol). The mixture was stirred for 5 h at 0°C. A solution of the alkyl halide (0.11 mol) in toluene (100 mL) was added and stirring maintained at 0°C for 3 h, then overnight at 20°C. The organic phase was separated, dried on $MgSO_4$ and concentrated by evaporation. Trithiocarbonates were separated from the aryl alkyl sulfide (due to non completion of the reaction with CS_2) by chromatography.

Methyl phenyl trithiocarbonate (4h). Reaction on a 0.1 mol scale with benzenethiol and iodomethane. Yield: 93% after chromatography (petroleum ether / dichloromethane 90:10). Yellow crystals, mp 40°C. ^{1}H NMR: 2.64 [s, 3H, SCH_3], 7.35-7.63 [m, 5H, aromatic CH] (erroneous report of the methyl signal in lit[30]). ^{13}C NMR: 20.7 [SCH_3], 129.7, 130.2, 131.0 [aromatic CH], 135.8 [aromatic CS], 226.1 [C=S].

Methyl (4-methylphenyl) trithiocarbonate (4i). Reaction on a 0.1 mol scale with 4-methylbenzenethiol and iodomethane. Yield: 65% after chromatography (petroleum ether / dichloromethane 90:10). Yellow oil. ^{1}H NMR: lit[30]. ^{13}C NMR: 20.7 [SCH_3], 21.7 [CH_3Ph], 126.9 [CCH_3], 130.5, 135.7 [aromatic C], 227.0 [C=S].

(4-Fluorophenyl) methyl trithiocarbonate (4j). Reaction on a 0.1 mol scale with 4-fluorobenzenethiol and iodomethane. Yield: 46% after chromatography (petroleum ether / ethyl acetate 90:10). Yellow oil. ^{1}H NMR: 2.65 [s, 3H, SCH_3], 7.13-7.62 [m, 4H, aromatic CH]. ^{13}C NMR: 20.8 [SCH_3], 117.0 [d, $^2J_{C-F}$ = 22.4 Hz, meta aromatic CH], 125.7 [d, $^4J_{C-F}$ = 3.5 Hz, aromatic CS], 138.0 [d, $^3J_{C-F}$ = 9.0 Hz, ortho aromatic CH], 164.4 [d, $^1J_{C-F}$ = 253.0 Hz, CF], 226.0 [C=S]. ^{19}F NMR: -81.74 to -81.19 [m]. MS: 218 (M^+, 74), 171 (F-PhSCS_2^+, 5), 127 (F-PhSC^+, 5), 95 (F-PhSC^+, 16), 91 (MeS_2C^+, 100), 83 (F-PhS^+, 23), 76 (CS_2^+, 6). Anal. calcd.: C, 44.01; H, 3.23; S, 44.00. Found: C, 44.15; H, 3.21; S, 43.86.

Methyl [2-methyl-5-(dimethylethyl)phenyl)] trithiocarbonate (4k). Reaction on a 0.1 mol scale with 2-methyl-5-tertiobutylbenzenethiol and iodomethane. Yield: 59% after chromatography (petroleum ether). Yellow oil. ^{1}H NMR: 1.32 [s, 9H, $C(CH_3)_3$], 2.41 [s, 3H, CH_3Ph], 2.62 [s, 3H, SCH_3], 7.25-7.57 [m, 3H, aromatic CH]. ^{13}C NMR: 20.1 [CH_3Ph], 20.7 [SCH_3], 31.3 [$C(CH_3)_3$], 34.7 [$C(CH_3)_3$], 124.2 [aromatic CS], 128.5, 130.7 and 133.7 [aromatic CH], 139.8 and 150.4 [aromatic C], 226.1 [C=S]. MS: 270 (M^+, 17), 91 ($MeCS_2^+$, 100), 57 (4). Anal. calcd.: C, 57.73; H, 6.71; S, 35.56. Found: C, 57.79; H, 6.65; S, 35.89.

(4-Fluorophenyl) 2-propenyl trithiocarbonate (4l). Reaction on a 5 mmol scale with 4-fluorobenzenethiol and allyl bromide. Yield: 40% after chromatography (petroleum ether / ethyl acetate 90:10). Yellow oil. ^{1}H NMR: 3.93 [d, J = 7.1 Hz, 2H, CH_2S], 5.15-5.32 [m, 2H, $=CH_2$], 5.72-5.88 [m, 2H, CH=], 7.12-7.21 [m, 2H, aromatic CH], 7.53-7.61 [m, 2H, aromatic CH]. ^{13}C NMR: 40.5 [SCH_2], 117.0 [d, $^2J_{C-F}$ = 23.4 Hz, meta aromatic CH], 120.1 [CH_2=], 125.6 [d, $^4J_{C-F}$ = 3.3 Hz, aromatic CS], 130.7 [CH=], 138.0 [d, $^3J_{C-F}$ = 8.9 Hz, ortho aromatic CH], 164.5 [d, $^1J_{C-F}$ = 253 Hz, CF], 224.3 [C=S]. ^{19}F NMR: -108.7 to -109.1 [m]. MS: 244 (M^+, 18), 127 (F-PhSC$^+$, 33), 117 ($C_3H_5S_2C^+$, 26), 57 (75), 41 ($C_3H_5^+$, 100).

Sulfines by Oxidation of Trithiocarbonates

General Procedure. To a solution of trithiocarbonate **4** (10 mmol) in dichloromethane (75 mL) cooled at 0°C, 70% mCPBA (10 mmol, 2.51 g) was added. The mixture was stirred at 0°C for 20 min. The solution was washed with an aqueous sodium hydrogen carbonate solution (3 x 50 mL) (with vigorous stirring), then with water (50 mL). The organic phase was dried over $MgSO_4$ and concentrated by evaporation. The resulting sulfine **2** was isolated by chromatography on silica gel or by cristallisation.

1,1-Bis(methylthio)-1-sulfinylmethane (2a). Reaction carried out on 17.5 mmol (2.41 g) of dimethyl trithiocarbonate **4a**. Yield: 73% after chromatography (dichloromethane). Yellow oil. ^{1}H NMR: 2.48 [s, 3H, *trans* SCH_3], 2.76 [s, 3H, *cis* SCH_3]. ^{13}C NMR: 15.9 [*trans* SCH_3], 20.4 [*cis* SCH_3], 192.2 [C=SO]. IR (neat): 2998, 2922, 1422, 1314, 1116, 1084, 1012, 974, 948, 930. MS: 154 (M^+, 8), 137 (9), 108 (CS_3^+, 3), 91 (MeS_2C^+, 100), 76 (CS_2^+, 21). Anal. calcd.: C, 23.36; H, 3.92; S, 62.35. Found: C, 23.72; H, 3.95; S, 61.73.

1,1-Bis(ethylthio)-1-sulfinylmethane (2b). Reaction carried out on 10.7 mmol (1.78 g) of diethyl trithiocarbonate **4b**. Yield: 75% after chromatography (dichloromethane). Yellow oil. ^{1}H NMR: 1.29 [t, J = 7.3 Hz, 3H, *trans* CH_3], 1.39 [t, J = 7,4 Hz, 3H, *cis* CH_3], 2.81 [q, J = 7.3 Hz, 2H, *trans* SCH_2], 3.40 [q, J = 7.4 Hz, 2H, *cis* SCH_2]. ^{13}C NMR: 13.9 [*trans* CH_3], 14.9 [*cis* CH_3], 27.5 [*trans* SCH_2], 31.0 [*cis* SCH_2], 186.2 [C=SO]. IR (KBr): 2966, 2926, 2868, 1448, 1374, 1260, 1124, 1054, 1006. MS: 182 (M^+, 87), 166 (M^+ - O, 7), 165 (54), 105 (EtS_2^+, 100), 77 (99), 76 (CS_2^+, 15), 61 (EtS^+, 14) . Anal. calcd.: C, 32.94; H, 5.53; S, 52.75. Found: C, 33.30; H, 5.50; S, 51.11.

1,1-Bis(2-methylpropylthio)-1-sulfinylmethane (2c). Reaction carried out on 12.8 mmol (2.84 g) of bis(2-methylpropyl) trithiocarbonate **4c**. Yield: 85% after chromatography (dichloromethane). Yellow oil. ^{1}H NMR: 1.02 [d, J = 6.7 Hz, 6H, *trans* $(CH_3)_2CH$], 1.05 [d, J = 6.7 Hz, 6H, *cis* $(CH_3)_2CH$], 1.87 [m, 1H, *trans* CH], 1.96 [m, 1H, *cis* CH], 2.67 [d, J = 6.9 Hz, 2H, *trans* CH_2S], 3.27 [d, J = 6.8 Hz, 2H, *cis* CH_2S]. ^{13}C NMR: 21.7 [CH_3], 28.1 [*trans* CH], 29.2 [*cis* CH], 41.4 [*trans* CH_2S], 45.6 [*cis* CH_2S], 188.8 [C=SO]. IR (neat): 2958, 2928, 2870, 1464, 1384, 1366, 1126, 1110, 1078, 1012. MS: 238 (M^+, 8), 165 (i-BuSCS$_2^+$, 17), 57 (i-Bu$^+$, 100). Anal. calcd.: C, 45.34; H, 7.61; S, 40.34. Found: C, 45.65; H, 7.49; S, 41.08.

1,1-Bis(phenylmethylthio)-1-sulfinylmethane (2d). Reaction carried out on 11.7 mmol (3.39 g) of bis(phenylmethylthio) trithiocarbonate **4d**. Yield: 78% after chromatography (dichloromethane). Yellow crystals, mp 54°C. ^{1}H NMR: 3.77 [s, 2H, *trans* CH_2], 4.58 [s, 2H, *cis* CH_2], 6.97 [m, 2H, para aromatic H], 7.24-7.38 [m, 8H, aromatic H]. ^{13}C NMR: 37.0 [*trans* CH_2S], 41.8 [*cis* CH_2S], 128.0 and 128.1 [para aromatic CH], 128.9, 129.0, 129.2 and 129.5 [aromatic CH], 135.3 and 136.0 [CCH_2S], 182.4 [C=SO]. IR (KBr): 3060, 3028, 1600, 1494, 1454, 1236, 1114, 1072, 1012, 948, 698. MS: 290 (M^+, 4), 167 ($PhCH_2S^+$, 9), 91 ($PhCH_2^+$, 41), 90 (100), 76 (CS_2^+, 9), 64 (11). Anal. calcd.: C, 58.79; H, 4.60; S, 31.38. Found: C, 58.83; H, 4.52; S, 31.27.

2-Sulfinyl-1,3-dithiolane (2e). Reaction carried out on 19.26 mmol (2.6 g) of commercial ethylene trithiocarbonate **4e**. Yield: 82%. Yellow crystals (cristallisation in dichloromethane / diethyl ether), mp 71-72°C. In the solid state this compound decomposes rapidly but can be stored for weeks in $CDCl_3$. ^{1}H NMR: 3.60-3.74 [m, 4H, CH_2S]. ^{13}C NMR: 38.8 [*trans* CH_2S], 41.4 [*cis* CH_2S], 199.8 [C=SO]. IR (neat): 1418, 1284, 1092, 996, 976, 948, 926, 884, 860, 666, 516. MS: 152 (M^+, 28), 136 (M^+ - O, 10), 104 (M^+ - SO, 4), 92 (M^+ - CSO, 5), 76 (CS_2^+, 100), 64 (44), 60 ($CH_2CH_2S^+$, 15).

2-Sulfinyl-1,3-dithiane (2f). Reaction carried out on 0.51 mmol (77 mg) of commercial ethylene trithiocarbonate **4f**. Yield: 98%. Yellow crystals (cristallisation in dichloromethane / diethyl ether): mp 38°C. ^{1}H NMR: 2.37 [m, 2H, CH_2CH_2S], 3.04 [m, 2H, *trans* CH_2S], 3.23 [m, 2H, *cis* CH_2S]. ^{13}C NMR: 24.9 [CH_2CH_2S], 29.1 [*trans* CH_2S], 30.4 [*cis* CH_2S], 193.5 [C=SO]. IR (neat): 1420, 1092, 994, 952, 912. MS: 166 (M^+, 41), 118 (M^+ - SO, 15), 108 (CS_3^+, 10), 106 (M^+ - CSO, 18), 92 (15), 85 (49), 76 (CS_2^+, 100), 71 (29).

(Z)-**1-(Methylthio)-1-(dimethylethyl)thio-1-sulfinylmethane (2g)**. Reaction carried out on 3 mmol (601 mg) of methyl (4-methylphenyl) trithiocarbonate **4g**. Yield: 78% after chromatography (dichloromethane). Yellow oil. A single *Z* isomer was obtained. ^{1}H NMR: 1.39 [s, 9H, t-Bu], 2.66 [s, 3H, CH_3S]. ^{13}C NMR: 116.7 [SCH_3], 30.6 [$C(CH_3)_3$], 50.7 [$C(CH_3)_3$], 185.2 [C=SO]. Anal. calcd.: C, 36.70; H, 3.16; S, 48.99. Found: C, 36.24; H, 6.17; S, 48.29.

1-(Methylthio)-1-phenylthio-1-sulfinylmethane (2h). Reaction carried out on 3 mmol (605 mg) of methyl phenyl trithiocarbonate **4h**. Yield: 94% after chromatography (dichloromethane). Yellow oil. A 70:30 mixture of *Z* and *E* isomers was obtained 1 h after reaction; 20:80 after 3 days (equilibrium). ^{1}H NMR of the *Z* isomer: 2.27 [s, 3H, SCH_3], 7.30-7.65 [m, 5H, aromatic **CH**]. ^{1}H NMR of the *E* isomer: 2.56 [s, 3H, SCH_3], 7.30-7.65 [m, 5H, aromatic **CH**]. ^{13}C NMR of the *Z* isomer: 19.1 [SCH_3], 127.0, 129.9, 130.6 and 135.5 [aromatic CH], 194.5 [C=SO]. ^{13}C NMR of the *E* isomer: 15.9 [SCH_3], 128.5, 128.8, 129. 8 and 132.8 [aromatic CH], 186.4 [C=SO]. IR (neat): 3056, 3002, 2924, 1580, 1476, 1440, 1426, 1118, 1080, 1020, 1000, 968, 930, 688. MS: 216 (M^+, 22), 153 (PhS_2C^+, 31), 140 (19), 123 (17), 121 ($PhSC^+$, 12), 91 (MeS_2C^+, 40), 77 (Ph^+, 100), 65 (19), 51 (25). Anal. calcd.: C, 41.15; H, 3.95; S, 47.07. Found: C, 41.01; H, 3.95; S, 46.71.

1-(Methylthio)-1-(4-methylphenylthio)-1-sulfinylmethane (2i). Reaction carried out on 9.3 mmol (2 g) of methyl 4-methylphenyl trithiocarbonate **4i**. Yield: 93% after chromatography (dichloromethane / petroleum ether 80:20). Yellow oil. A 80:20 mixture of *Z* and *E* isomers was obtained 1 h after reaction; 25:75 at equilibrium. ^{1}H NMR of the *Z* isomer: 2.27 [s, 3H, SCH_3], 2.41 [s, 3H, CH_3Ph], 7.26 and 7.46 [AB system, J = 8.0 Hz, 4H, aromatic **CH**]. ^{1}H NMR of the *E* isomer: 2.36 [s, 3H, CH_3Ph], 2.56 [s, 3H, SCH_3], 7.19 and 7.31 [AB system, J = 8.3 Hz, 4H, aromatic CH]. ^{13}C NMR of the *Z* isomer: 15.9 [SCH_3], 21.3 [CH_3Ph], 126.0 [CCH_3], 129.4 and 130.6 [aromatic CH], 139.1 [CS], 187.5 [C=SO]. ^{13}C NMR of the *E* isomer: 18.9 [SCH_3], 21.5 [CH_3Ph], 129.0 [CCH_3], 130.5 and 135.6 [aromatic CH], 141.3 [CS], 196.5 [C=SO]. IR (neat): 3020, 2922, 1490, 1448, 1426, 1398, 1120, 1080, 1016, 968, 936, 926, 806. MS: 230 (M^+, 6), 167 ($MePhS_2C^+$, 10), 135 ($MePhSC^+$, 11), 123 ($MePhS^+$, 21), 91 ($MePh^+$, 35), 65 (15), 57 (100). Anal. calcd.: C, 46.93; H, 4.38; S, 41.75. Found: C, 47.0; H, 4.34; S, 41.95.

1-(Methylthio)-1-(4-fluorophenylthio)-1-sulfinylmethane (2j). Reaction carried out on 2.61 mmol (570 mg) of methyl 4-fluorophenyl trithiocarbonate **4j**. Yield: 88% after chromatography (petroleum ether / ethyl acetate 95:5 then 90:10). Yellow oil. A 90:10 mixture of *Z* and *E* isomers was obtained 1 h after reaction; 25:75 at equilibrium (20 days). ^{1}H NMR of the *Z* isomer: 2.59 [s, 3H, SCH_3], 7.06-7.12 [m, 2H, aromatic **CH**], 7.39-7.44 [m, 2H, aromatic **CH**]. ^{1}H NMR of the *E* isomer: 2.29 [s, 3H, SCH_3], 7.10-7.19 [m, 2H, aromatic **CH**], 7.54-7.60 [m, 2H, aromatic **CH**]. ^{13}C NMR of the *Z* isomer: 19.0 [SCH_3], 117.0 [d, $^2J_{C\text{-}F}$ = 22.4 Hz, meta aromatic CH], 122.0 [aromatic CS], 137.8 [d, $^3J_{C\text{-}F}$ = 13.4 Hz, ortho aromatic CH], 164.3 [d, $^1J_{C\text{-}F}$ = 253.0 Hz, CF], 194.6 [C=SO]. ^{13}C NMR of the *E* isomer: 16.0 [SCH_3], 117.1 [d, $^2J_{C\text{-}F}$ = 22.4 Hz, meta aromatic CH], 127.6 [aromatic CS], 131.7 [d, $^3J_{C\text{-}F}$ = 8.8 Hz, ortho aromatic CH], 163.0 [d, $^1J_{C\text{-}F}$ = 250.3 Hz, CF], 286.8 [C=S]. ^{19}F NMR: -84.75 to -84.23 [m, *E* isomer], -81.88 to -81.52 [m, *Z* isomer]. IR (neat): 3064, 2926, 1588, 1490, 1230, 1158, 1118, 1012, 832. MS: 234 (M^+, 36), 171 ($FPhS_2C^+$, 26), 139 (F-$PhSC^+$, 41), 123 ($MeCS_3^+$, 8), 95 (F-Ph^+, 44), 91 (MeS_2C^+, 43), 76 (CS_2^+, 30), 75 (63), 57 (59), 50 (51) 47 (62), 45 (100). Anal. calcd.: C, 41.01; H, 3.01; S. 41,05. Found: C, 41.12; H, 2.99; S, 40.74.

1-Methylthio-1-[2-methyl-5-(dimethylethyl)phenylthio]-1-sulfinylmethane (2k). Reaction carried out on 9.3 mmol (2 g) of methyl 2-methyl-5-tertiobutylphenyl trithiocarbonate **4k**. Yield: 88% after chromatography (dichloromethane / petroleum ether 50:50). Yellow oil. A 85:15 mixture of *Z* and *E* isomers was obtained 1 h after reaction; 35:65 at equilibrium (8 days). ^{1}H NMR of the *Z* isomer: 1.32 [s, 9H, $C(CH_3)_3$], 2.26 [s, 3H, SCH_3], 2.40 [s, 3H, CH_3Ph], 7.13-7.55 [m, 3H, aromatic **CH**]. ^{1}H NMR of the *E* isomer: 1.29 [s, 9H, $C(CH_3)_3$], 2.43 [s, 3H, CH_3Ph], 2.54 [s, 3H, SCH_3], 7.13-7.55 [m, 3H, aromatic **CH**]. ^{13}C NMR of the *Z* isomer: 18.3 [SCH_3], 20.3 [CH_3Ph], 31.2 [$C(CH_3)_3$], 34.5 [$C(CH_3)_3$], 128.3, 130.8 and 134.0 [aromatic CH], 125.2, 140.3 and 150.3 [aromatic C], 196.3 [C=SO]. ^{13}C NMR of the *E* isomer: 15.8 [SCH_3], 18.6 [CH_3Ph], 31.3 [$C(CH_3)_3$], 34.9 [$C(CH_3)_3$], 125.8, 136.4 and 130.9 [aromatic CH], 130.7, 135.0 and 150.9 [aromatic C], 188.5 [C=SO]. IR (neat): 2962, 2868, 1486, 1464, 1428, 1362, 1118, 1082, 1016, 968, 934, 824. MS: 286 (M^+, 4), 270 (M^+ - O, 10), 223 (M^+ - OMeS, 6), 179 (M^+ - CS_2OMe, 4), 123 (78), 117 (40), 115 (44), 91 ($MePh^+$, 100), 77 (Ph^+, 13), 57 (20), 41 (30). Anal. calcd.: C, 54.51; H, 6.33; S, 33.57. Found: C, 54.42; H, 6.34; S, 33.09.

1-(2-Propenylthio)-1-(4-fluorophenylthio)-1-sulfinylmethane (2l). Reaction carried out on 0.39 mmol (95 mg) of 2-propenyl 4-fluorophenyl trithiocarbonate **4l**. Yield: 78% after chromatography (dichloromethane). Yellow oil. A 30:70 mixture of *Z* and *E* isomers was obtained at equilibrium (15 days). ^{1}H NMR: 3.06 [d, J = 7,3 Hz, 2H, CH_2S, *Z* isomer], 3.93 [d, J = 7,0 Hz, 2H, CH_2S, *E* isomer], 5.06-5.27 [m, 2H, =CH_2], 5.47-5.66 [m, 2H, CH=], 7.05-7.20 [m, 2H, aromatic **CH**], 7.38-7.46 [m, 2H, aromatic **CH**, *E* isomer], 7.50-7.56 [m, 2H, aromatic **CH**, *Z* isomer]. ^{13}C NMR of the *Z* isomer: 38.9 [SCH_2], 116.8 [d, $^2J_{C\text{-}F}$ = 22.4 Hz, meta aromatic CH], 120.8 [CH_2=], 122.7 [aromatic CS], 130.8 [CH=], 132.9 [d, $^3J_{C-F}$ = 8 Hz, ortho aromatic CH], 164.1 [d, $^1J_{C-F}$ = 252 Hz, CF], 186.3 [C=SO]. ^{13}C NMR of the *E* isomer: 35.5 [SCH_2], 116.9 [d, $^2J_{C-F}$ = 22.4 Hz, meta aromatic CH], 120.4 [CH_2=], 127.6 [aromatic CS], 130.2 [CH=], 137.3 [d, $^3J_{C-F}$ = 8 Hz, ortho aromatic CH], 163.2 [d, $^1J_{C-F}$ = 252 Hz, CF], 183.6 [C=SO]. ^{19}F NMR: -111.60 [m, *E* isomer], -109.66 [m, *Z* isomer]. IR (neat): 3090, 3066, 2924, 1588, 1490, 1398, 1332, 1120, 1012, 832.

Thiophilic Addition of Organolithiums to Sulfines

Synthesis of Trithioorthoester Oxides (11)

General Procedure. A solution of alkyl- or aryllithium (1 eq., 1.15 mmol) was added to a solution of sulfine **2** (1.15 mmol) in anhydrous THF (15 mL) at -78°C, which resulted in a rapid discharge of the yellow colour of the sulfine. After stirring for 10 min at -78°C the reaction was quenched by addition of water (1 mL). The organic layer was extracted with dichloromethane (20 mL), washed with water (2 x 10 mL), dried over magnesium sulfate. After concentration under vacuum (at room temperature) the crude material was immediately analysed by NMR. Due to their instability, the trithioorthoester oxides **11** could not be purified by chromatography but were obtained in quantitative yields in acceptable purity (>95%).

Bis(methylthio)(methylsulfinyl)methane (11aa). Reaction carried out on 1.28 mmol (197 mg) of sulfine **4a** and a solution of methyllithium (1.6 M in diethyl ether). Pale pink crystals: mp 66-67 °C [Litt.[57]: 69-70 °C]. ^{1}H NMR: 2.37 [s, 6H, CH_3S], 2.74 [s, 3H, CH_3SO], 4.55 [s, 1H, CH]. ^{13}C NMR: 15.9 and 16.3 [CH_3S], 35.9 [CH_3SO], 73.0 [CHS_3]. IR (KBr): 1422, 1320, 1034, 954.

Bis(ethylthio)(methylsulfinyl)methane (11ba). Reaction carried out on 1.85 mmol (336 mg) of sulfine **4b**. Colourless oil. ^{1}H NMR: 1.33 and 1.34 [2t, *J* = 7.4 Hz, 6H, CH_3CH_2], 2.69 [s, 3H, CH_3SO], 2.87 and 2.89 [2q, *J* = 7.4 Hz, 4H, CH_3CH_2], 4.73 [s, 1H, CH]. ^{13}C NMR: 14.6 and 14.8 [CH_3CH_2], 27.6 and 27.8 [CH_2S], 47.2 [CH_3SO], 69.1 [CHS_3].

Bis(2-methylpropylthio)(methylsulfinyl)methane (11ca). Reaction carried out on 1.45 mmol (345 mg) of sulfine **4c**. Colourless oil. ^{1}H NMR: 1.02 [d, *J* = 6.6 Hz, 12H, $(CH_3)_2CH$], 1.88 [m, 2H, CH], 2.69 [s, 3H, CH_3SO], 2.76 [m, 4H, CH_2S], 4.66 [s, 1H, CH]. ^{13}C NMR: 21.9 [$(CH_3)_2CH$], 28.9 and 29.0 [$(CH_3)_2CH$], 34.4 [CH_3SO], 42.3 and 42.6 [CH_2S], 70.7 [CHS_3].

Bis(phenylmethylthio)(methylsulfinyl)methane (11da). Reaction carried out on 1.15 mmol (353 mg) of sulfine **4d**. Colourless oil. ^{1}H NMR: 2.51 [s, CH_3SO], 3.73 and 3.93 [AB system, *J* = 13.3 Hz, 2H, CH_2Ph], 3.81 and 4.04 [AB system, *J* = 13.2 Hz, 2H, CH_2Ph], 4.38 [s, 1H, S_3CH], 7.10-7.35 [m, 10H, aromatic H]. ^{13}C NMR: 34.6 [CH_3SO], 37.2 and 37.3 [CH_2Ph], 65.9 [CHS_3], 127.7, 127.8, 128.6, 128.9, 129.3 and 129.4 [aromatic CH], 136.4 and 136.8 [aromatic C]. IR (neat): 3060, 3028, 3002, 1494, 1454, 1418, 1058, 766, 700.

2-(Methylsulfinyl)-1,3-dithiane (11fa). Reaction carried out on 0.29 mmol (49 mg) of sulfine **4f**. Colourless oil. ^{1}H NMR: 1.92-2.15 [m, 2H, $CH_2CH_2CH_2$], 2.48-2.56 [m, 2H, CH_2S], 2.76 [s, 3H, CH_3SO], 3.10-3.28 [m, 3H, CH_2S and CH]. ^{13}C NMR: 24.2, 25.0 and 25.8 [CH_2], 32.2 [CH_3SO], 62.5 [CHS_3].

(1,1-Dimethylethylthio)(methylsulfinyl)(methylthio)methane (11ga). Reaction carried out on 0.45 mmol (88 mg) of sulfine **4g**. Colourless oil. ^{1}H NMR: 1.42 and 1.45 [2s, 9H, $(CH_3)_3C$], 2.36 and 2.47 [2s, 3H, CH_3S], 2.63 and 2.66 [2s, 3H, CH_3SO], 4.60 and 4.78 [2s, 1H, CH]. ^{13}C NMR: 15.9 and 17.4 [CH_3S], 31.0 and 31.03 [$(CH_3)_3C$], 32.5 and 34.2 [CH_3SO], 46.3 and 46.6 [$(CH_3)_3C$], 66.5 and 68.3 [CHS_3].

(Methylsulfinyl)(methylthio)(phenylthio)methane (11ha). Reaction carried out on 0.35 mmol (71 mg) of sulfine **4h**. Colourless oil. ^{1}H NMR: 2.39 and 2.45 [2s, 3H, CH_3S], 2.72 and 2.74 [2s, 3H, CH_3SO], 4.78 and 4.91 [2s, 1H, CH], 7.24-7.65 [m, 5H, H aromatic]. ^{13}C NMR: 16.2 and 16.6 [CH_3S], 34.4 and 35.5 [CH_3SO], 74.8 and 75.4 [CHS_3], 132.0 and 135.5 [aromatic C], 129.0 and 129.1 [para aromatic CH], 129.5 and 129.6 [meta aromatic CH], 133.3 and 133.7 [ortho aromatic CH].

Bis(methylthio)(butylsulfinyl)methane (11ab). Reaction carried out on 1.28 mmol (197 mg) of sulfine **4a** and a solution of butyllithium (1.4 M in hexane). Colourless oil. ^{1}H NMR: 0.98 [t, *J* = 4.3 Hz, 3H, CH_3CH_2], 1.51 [m, 2H, CH_3CH_2], 3.37 [m, 2H, CH_2CH_2SO], 2.35 and 2.36 [2s, 6H, CH_3S], 2.94 [m, 2H, CH_2SO], 4.55 [s, 1H, CH]. ^{13}C NMR: 13.6 [CH_3CH_2], 15.2 and 15.7 [CH_3S], 22.2 [CH_3CH_2], 25.0 [CH_2CH_2SO], 49.8 [CH_2SO], 71.6 [CHS_3].

Bis(methylthio)(phenylsulfinyl)methane (11ac). Reaction carried out on 0.35 mmol (71 mg) of sulfine **4a** and a solution of phenyllithium (1.6 M in diethyl ether hexane). Colourless oil. Diastereomer ratio 1:1.

^{1}H NMR: 2.09 and 2.30 [2s, 6H, CH_3S], 4.49 [s, 1H, CH], 7.29-7.85 [m, 5H, aromatic **H**]. ^{13}C NMR: 15.3 and 15.4 [CH_3S], 76.3 [CHS_3], 126.1, 128.8, and 132.0 [aromatic CH], 141.6 [aromatic CSO].

Transformations of Trithioorthoester Oxides (11)

Compounds **11** were left at ambient temperature. The transformations and the mixture compostions were determined by NMR. Some of the products were separated by chromatography. Two rearrangement pathways were identified: - an intramolecular pathway (route A), which led to thiolester **12** and disulfide **13**, and an intermolecular one (route B) which gave thiolester **12**, trithioorthoester **14** and methyl methanethiosulfinate **15**.

Transformation of trithioorthoester oxide (11aa). Complete after 6 days at room temperature. Ratio A/B 40:60. Compounds **14a** and **15a** were isolated by chromatography on silica gel (petroleum ether).

S-Methyl thioformate (12a). Yield: 70% (crude). ^{1}H NMR: 2.37 [s, 3H, CH_3S], 10.15 [s, 1H, CHO]. ^{13}C NMR: 22.3 [CH_3S], 187.9 [SCHO].

Dimethyl disulfide (13aa). Yield: 40% (crude). ^{1}H NMR: 2.43 [s, 6H, CH_3S].

Tris(methylthio)methane (14a). Yield: 30% (crude). ^{1}H NMR: 2.29 [s, 9H, CH_3S], 4.66 [s, 1H, CH]. ^{13}C NMR: 14.9 [CH_3S], 49.4 [CH].

S-Methyl methanethiosulfinate (15a). Yield: 60% (crude). ^{1}H NMR: 2.68 [s, 3H, CH_3S], 2.99 [s, 1H, CH_3SO]. IR (neat): 2928, 1430, 1330, 1304, 1134, 956.

Transformation of trithioorthoester oxide (11ba). Complete after 3 days at room temperature. Ratio A/B 60:40. Compounds **14b** and **15a** were isolated by chromatography on silica gel (petroleum ether).

S-Ethyl thioformate (12b). Yield: 80% (crude). ^{1}H NMR: 1.30 [t, J = 7.4 Hz, 3H, CH_3CH_2], 2.99 [q, J = 7.4 Hz, 2H, CH_2S], 10.15 [s, 1H, CHO]. ^{13}C NMR: 187.9 [CHO].

Ethyl methyl disulfide (13ba). Yield: 60% (crude). ^{1}H NMR: 1.34 [t, J = 7.3 Hz, 3H, CH_3CH_2], 2.41 [s, 6H, CH_3S], 2.73 [q, J = 7.3 Hz, 2H, CH_2S].

Tris(ethylthio)methane (14b). Yield: 20% (crude). ^{1}H NMR: 2.29 [s, 9H, CH_3S], 4.66 [s, 1H, CH]. ^{13}C NMR: 14.9 [CH_3S], 49.4 [CH]. ^{13}C NMR: 14.5 [CH_3], 26.0 [SCH_2], 53.9 [CH]. IR (neat): 2968, 2926, 2870, 1450, 1420, 1374, 1264. MS: 196 (M^+, 2), 135 (M^+ - EtS, 100), 106 ($SCHSEt^+$, 21), 78 (12), 61 (EtS^+, 11), 45 (48).

Transformation of trithioorthoester oxide (11ca). Complete after 8 days at room temperature. Ratio A/B 40:60.

S-(2-Methylpropyl) thioformate (12c). Yield: 70% (crude). ^{1}H NMR: 1.01 [d, J = 6.6 Hz, 3H, $(CH_3)_2CH$], 1.86 [m, 1H, $(CH_3)_2CH$], 2.91 [d, J = 6.7 Hz, 2H, CH_2S], 10.14 [s, 1H, CHO]. ^{13}C NMR: 21.6 [$(CH_3)_2CH$], 28.4 [$(CH_3)_2CH$], 42.7 [CH_2S], 187.8 [CHO]. IR (neat): 1674 ($\nu_{C=O}$).

Methyl 2-methylpropyl disulfide (13ca). ^{1}H NMR: 2.41 [s, 3H, CH_3S].

Tris(2-methylpropylthio)methane (14c). Yield: 30% (crude). ^{1}H NMR: 1.00 [d, J = 6.6 Hz, 18H, $(CH_3)_2CH$], 1.86 [m, 3H, $(CH_3)_2CH$], 2.61 [d, J = 6.9 Hz, 6H, CH_2S], 4.76 [s, 1H, CHS_3]. ^{13}C NMR: 22.2 [$(CH_3)_2CH$], 28.5 [$(CH_3)_2CH$], 40.9 [CH_2S], 56.1 [CHS_3].

Transformation of trithioorthoester oxide (11da). Complete after 8 days at room temperature. Ratio A/B 40:60. Compounds **14d** and **15a** were isolated by chromatography on silica gel (petroleum ether).

S-Phenylmethyl thioformate (12d). Yield: 70% (crude). ^{1}H NMR: 4.20 [s, 2H, CH_2S], 10.17 [s, 1H, SCHO]. ^{13}C NMR: 30.9 [CH_2S], 127.7, 128.9 and 129.5 [aromatic CH], 136.9 [CCH_2S], 186.9 [SCHO].

Methyl phenylmethyl disulfide (13da). ^{1}H NMR: 2.11 [s, 3H, CH_3S], 3.90 [s, 2H, CH_2], 7.26-7.36 [m, 5H, aromatic **H**]. ^{13}C NMR: 23.0 [CH_3S], 43.1 [CH_2S], 127.4, 128.5 and 129.2 [aromatic CH], 137.6 [CCH_2S].

Tris(phenylmethylthio)methane (14d). Yield: 30% (crude). Colourless crystals, mp 138-139 °C. ^{1}H NMR: 3.61 [s, 6H, CH_2S], 4.12 [s, 1H, CHS_3], 6.76-6.78 [m, 3H, para aromatic **H**], 7.10-7.25 [m, 12H, ortho and meta **H** aromatic]. ^{13}C NMR: 36.6 [CH_2S], 49.6 [CHS_3], 126.9, 128.8 and 129.0 [aromatic CH], 138.1 [CCH_2S].

Transformation of trithioorthoester Oxide (11ea). Complete after 15 days at room temperature. Compounds **19** was isolated by chromatography on silica gel (petroleum ether / ethyl acetate 95:5).

S-[(Methyldithio)propyl thioformate (12e). Yield: 56%. ^{1}H NMR: 1.98-2.10 [m, 2H, SCH_2CH_2], 2.41 [s, 3H, CH_3S], 2.75 [t, J = 7.2 Hz, 2H, CH_2SS], 3.10 [t, J = 7.1 Hz, 2H, CH_2SCO], 10.15 [s, 1H, CHO]. ^{13}C NMR: 23.3 [CH_3S], 25.3 [SCH_2CH_2], 28.9 [CH_2SS], 36.3 [CH_2SCO], 187.5 [CHO].

Transformation of trithioorthoester oxide (11ga). Complete after 8 days at room temperature. The two thiolesters **14a** and **14g** are formed in a 70:30 ratio.

S-(1,1-Dimethylethyl) thioformate (12g). [1]H NMR: 10.17 [s, 1H, CHO]. [13]C NMR: 30.1 [CH_3], 190.6 [CHO].

Transformation of trithioorthoester oxide (11ha). Complete after 8 days at room temperature. The two thiolesters **14a** and **14b** are formed.

S-Phenyl thioformate (12h). [1]H NMR: 10.23 [s, 1H, CHO]. [13]C NMR: 190.6 [CHO].

Thiophilic Addition to Sulfines and Michael Addition

Synthesis of Trithioorthoester Oxides (21)

General Procedure. A solution of 1.6 M methyllithium in diethyl ether (0.69-0.98 mmol, 1 eq) was added to a solution of sulfine **2** (0.69-0.98 mmol, 1 eq) in anhydrous THF (15 mL) at -78°C, which resulted in a rapid discharge of the yellow colour of the sulfine. After stirring for 10 min at -78°C the reaction was treated with an unsaturated ketone **20** (0.69-0.98 mmol, 1 eq). After stirring the temperature of the mixture was allowed to rise to to 20°C in 3-7 h. It was then quenched by addition of water (1 mL). The organic layer was extracted with dichloromethane (20 mL), washed with water (2 x 10 mL), dried over magnesium sulfate. After concentration under vacuum (at room temperature) the crude material was immediately analysed by NMR. Due to their instability, the trithioorthoester oxides **21** could not be purified by chromatography but were obtained in quantitative yields in acceptable purity (>95%).

5,5-Bis(methylthio)-5-(methylsulfinyl)pentan-2-one (21aa). Reaction carried out with sulfine **2a** (230 mg, 1.49 mmol) with 3-buten-2-one at -78°C for 10 min. Yield: 80% (crude). [1]H NMR: 2.23 [s, 6H, CH_3S], 2.31 [s, 3H, CH_3CO], 2.47 [m, 2H, CH_2CO], 2.80 [s, 3H, CH_3SO], 2.93 [m, 2H, CH_2CH_2CO]. [13]C NMR: 12.9 and 13.0 [CH_3S], 25.5 [CH_3CO], 30.3 [CH_2CO], 34.5 [CH_3SO], 38.3 [CH_2CH_2CO], 75.6 [CS_3], 206.8 [CO].

6,6-Bis(methylthio)-6-(methylsulfinyl)hexan-3-one (21ab). Reaction carried out with sulfine **2a** (98 mg, 0.64 mmol) with 1-penten-3-one at -78°C for 10 min. Yield: 70% (crude). [1]H NMR: 1.09 [t, J = 7.3 Hz, 3H, CH_3CH_2], 2.23 [s, 6H, CH_3S], 2.31 [s, 3H, CH_3CH_2CO], 2.50 [m, 4H, CH_2CO], 2.80 [s, 3H, CH_3SO], 2.90 [m, 2H, CH_2CH_2CO]. [13]C NMR: 7.9 [CH_3CH_2], 12.9 and 13.1 [CH_3S], 25.6 [CH_3CH_2CO], 34.6 [CH_2CO], 36.3 [CH_3SO], 36.9 [CH_2CH_2CO], 75.8 [CS_3], 209.6 [CO].

5,5-Bis(ethylthio)-5-(methylsulfinyl)pentan-2-one (21ba). Reaction carried out with sulfine **2b** (100 mg, 0.55 mmol) with 3-buten-2-one from -78°C to 20°C for 6 h. Yield: 50% (crude). [1]H NMR: 1.18-1.30 [m, 6H, CH_3CH_2], 2.25 [s, 3H, CH_3CO], 2.48 [m, 2H, CH_2CO], 2.80 [s, 3H, CH_3SO], 2.82-3.05 [m, 4H, CH_2CH_2]. [13]C NMR: 14.4 and 14.8 [CH_3CH_2], 24.2 [CH_3CO], 26.3 and 27.0 [CH_2S], 30.3 [CH_2CO], 34.6 [CH_3SO], 38.5 [CH_2CH_2CO], 76.7 [CS_3], 206.8 [CO].

5,5-Bis(phenylmethylthio)-5-(methylsulfinyl)pentan-2-one (21da). Reaction carried out with sulfine **2d** (79 mg, 0.26 mmol) with 3-buten-2-one from -78°C to 20°C for 6 h. [1]H NMR: 2.18 [s, 3H, CH_3CO], 2.83 [s, 3H, CH_3SO], 4.09 and 4.17 [AB system, J = 12 Hz, 4H, CH_2Ph], 7.1-7.4 [m, 10H, CH aromatic]. [13]C NMR: 26.5 [CH_3CO], 30.2 [CH_2CO], 34.9 [CH_3SO], 38.5 [CH_2S], 77.9 [CS_3], 127.8, 128.6 and 129.4 [CH aromatic], 136.2 [CCH_2S], 206.7 [CO].

Formation of Ketene Dithioacetals (22) from Trithioorthoester Oxides (21)

Compounds **21** were left at ambient temperature for a few days. A mixture of ketene dithioacetals **22** and methyl methanethiosulfonate was obtained, which was rather moisture sensitive. Only one product, **22aa**, could be isolated by flash chromatography without any further transformation. Other products were analysed as crude materials, chromatography producing thiolesters **23** (*vide infra*).

5-Bis(methylthio)-4-penten-2-one (22aa). Isolated by chromatography (petroleum ether / ethyl acetate 90:10) of trithioorthoester oxide **21aa**. Colourless oil. [1]H NMR: 2.18 [s, 3H, CH_3CO], 2.31 [s, 6H, CH_3S], 3.53 [d, J = 7,0 Hz, 2H, CH_2CO], 5.49 [t, J = 7,0 Hz, 1H, CH=] . [13]C NMR: 16.6 and 16.8 [CH_3S], 29.7 [CH_3CO], 44.9 [CH_2CO], 123.6 [CH=], 136.4 [C=], 206.3 [CO]. IR (neat): 2984, 2918, 1718 ($\nu_{C=O}$), 1420, 1358, 1314, 1084. **MS**: 176 (M^+, 10), 143 (12), 42 (100).

6,6-Bis(methylthio)-5-hexen-3-one (22ab). Trithioorthoester oxide **21aa** was left 15 h at ambient temperature. [1]H NMR: 1.07 [t, J = 7.3 Hz, 3H, CH_3CH_2], 2.31 [s, 6H, CH_3S], 2.48 [q, J = 7.3 Hz, 2H, CH_3CH_2], 3.51 [d, J = 7.0 Hz, 2H, CH_2CO], 5.96 [t, J = 7.0 Hz, 1H, CH=] . [13]C NMR: 7.8 [CH_3CH_2], 16.8 [CH_3S], 35.7 [CH_3CH_2], 43.8 [$CHCH_2CO$], 124.1 [CH=], 136.3 [C=], 208.4 [CO].

5,5-Bis(2-methylpropylthio)-4-penten-2-one (22ca). Trithioorthoester oxide **21aa** was not detected and compound **22ca** was directly obtained. Yield: 50% (crude). ^{1}H NMR: 0.94-1.1 [m, $(CH_3)_2CH$], 2.17 [s, 3H, CH_3CO], 3.53 [d, J = 7.0 Hz, 2H, CH_2CO], 6.13 [t, J = 7,0 Hz, 1H, CH=]. ^{13}C NMR: 22.0 [$(CH_3)_2CH$], 28.2 [$(CH_3)_2CH$], 29.8 [CH_3CO], 41.7 [CH_2CO], 128.0 [CH=], 135.5 [C=], 205.7 [CO].

Thiolesters (23) from Ketene Dithioacetals (22)

Compounds **22** were left at ambient temperature for a few days. They were hydrolyzed into thiolesters **23** during this period or on chromatography on silica gel.

S-Methyl 4-oxopentanethioate (23aa). Ketene dithioacetal **22aa** was left at r.t. for 7 days. Separation by chromatography (petroleum ether / ethyl acetate 90:10) gave **23aa**. Yield: 52%. Colourless oil. ^{1}H NMR: 2.19 [s, 3H, CH_3CO], 2.30 [s, 3H, CH_3SCO], 2.83 [m, 4H, CH_2CH_2CO]. ^{13}C NMR: 11.6 [CH_3S], 28.9 [CH_3CO], 37.3 and 38.2 [CH_2], 198.8 [SCO], 206.2 [CO]. IR (neat): 2930, 1716 ($\nu_{C=O}$), 1694 ($\nu_{SC=O}$), 1416, 1312, 1164, 1074, 1008, 946. MS: 112 (48), 99 (M^+ - MeS, 100), 84 ($OCCH_2CH_2CO^+$, 5), 75 ($MeSCO^+$, 15), 71 ($MeCO^+$, 30), 56 ($CH_2CH_2CO^+$, 4), 55 (27), 43 ($MeCO^+$, 27).

S-Methyl 4-oxohexanethioate (23ab). Ketene dithioacetal **22ab** was left at r.t. for 6 days. Separation by chromatography (petroleum ether / ethyl acetate 90:10) gave **23aa**. Yield: 41%. Colourless oil. ^{1}H NMR: 1.07 [t, J = 7.3 Hz, 3H, CH_3CH_2], 2.30 [s, 3H, CH_3SCO], 2.48 [q, J = 7.3 Hz, 2H, CH_3CH_2], 2.73-2.92 [m, 4H, CH_2CH_2CO]. ^{13}C NMR: 7.7 [$(CH_3CH_2$], 11.6 [CH_3S], 35.8 [CH_3CH_2CO], 36.8 and 37.4 [CH_2CH_2], 198.9 [SCO], 209.0 [CO]. MS: 132 (10), 131 (M^+ - Et, 4), 113 (M^+ - MeS, 27), 112 (100), 74 (56), 56 ($CH_2CH_2CO^+$, 41).

S-Methyl 2-methyl-4-oxopentanethioate (23ac). Trithioorthoester oxide **5ac** and ketene dithioacetal **22ac** were not detected and compound **23ac** was directly obtained. Separation by chromatography (petroleum ether / ethyl acetate 90:10) gave **23ac**. Yield: 37%. Colourless oil. ^{1}H NMR: 1.24 [d, J = 7.1 Hz, 3H, CH_3CH], 2.16 [s, 3H, CH_3CO], 2.29 [s, 3H, CH_3SCO], 2.49 and 2.99 [AB part of an ABX system, J_{AB} =17.8 Hz, J_{AX} = 7.5 Hz, J_{BX}= 5.9 Hz, 2H, CH_2CO], 3.18 [X part of an ABX system, 1H, CH_3CH]. ^{13}C NMR: 11.5 [CH_3S], 18.1 [CH_3CH], 30.2 [CH_3CO], 43.3 [$CHCH_2$], 46.8 [$CHCH_2$], 203.2 [SCO], 206.2 [CO]. IR (neat): 2972, 2932, 1718 (ν_{CO}), 1684 (ν_{SCO}), 1364, 1268, 1170, 1136, 998. MS: 113 (M^+ - MeS, 100), 112 (87), 99 (43), 85 (M^+ - MeSCO, 14), 75 (31), 57 ($CH_3COCH_2^+$, 1), 55 (31), 43 ($MeCO^+$, 89).

S-Ethyl 4-oxopentanethioate (23ba). Ketene dithioacetal **22ba** was left at r.t. for 7 days. Separation by chromatography (petroleum ether / ethyl acetate 90:10) gave **23ba**. Yield: 37%. Colourless oil. ^{1}H NMR: 1.24 [t, J = 7.4 Hz, 3H, CH_3CH_2], 2.19 [s, 3H, CH_3CO], 2.74-2.88 [m, 2H, CH_2CH_2], 2.88 [q, J = 7.4 Hz, 2H, CH_3CH_2]. ^{13}C NMR: 14.8 [CH_3CH_2S], 23.4 [CH_3CH_2S], 29.8 [CH_3CO], 37.5 and 38.1 [CH_2], 198.5 [SCO], 206.3 [CO]. IR (neat): 2970, 2932, 1720 (ν_{CO}), 1688 (ν_{SCO}), 1416, 1368, 1164, 1072, 992, 956. Anal. calcd.: C, 52.47; H, 7.55; S, 20.01. Found: C, 52.40; H, 7.54; S, 20.00.

S-(2-Methylpropyl) 4-oxopentanethioate (23ca). Ketene dithioacetal **22ca** was left at r.t. for 6 days. Separation by chromatography (petroleum ether / ethyl acetate 95:5) gave **23ca**. Yield: 56%. Colourless oil. ^{1}H NMR: 0.95 [d, J = 6.7 Hz, 6H, $(CH_3)_2CH$], 1.79 [nonuplet, J = 6.7 Hz, 1H, $(CH_3)_2CH$], 2.18 [s, 3H, CH_3CO], 2.79 [d, J = 6.7 Hz, 2H, CH_2S], 2.82 [m, 4H, CH_2CH_2]. ^{13}C NMR: 21.8 [$(CH_3)_2CH$], 28.8 [$(CH_3)_2CH$], 29.9 [CH_3CO], 37.3 [CH_2S], 37.8 and 38.2 [CH_2CH_2], 198.5 [SCO], 206.3 [CO]. IR (neat): 2960, 2924, 2870, 1720 (ν_{CO}), 1690 (ν_{SCO}), 1368, 1162, 1072, 996. MS: 117 (i-$PrSCO^+$, 3), 99 (M^+ - i-PrS, 100), 71 (M^+ - i-PrSCO, 23), 57 ($CH_3COCH_2^+$ or i-Pr^+, 11), 43 ($MeCO^+$, 28).

S-(2-Methylpropyl) 2-methyl-4-oxopentanethioate (23cc). . Trithioorthoester oxide **21cc** and ketene dithioacetal **22cc** were not detected and compound **23cc** was directly obtained. Separation by chromatography (petroleum ether / ethyl acetate 95:5) gave **23cc**. Yield: 42%. Pale yellow oil. ^{1}H NMR: 0.96 [d, J = 6.6 Hz, 6H, $(CH_3)_2CH$], 1.21 [d, J = 7.1 Hz, 3H, CH_3CH], 1.74-1.85 [m, 1H, $(CH_3)_2CH$], 2.15 [s, 3H, CH_3CO], 2.49 and 2.96 [AB part of ABX, J_{AB} =17.7 Hz, J_{AX} = 7.5 Hz, J_{BX} = 5.9 Hz, 2H, CH_2CO], 3.17 [X part of ABX, J_{AX} = 7.5 Hz, J_{BX} = 5.9 Hz, 1H, CH_3CH]. ^{13}C NMR: 11.5 [CH_3S], 18.1 [CH_3CH], 30.2 [CH_3CO], 43.3 [$CHCH_2$], 46.8 [$CHCH_2$], 203.2 [SCO], 206.2 [CO]. IR (neat): 2972, 2932, 1718 (ν_{CO}), 1684 (ν_{SCO}), 1364, 1268, 1170, 1136, 998.

S-(Phenylmethyl) 4-oxopentanethioate (23da). Ketene dithioacetal **22da** was left at r.t. for 30 days. Separation by chromatography (petroleum ether / ethyl acetate 95:5) gave **23da**. Yield: 54%. Colourless oil. ^{1}H NMR: 2.19 [s, 3H, CH_3CO], 2.78-2.89 [m, 4H, CH_2CH_2], 4.12 [s, 2H, CH_2Ph], 7.26-7.29 [m, 5H, aromatic H]. ^{13}C NMR: 29.9 [CH_3CO], 33.3 [CH_2S], 37.3 and 38.1 [CH_2CH_2], 127.4, 128.7, 128.9 [aromatic CH], 137.8 [aromatic CCH_2], 197.8 [SCO], 206.2 [CO].

Thiophilic Addition to a Sulfine and Methylation

1,1-Bis(ethylthio)-1-(methylsufinyl)ethane (24). A solution of 1.6 M methyllithium in diethyl ether (0.645 mL, 1.03 mmol) was added to a solution of sulfine **2** (188 mg, 1.03 mmol, 1 eq) in anhydrous THF (15 mL) at -78°C, which resulted in a rapid discharge of the yellow colour of the sulfine. After stirring for 10 min at -78°C an addition of HMPA (2 eq., 0.366 mL) and then iodomethane (1 equiv., 0.065 mL) was effected. The temperature of the mixture was allowed to rise to 20°C in 7 h. It was then quenched by addition of water (1 mL). The organic layer was extracted with dichloromethane (20 mL), washed with water (2 x 10 mL), dried over magnesium sulfate. After concentration under vacuum (at room temperature) the crude material was immediately analysed by NMR. Due to its instability, the ketene dithioacetal **25** could not be purified by chromatography but was obtained in a 94% yield in acceptable purity (>95%). Colourless oil. ^{1}H NMR: 1.27 and 1.28 [2t, J = 7.5 Hz, 6H, CH_3CH_2S], 1.90 [s, 3H, CH_3CS_3], 2.70 [s, 3H, CH_3SO], 2.80-2.95 [m, 4H, CH_3CH_2S]. ^{13}C NMR: 14.2 and 14.4 [CH_3CH_2], 21.1 [CH_3CS_3], 24.4 and 24.6 [CH_2S], 34.4 [CH_3SO], 73.8 [CS_3].

Bis(ethylthio)ethene (25). Compound **24** was left at ambient temperature for 15 h producing compound **25**, whose instability obliged analysis and use to be carried out on the crude material . Yield: quantitative. ^{1}H NMR: 1.28 [2t, J = 7.4 Hz, 6H, CH_3CH_2S], 2.79 [q, J = 7.4 Hz, 4H, CH_3CH_2S], 5.40 [s, 2H, CH_2=]. ^{13}C NMR: 14.0 [CH_3CH_2], 27.5 [CH_2S], 114.1 [CH_2=], 139.5 [S_2C=].

Addition to Silanes

Procedure. To a solution of anhydrous[58] TBAF, prepared from TBAF.3H_2O (0.27 mmol), in dry DMF (2.6 mL), containing activated molecular sieves 4Å (300 mg), was added, under inert atmosphere, a solution of sulfine **2e** (0.21 mmol) and the appropriate silane (0.27 mmol) in dry DMF (2.6 mL). The mixture was stirred at room temperature and progress of the reaction was monitored by TLC. After quenching with aqueous saturated ammonium chloride, the product was extracted with diethyl ether and dried over sodium sulfate. Evaporation of the solvent afforded the crude material, which was purified on silica gel (elution with hexanes / EtOAc).

2-[2-Propenyl]sulfinyl-1,3-dithiolane (26a). Reaction with allyl silane. ^{1}H NMR: 3.29-3.46 [m, 4H, S-$(CH_2)_2$-S], 3.51 [dd, J = 8.6 Hz and 12.3 Hz, 1H, S-CH_2-CH=], 3.68 [dd, J = 8.6Hz and 12.3 Hz, 1H, S-CH_2-CH=], 5.14 [s, 1H, CH(S_3)], 5.36-5.50 [m, 2H, CH_2=CH], 5.89-6.02 [m, 1H, =CH]. ^{13}C NMR: 38.0, 38.7, 54.8, 70.7, 123.4, 126.6.

2-Benzylsulfinyl-1,3-dithiolane (26b). Reaction with benzyl silane. ^{1}H NMR: 3.24-3.44 [m, 4H, ring protons], 4.05 [d, J = 13.1 Hz, 1H, CHPh], 4.16 [d, J = 13.1 Hz, 1H, CHPh], 4.81 [s, 1H, CHS_3], 7.28-7.41 [m, 5H, Ph]. ^{13}C NMR: 38.2, 38.8, 56.3, 69.6, 128.4, 129.0, 129.1, 130.4.

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