α-Oxosulfines, IV[‡]

Intramolecular Hetero Diels−Alder Reactions of α,α'-Dioxosulfines − A New Access to the [3.3.1]-Bicyclic Skeleton

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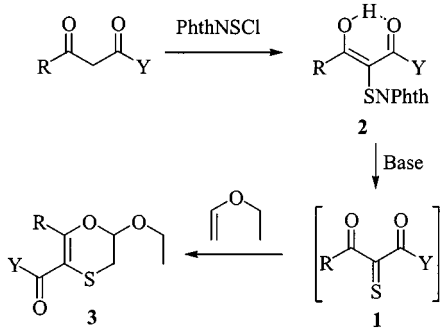
Simple transformations of *tert*-butylthio-substituted 1,4-oxathiin permitted the preparation of oxathiin *S*-oxides. These in turn were suitable precursors of corresponding α,α′-dioxosulfine dienes with tethered internal electron-rich double bonds. Examining the synthetic utility of these sulfines, we observed either hydrolysis or intramolecular cycloaddition, depending on the distance between the reactive centres and the substitution on the double bond. Bicyclic derivatives with a [3.3.1] skeleton and an sp^2 bridgehead carbon were obtained from the cycloadditions.

Introduction

The intramolecular Diels−Alder reaction represents a valuable tool for stereoselective access to polycyclic systems.[1] Although cycloaddition reactions are one of the main features of thiocarbonyl compounds, rather few examples of intramolecular reactions involving thiones as dienes[2] or dienophiles[3] are actually reported in the literature. We have demonstrated the flexibility of α,α′-dioxothiones **1** in sulfur organic chemistry, covering their ability to behave as electron-poor dienophiles,[4] enophiles[5] and bis-heterodienes.[6] α,α′-Dioxothiones **1** can be generated simply from β-dicarbonyls: by phthalimidesulfenylation followed by base-catalysed elimination,[4] as reported in Scheme 1.

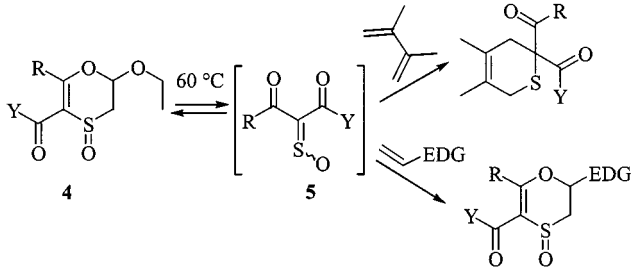


R = Alkyl, Aryl; Y = Alkyl, Aryl, OR, SR; PhthN = Phthaloyl

Scheme 1. Generation and trapping as hetero dienes of α,α′-dioxothiones

In particular, when thiones **1** are generated, using a tertiary amine base, from the corresponding dioxothiophthalimides **2** in the presence of an electron-rich alkene like ethyl vinyl ether, they undergo an inverse electron demand cycloaddition to give the 1,4-oxathiin cycloadducts **3**[6] with complete regio- and chemoselectivity (Scheme 1).

Interestingly, we found that oxidation of derivatives **3** to the corresponding *S*-oxides **4** greatly facilitates a retro Diels−Alder process, which occurs under mild conditions ($CHCl_3$, 60 °C) and leads to the formation of α,α′-dioxosulfines **5**. These, in turn, are dienophiles and heterodienes[7] even more efficient than the corresponding oxothiones (Scheme 2).



Scheme 2. Generation, from oxathiin *S*-oxides, and trapping of α,α′-dioxosulfines

We became interested in performing an intramolecular cycloaddition with **1** or **5** acting as a heterodiene, and so needed to generate such a species bearing an internal dienophile. Examination of the rational disconnections for this target suggested that direct use of a β-dicarbonyl compound containing an electron-rich alkene would be impracticable, since sulfenylation would occur at both of the nucleophilic centres: − i.e., the enolizable carbon and the double bond[8] (Scheme 3, Equation 1). Hence we decided to adapt a cycloadduct of type **3**, by introduction of an electron-rich double bond and subsequent oxidation, to generate an α,α′-dioxos-

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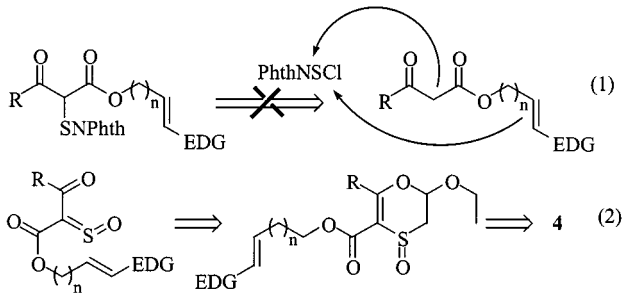
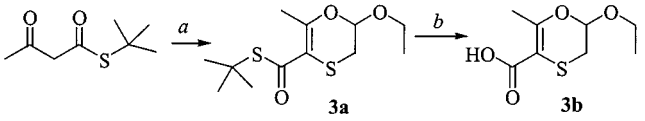
ulfine with a tethered dienophile thermally (Scheme 3, Equation 2).



Scheme 3. Possible disconnections for intramolecular cycloaddition reactions with oxothiones

Our efforts were concentrated on oxathiin **3a**, (R = Me, Y = S*t*Bu), which was easily prepared from *S*-*tert*-butyl acetothioacetate, following the general procedure depicted in Scheme 1. Hydrolysis of thiol ester **3a** with tetrabutylammonium hydroxide (TBAH) in THF/H_2O afforded acid **3b**[9] (R = Me, Y = OH), as reported in Scheme 4.



a) PhthNSCl, CH_2Cl_2, rt; then Py, ethyl vinyl ether, $CHCl_3$, rt, 86% overall

b) TBAH, THF/H_2O 1/1, rt, 72 h, 80%

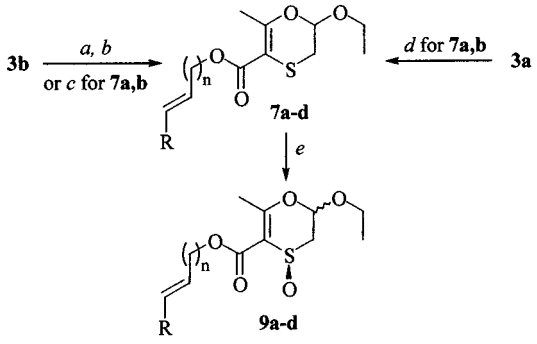
Scheme 4. Synthesis of oxathiin derivatives **3a** and **3b**

We were indeed able to introduce an internal dienophile onto the oxathiin skeleton, using either **3a** or **3b**. The conversion of acid **3b** into the corresponding chloride **3c** (R = Me, Y = Cl), followed by treatment with unsaturated alcohols **6a–d**, afforded the unsaturated esters **7a–d** (Scheme 5). Alternatively, direct treatment of acid **3b** with allyl and cinnamyl bromides (**8a** and **8b**) in the presence of DBU provided a different option for the preparation of esters **7a** and **7b** as reported in Scheme 5. On the other hand, the utility of the thiol ester **3a** for the preparation of these modified oxathiins was further demonstrated by the more convenient means of obtaining compounds **7a** and **7b** by direct transesterification of **3a** with the lithium salt of the corresponding alcohols **6a** and **6b** in refluxing THF[10] (Scheme 5).

Oxidation of esters **7a–d** to the corresponding sulfoxides **9a–d**, obtained as mixture of diastereoisomers (see Experimental Section), was then easily achieved using *m*-chloroperoxybenzoic acid (*m*-CPBA) in dichloromethane at −18 °C, as reported in Scheme 5.[7]

The synthesis of derivatives **9** thus offered the opportunity to verify whether or not the corresponding sulfines may be obtained thermally, and whether these species are able to undergo intramolecular cycloaddition.

Consequently, derivatives **9a–d** were heated at 60 °C in chloroform and the reactions monitored by ^{1}H NMR. The formation of the corresponding sulfines **10a–d** was demonstrated by the presence of ethyl vinyl ether in the reaction



a) $(CO)_2Cl_2$, DMF cat., C_6H_6, rt, 10min or $SOCl_2$, C_6H_6 reflux, 30min

b) HO(CH$_2$)$_n$CH=CHR^1 (**6a-d**), Py, C_6H_6, rt

6a : R^1 = H, n = 1; **6b** : R^1 = Ph, n = 1

6c: R^1 = 4-MeOPh, n = 1; **6d**: R^1 = 4-MeOPh, n = 2

c) Br(CH$_2$)$_n$CH=CHR^2 (**8a,b**), DBU, C_6H_6, rt

8a : R^2 = H, n = 1; **8b** : R^2 = Ph, n = 1

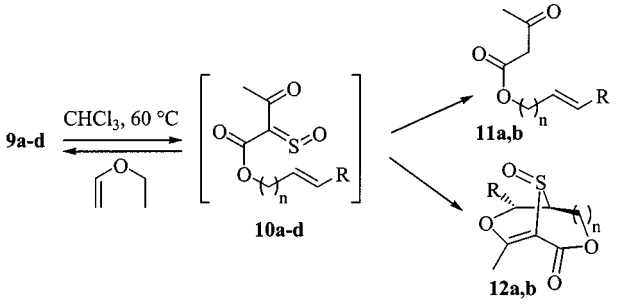
d) **6a,b**, BuLi, THF reflux

e) *m*-CPBA, CH_2Cl_2, -18 °C, 20 min

7a, 9a: R = H, n = 1	**7b, 9b**: R = Ph, n = 1
7c, 9c: R = 4-MeOPh, n = 1	**7d, 9d**: R = 4-MeOPh, n = 2

Scheme 5. Synthesis of oxathiin *S*-oxides **9a–d**

mixture and by the isolation of β-keto esters **11a** and **11b** or cycloadducts **12a** and **12b** as reported in Scheme 6.



entry	sulfine	R	n	Reac Time (h)	**11** yield (%)	**12** yield (%)
1	**10a**	H	1	300	**11a** (41)	/
2	**10b**	Ph	1	240	/	**12a** (43)
3	**10c**	4-MeOPh	1	72	/	**12b** (48)
4	**10d**	4-MeOPh	2	120	**11b** (53)	/

Scheme 6. Intramolecular Diels–Alder reactions with α,α′-dioxosulfines

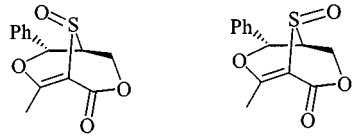
Derivatives **11a** and **11b** and **12a** and **12b** are products of the intermediate sulfines **10a–d**. Or, to be precise, hydrolysis[11] of sulfines **10a** and **10d** (entries 1, 4, Scheme 6), probably due to chance presence of water, gave rise to the corresponding keto esters **11a** and **11b** as the main side products. On the other hand, cycloadducts **12a** and **12b** clearly derive from an intramolecular hetero Diels–Alder

reaction undergone by oxosulfines **10b** and **10c** (entries 2, 3, Scheme 6). These results indicate that quite rigid stereoelectronic requirements need to be respected to allow the intramolecular cycloaddition. An electron-rich double bond is necessary for the reaction; on heating allylic ester **9a** we observed only decomposition of the corresponding sulfine **10a** (entry 1, Scheme 6). Moreover, an appreciable increase in the rate of cycloaddition was observed on going from sulfine **10b**[12] to **10c** (entries 2, 3, Scheme 6) as a result of the introduction of a *p*-methoxy group, causing a decrease in the energy gap between the molecular orbitals involved in the cycloaddition.

From the steric point of view, it is clear how the formation of the [3.3.1] skeleton, obtained when $n = 1$, is a favoured situation. It has to be borne in mind that in our case we obtained a [3.3.1] bicyclic compound with three adjacent sp^2 carbons, one of these a bridgehead one, which seems to suggest a high strain for this particular structure. On the other hand, sulfine **10d** ($n = 2$), which would mean a release of this strain, gave rise mainly to decomposition with hydrolysis, without any evidence of the corresponding cycloadduct (entry 4, Scheme 6).

Both compounds **12a** and **12b** were obtained as single regio- and stereoisomers. Our earlier results on the intermolecular reactions of α,α′-dioxothiones[6] and α,α′-dioxosulfines,[7] support the assumption for these reactions of an attack of the ketone oxygen on the benzylic carbon and the retention of the geometry of the double bond as the keys to interpret the regiochemistry and the stereochemistry, on the former double bond, of the cycloadducts **12a** and **12b**.

The position of sulfoxide oxygen is more difficult to understand and spectroscopic evidence is not helpful for this purpose. From our previous work, we know that the stereochemistry of the starting sulfoxide[13] does not affect the geometry of the intermediate sulfine. This, in turn, is not the cause of the stereochemistry of the final product.[7] Indeed, we may assume that the formation of the thermodynamic sulfoxide is the result of an equilibration process via cycloaddition/retro-cycloaddition reactions. Thus, as preliminary evidence for explaining the stereochemistry at the sulfoxide stereogenic centre, molecular mechanics calculations[14] carried out on *anti*-S=O/C=C bonds **12a** and *sin*-S=O/C=C **13** (Figure 1) showed that **12a** is about 8 kcal/mol more stable than **13**.



sin-S=O/C=C **12a** *anti*-S=O/C=C **13**

Figure 1. Diastereoisomers at sulfoxide stereogenic centres

To the best of our knowledge, this work represents the first example of intramolecular Diels−Alder reactions involving a dioxothionic species acting as a heterodiene. Taking advantage of the generation of α,α′-dioxosulfines from 1,4-oxathiin *S*-oxides, it has been possible to obtain several oxosulfine dienes possessing an electron-rich double bond as a potential dienophile. As a function of the quite narrowly defined stereoelectronic requirements, an intramolecular cycloaddition can occur, affording [3.3.1] bicyclic compounds with interesting and individual structural characteristic, as well as synthetic opportunities.[15] Moreover, it should be pointed out that several natural compounds possessing this bicyclic structure exhibit a range of biological activities, making them valuable synthetic targets.[16]

Further aspects of this chemistry, as well as of the opportunities offered by synthetic transformation of these bicyclic species, are under investigation in these groups.

Experimental Section

NMR: Varian Gemini-200 (200 and 50 MHz, for ^1H and ^{13}C, respectively). For ^1H and ^{13}C NMR, $CDCl_3$ as solvent $\delta_H = 7.26$; $\delta_C = 77.0$ respectively. − MS: Carlo Erba QMD100 (70 eV). − Melting points are uncorrected. − Solvents were dried following standard procedures, all commercial reagents were used without further purification as obtained from freshly opened containers.

Oxathiin **3a** was prepared as reported elsewhere from the corresponding *N*-thiophthalimide.[7]

***S-tert*-Butyl 6-Ethoxy-5,6-dihydro-2-methyl-1,4-oxathiin-3-carbothioate (3a):** Yellow oil. − ^1H NMR: δ = 5.24 (dd, X part of an ABX system, J = 2.8, 5.0 Hz, 1 H, OCHO), 4.00−3.85 and 3.74−3.54 (m, AB part of an ABX_3 system, 2 H, OCH_2), 2.92−2.74 (AB part of an ABX system, J_{AB} = 12.8 Hz, SCH_2), 2.24 (s, 3 H, CH_3C), 1.47 (s, 9 H, $(CH_3)_3C$), 1.24 (t, X_3 part of an ABX_3 system, J = 7.4 Hz, 3 H, CH_3CH_2). − MS; *m/z* (%): 276 (16) [M^+], 159 (60), 57 (100). − $C_{12}H_{20}O_3S_2$ (276.4): calcd. C 52.14, H 7.29; found C 52.29, H 7.37.

6-Ethoxy-5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxylic Acid (3b): A solution of thiol ester **3a** (680 mg, 2.45 mmol) in THF (30 mL), 3 M lithium hydroxide (5 mL) and TBAH (2.45 mmol) in water was kept stirring at room temperature for 72 h. Then 3% HCl was added until pH 2 was reached, and the mixture was extracted with CH_2Cl_2 (4×15 mL). Combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Silica gel flash chromatography (eluent CH_2Cl_2/CH_3OH 20:1) gave acid **3b** as a white solid (80%); m.p. 137−140 °C. − ^1H NMR: δ = 5.28 (dd, X part of an ABX system, J = 2.6, 5.2 Hz, 1 H, OCHO), 4.03−3.88 and 3.78−3.63 (m, AB part of an ABX_3 system, 2 H, OCH_2), 2.98−2.80 (AB part of an ABX system, J_{AB} = 13.2 Hz, SCH_2), 2.36 (s, 3 H, CH_3C), 1.28 (t, X_3 part of an ABX_3 system, J = 7.4 Hz, 3 H, CH_3CH_2). − ^{13}C NMR: δ = 170.4 (s), 161.5 (s), 97.2 (s), 96.4 (d), 65.0 (t), 28.7 (t), 21.9 (q), 15.1 (q). − MS; *m/z* (%): 204 (43) [M^+], 186 (40), 115 (70), 72 (100). − $C_8H_{12}O_4S$ (204.2): calcd. C 47.04, H 5.92; found C 47.22, H 5.77.

6-Ethoxy-5,6-dihydro-2-methyl-1,4-oxathiin-3-carbonyl Chloride (3c): A suspension of acid **3b** in dry C_6H_6 was treated with oxalyl chloride (4 equiv.) and DMF (5 μL) for 10 min at room temp. Evaporation of the solvent and of excess of reagents afforded acyl chloride **3c**, which was used directly for the synthesis of the esters. − ^1H NMR: δ = 5.34 (dd, X part of an ABX system, J = 2.4, 4.6 Hz, 1 H, OCHO), 4.01−3.92 and 3.77−3.68 (m, AB part of an ABX_3 system, 2 H, OCH_2), 2.98−2.85 (AB part of an ABX system, J_{AB} = 11.4 Hz, SCH_2), 2.33 (s, 3 H, CH_3C), 1.28 (t, X_3 part of an ABX_3 system, J = 7.0 Hz, 3 H, CH_3CH_2).

Chloride **3c** can also be prepared by treating **3b** with thionyl chloride (2 equiv.) in refluxing C_6H_6 for 30 min.

Synthesis of Sulfides 7a−d. − Method A: Pyridine (1.2 equiv.) and the required alcohol **6** (1 equiv.) were added at room temp to a solution of chloride **3c** in dry CH_2Cl_2. The reaction mixture was stirred at room temperature until the complete disappearance of starting materials, as monitored by TLC. The mixture was then diluted with CH_2Cl_2 (20 mL), washed with H_2O (2× 20 mL), dried with anhydrous Na_2SO_4, and concentrated. The crude esters were then purified by column chromatography (petroleum ether/ethyl acetate).

Method B: DBU (1.2 equiv.) and the required bromide **8** were added to a suspension of acid **3b** (1 equiv.) in dry C_6H_6, and the reaction mixture was stirred at room temperature until complete disappearance of starting materials, as monitored by TLC. The mixture was then diluted with CH_2Cl_2 (20 mL), washed with H_2O (2× 20 mL), dried with anhydrous Na_2SO_4, and concentrated. The crude product was purified by column chromatography.

Method C: *n*BuLi (1.6 M in hexane, 1 equiv.) was added at 0 °C to a solution of allyl or cinnamyl alcohol (**6a** or **6b**) in dry THF; after 10 min the reaction was allowed to come to room temp., and ester **3a** (1 equiv.) was added. The mixture was then refluxed until disappearance of starting materials, as monitored by TLC. The reaction mixture was then diluted with CH_2Cl_2 (20 mL), washed with saturated NH_4Cl, dried with anhydrous Na_2SO_4, concentrated and purified by column chromatography

Oxathiins **7** were used directly for the following steps without further purification. For compounds **7a** and **7b**, yields refer to the best result obtained when using the method reported in parenthesis.

Prop-2-enyl 6-Ethoxy-5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxylate (7a): (petroleum ether/ethyl acetate 50:1). Colourless oil, 70% (Method C). − ^{1}H NMR: δ = 5.86 (m, 1 H, vinyl), 5.36 (dq, *J* = 1.4, 17.2 Hz, 1 H, vinyl), 5.26 (dd, X part of an ABX system, *J* = 2.6, 4.8 Hz, 1 H, OCHO), 5.24 (dq, *J* = 1.4, 10.2 Hz, 1 H, vinyl), 4.65 (dt, *J* = 1.4, 5.4 Hz, 2 H, OCH_2 allyl), 4.02−3.87 and 3.78−3.62 (m, AB part of an ABX_3 system, 2 H, OCH_2CH_3), 2.96−2.78 (AB part of an ABX system, J_{AB} = 12.8 Hz, SCH_2), 2.35 (s, 3 H, CH_3C), 1.27 (t, X_3 part of an ABX_3 system, *J* = 7.2 Hz, 3 H, CH_3CH_2).

(2*E*)-3-Phenylprop-2-enyl 6-Ethoxy-5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxylate (7b): (petroleum ether/ethyl acetate 30:1). Yellow oil, 78% (Method B). − ^{1}H NMR: δ = 7.46−7.26 (m, 5 H, arom), 6.70 (d, *J* = 15.8 Hz, 1 H, vinyl), 6.32 (dt, *J* = 6.2, 15.8 Hz, 1 H, vinyl), 5.27 (dd, X part of an ABX system, *J* = 2.2, 4.8 Hz, 1 H, OCHO), 4.82 (d, *J* = 6.2 Hz, 2 H, OCH_2 allyl), 3.99−3.84 and 3.78−3.58 (m, AB part of an ABX_3 system, 2 H, OCH_2CH_3), 2.98−2.78 (AB part of an ABX system, J_{AB} = 14.0 Hz, SCH_2), 2.36 (s, 3 H, CH_3C), 1.27 (t, X_3 part of an ABX_3 system, *J* = 7.4 Hz, 3 H, CH_3CH_2).

(2*E*)-3-(4-Methoxyphenyl)prop-2-enyl 6-Ethoxy-5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxylate (7c): (petroleum ether/ethyl acetate 6:1). Yellow oil, 48% (Method A). − ^{1}H NMR: δ = 7.35−7.31 (m, 2 H, arom), 6.87−6.83 (m, 2 H, arom), 6.63 (d, *J* = 16.0 Hz, 1 H, vinyl), 6.18 (dt, *J* = 6.2, 16.0 Hz, 1 H, vinyl), 5.26 (dd, X part of an ABX system, *J* = 2.6, 4.8 Hz, 1 H, OCHO), 4.78 (d, *J* = 6.2 Hz, 2 H, OCH_2 allyl), 3.98−3.86 and 3.77−3.62 (m, AB part of an ABX_3 system, 2 H, OCH_2CH_3), 3.81 (s, 3 H, OCH_3), 2.95−2.78 (AB part of an ABX system, J_{AB} = 12.8 Hz, SCH_2), 2.36 (s, 3 H, CH_3C), 1.27 (t, X_3 part of an ABX_3 system, *J* = 7.2 Hz, 3 H, CH_3CH_2). − MS; *m*/*z* (%): 350 (0.5) [M^+], 147 (100), 115 (16).

(3*E*)-4-(4-Methoxyphenyl)but-3-enyl 6-ethoxy-5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxylate (7d): (petroleum ether/ethyl acetate 6:1). Yellow oil, 56% (Method A). − ^{1}H NMR: δ = 7.30−7.26 (m, 2 H, arom), 6.86−6.81 (m, 2 H, arom), 6.44 (d, *J* = 15.8 Hz, 1 H, vinyl), 6.06 (dt, *J* = 6.6, 15.8 Hz, 1 H, vinyl), 5.25 (dd, X part of an ABX system, *J* = 2.6, 4.8 Hz, 1 H, OCHO), 4.25 (t, *J* = 6.6 Hz, 2 H, OCH_2CH_2), 4.02−3.86 and 3.80−3.61 (m, AB part of an ABX_3 system, 2 H, OCH_2CH_3), 3.80 (s, 3 H, OCH_3), 2.95−2.78 (AB part of an ABX system, J_{AB} = 13.2 Hz, SCH_2), 2.56 (br. q, *J* = 6.6 Hz, 2 H, allyl), 2.33 (s, 3 H, CH_3C), 1.27 (t, X_3 part of an ABX_3 system, *J* = 7.2 Hz, 3 H, CH_3CH_2).

General Procedure for the Synthesis of Sulfoxides:[7] To a solution of derivatives **7** in CH_2Cl_2, kept at −18 °C, was added *m*-CPBA (1 equiv.) in CH_2Cl_2. The mixture was stirred until the complete disappearance of starting sulfide, as monitored by TLC (10−20 min). Then, saturated $Na_2S_2O_3$ (3 mL) and CH_2Cl_2 (20 mL) were added, and the organic layer was separated, washed with saturated Na_2CO_3 (2× 20 mL) and H_2O (2× 20 mL), dried with anhydrous Na_2SO_4, and concentrated. ^{1}H NMR analysis of the crude product gave the *cis*/*trans* ratio by integration of the signals due to acetal protons for the two diastereoisomers; flash chromatography allowed the isolation of pure samples of major (*trans*) isomers, as reported in the following data.

Prop-2-enyl 6-Ethoxy-5,6-dihydro-2-methyl-4-oxo-1,4-oxathiin-3-carboxylate (9a): Yellow oil, 70%, *cis*/*trans* 25:75. − ^{1}H NMR: δ = 6.06−5.87 (m, 1 H, vinyl), 5.53 (dd, *J* = 1.6, 10.6 Hz, 1 H, OCHO), 5.40 (br. d, *J* = 18.0 Hz, 1 H, vinyl), 5.28−5.22 (m, 1 H, vinyl), 4.84−4.66 (m, 2 H, OCH_2 allyl), 4.17−4.01 and 3.88−3.74 (m, AB part of an ABX_3 system, 2 H, OCH_2CH_3), 3.20 (dd, *J* = 1.6, 14.0 Hz, 1 H, CH_2S), 2.59 (dd, *J* = 10.6, 14.0 Hz, 1 H, CH_2S), 2.47 (s, 3 H, CH_3C), 1.30 (t, X_3 part of an ABX_3 system, *J* = 7.2 Hz, 3 H, CH_3CH_2). − ^{13}C NMR: δ = 171.4 (s), 164.0 (s), 131.7 (d), 118.5 (t), 109.0 (s), 95.0 (d), 66.8 (t), 65.8 (t), 46.7 (t), 22.0 (q), 15.0 (q). − $C_{11}H_{16}O_5S$ (260.3): calcd. C 50.75, H 6.20; found C 50.46, H 6.08.

(2*E*)-3-Phenylprop-2-enyl 6-Ethoxy-5,6-dihydro-2-methyl-4-oxo--1,4-oxathiin-3-carboxylate (9b): Yellow oil, 77%, *cis*/*trans* 20:80. − ^{1}H NMR: δ = 7.42−7.24 (m, 5 H, arom), 6.72 (d, *J* = 15.6 Hz, 1 H, vinyl), 6.33 (dt, *J* = 6.6, 15.6 Hz, 1 H, vinyl), 5.54 (dd, *J* = 1.4, 10.2 Hz, 1 H, OCHO), 5.03−4.81 (A part of an ABMX system, J_{AB} = 10.2 Hz, 2 H, OCH_2 allyl), 4.18−4.03 and 3.88−3.78 (m, AB part of an ABX_3 system, 2 H, OCH_2CH_3), 3.20 (dd, *J* = 1.4, 14.0 Hz, 1 H, CH_2S), 2.60 (dd, *J* = 10.2, 14.0 Hz, 1 H, CH_2S), 2.49 (s, 3 H, CH_3C), 1.31 (t, X_3 part of an ABX_3 system, *J* = 7.2 Hz, 3 H, CH_3CH_2). − ^{13}C NMR: δ = 171.3 (s), 164.1 (s), 136.2 (s), 134.5 (d), 128.0 (2d), 126.6 (d), 122.7 (d), 109.4 (s), 95.0 (d), 66.7 (t), 65.8 (t), 46.7 (t), 22.1 (q), 14.9 (q). − MS; *m*/*z* (%): 336 (0.5) [M^+], 216 (25), 133 (55), 117 (100).). − $C_{17}H_{20}O_5S$ (336.4): calcd. C 60.70, H 5.99; found C 60.85, H 6.21.

(2*E*)-3-(4-Methoxyphenyl)prop-2-enyl 6-Ethoxy-5,6-dihydro-2-methyl-4-oxo-1,4-oxathiin-3-carboxylate (9c): Yellow oil, 73%, *cis*/*trans* 25:75. − ^{1}H NMR: δ = 7.36−7.31 (m, 2 H, arom), 6.87−6.83 (m, 2 H, arom), 6.67 (d, *J* = 15.8 Hz, 1 H, vinyl), 6.21 (dt, *J* = 6.6, 15.8 Hz, 1 H, vinyl), 5.55 (dd, X part of an ABX system, *J* = 1.4, 10.6 Hz, 1 H, OCHO), 5.00−4.78 (A part of an ABMX system, J_{AB} = 12.0 Hz, 2 H, OCH_2 allyl), 4.14−4.06 and 3.83−3.72 (m, AB part of an ABX_3 system, 2 H, OCH_2CH_3), 3.80 (s, 3 H, OCH_3), 3.20 (dd, *J* = 1.4, 14.2 Hz, 1 H, CH_2S), 2.50 (dd, *J* = 10.6, 14.2 Hz, 1 H, CH_2S), 2.49 (s, 3 H, CH_3C), 1.31 (t, X_3 part of an ABX_3 system, *J* = 7.0 Hz, 3 H, CH_3CH_2). − ^{13}C NMR: δ = 171.3

(s), 164.2 (s), 159.6 (s), 134.4 (s), 128.9 (d), 128.0 (d), 120.4 (d), 114.0 (d), 109.1 (d), 95.0 (d), 66.8 (t), 66.2 (t), 55.3 (q), 46.7 (t), 22.1 (q), 15.0 (q). − $C_{18}H_{22}O_6S$ (366.4): calcd. C 59.00, H 6.05; found C 59.14, H 6.26.

(3*E*)-4-(4-Methoxyphenyl)but-3-enyl 6-Ethoxy-5,6-dihydro-2-methyl-4-oxo-1,4-oxathiin-3-carboxylate (9d): Yellow oil, 75%, *cis*/*trans* 15:85. ^{1}H NMR: δ = 7.31−7.26 (m, 2 H, arom), 6.85−6.81 (m, 2 H, arom), 6.45 (d, *J* = 15.8 Hz, 1 H, vinyl), 6.07 (dt, *J* = 7.0, 15.8 Hz, 1 H, vinyl), 5.53 (dd, X part of an ABX system, *J* = 1.4, 10.6 Hz, 1 H, OCHO), 4.42−4.29 (m, 2 H, OCH_2CH_2), 4.17−4.02 and 3.86−3.71 (m, AB part of an ABX_3 system, 2 H, OCH_2CH_3), 3.79 (s, 3 H, OCH_3), 3.19 (dd, *J* = 1.4, 13.8 Hz, 1 H, SCH_2), 2.66−2.51 (m, 3 H, CH_2 allyl + SCH_2), 2.46 (s, 3 H, CH_3C), 1.31 (t, X_3 part of an ABX_3 system, *J* = 7.0 Hz, 3 H, CH_3CH_2). − ^{13}C NMR: δ = 171.1 (s), 164.0 (s), 159.0 (s), 132.1 (s), 130.1 (d), 128.0 (d), 122.7 (d), 113.9 (d), 109.3 (d), 95.0 (d), 66.8 (t), 64.9 (t), 55.3 (q), 46.8 (t), 29.6 (t), 22.1 (q), 15.0 (q). − $C_{19}H_{24}O_6S$ (380.5): calcd. C 59.98, H 6.36; found C 59.70, H 6.68.

General Procedure for the Generation of Sulfines 10: A solution of sulfoxides **9** in $CHCl_3$ (about 0.1 M) was heated at 60 °C until the complete disappearance of starting sulfoxide, as monitored by TLC and ^{1}H NMR. After complete consumption of the starting material, evaporation of the solvent and flash chromatography gave the β-keto esters **11** or the cycloadducts **12** (see Scheme 6). Spectroscopic data are as follows:

Prop-2-enyl 3-oxobutanoate (11a): ^{1}H NMR: δ = 6.02−5.82 (m, 1 H, vinyl), 5.39−5.30 (m, 2 H, vinyl), 4.64 (dt, *J* = 1.4, 5.4 Hz, OCH_2 allyl), 3.48 (s, 2 H, $COCH_2CO$), 2.27 (s, 3 H, CO CH_3).

(3*E*)-4-(4-Methoxyphenyl)but-3-enyl 3-Oxobutanoate (11b): ^{1}H NMR: δ = 7.30−7.26 (m, 2 H, arom), 6.86−6.82 (m, 2 H, arom), 6.41 (d, *J* = 15.8 Hz, 1 H, vinyl), 6.00 (dt, *J* = 7.0, 15.8 Hz, 1 H, vinyl), 4.25 (t, *J* = 7.0, 2 H, OCH_2), 3.80 (s, 3 H, OCH_3), 3.45 (s, 2 H, $COCH_2CO$), 2.54 (q, 2 H, *J* = 7.0 Hz, CH2 ally), 2.25 (s, 3 H, CO CH_3).). − MS; *m*/*z* (%): 262 (3) [M^+], 160 (100), 129 (34).

8-Methyl-6-phenyl-9-thia-3,7-dioxabicyclo[3.3.1]non-1(8)-ene-2,9-dione (12a): White solid,[17] 43%. − ^{1}H NMR: δ = 7.45−7.37 (m, 5 H, arom), 5.02 (d, *J* = 8.4 Hz, 1 H, OCHPh), 4.35 (dd, *J* = 7.4, 9.8 Hz, 1 H, OCH_2), 4.31 (dd, *J* = 2.6, 9.8 Hz, 1 H, OCH_2), 3.92−3.83 (m, 1 H, SOCH), 2.54 (s, 3 H, CH_3). − ^{13}C NMR: δ = 179.3 (s), 172.3 (s), 135.4 (s), 129.9 (d), 129.1 (d), 127.0 (d), 97.6 (s), 76.4 (d), 68.1 (t), 52.2 (d), 26.9 (t). − MS; *m*/*z* (%): 264 (3) [M+], 216 (100), 115 (53). − $C_{13}H_{12}O_4S$ (264.3): calcd. C 59.08, H 4.58; found C 58.85, H 4.45.

6-(4-Methoxyphenyl)-8-methyl-9-thia-3,7-dioxabicyclo[3.3.1]non-1(8)-ene-2,9-dione (12b): White solid,[17] 48%. − ^{1}H NMR: δ = 7.45−7.37 (m, 2 H, arom), 6.95−6.92 (m, 2 H, arom), 4.97 (d, *J* = 8.8 Hz, 1 H, OCHPh), 4.47 (dd, *J* = 7.0, 10.0 Hz, 1 H, OCH_2), 4.27 (dd, *J* = 2.4, 10.0 Hz, 1 H, OCH_2), 3.82 (s, 3 H, OCH_3), 3.90−3.81 (m, 1 H, SOCH), 2.54 (s, 3 H, CH_3). − MS; *m*/*z* (%): 294 (2) [M+], 246 (100), 155 (25). − $C_{14}H_{14}O_5S$ (294.3): calcd. C 57.13, H 4.79; found C 57.01, H 4.63.

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