α,α′-Dioxothiones, III[+]

Regio- and Stereoselective Ene and Tandem "Ene-Cycloaddition" Reactions of 2,4-Dioxopentane-3-thione

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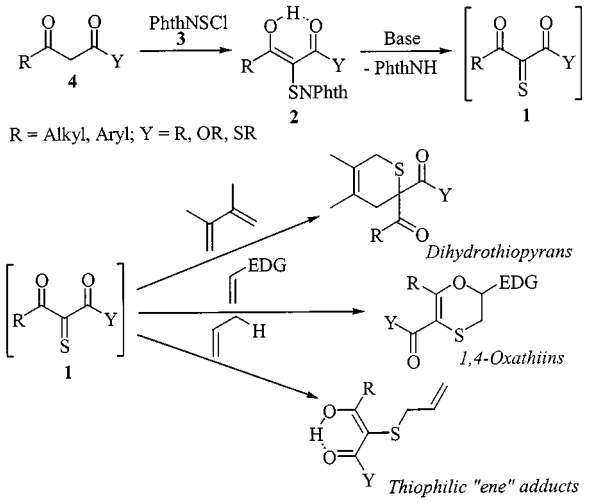
Keywords: α,α′-Dioxothiones / Ene reactions / Cyclo additions / Sulfur heterocycles / Stereoselectivity

2,4-Dioxopentane-3-thione **1a** reacts as an enophile with various allyl derivatives affording thiophilic ene adducts as single regioisomers with high (*E*) stereoselectivity. Using allyl ethers or allenes as ene counterparts, the formation of the thiophilic adduct is followed by a fast cycloaddition reaction in which **1a** behaves as a diene or a dienophile, respectively.

A few years ago we reported a new procedure for the generation of α,α′-dioxothiones **1** from α,α′-dioxothiophthalimides **2**, which, in turn, were prepared by reaction of β-dicarbonyl compounds **4** with the key reagent phthalimidesulfenyl chloride[1] (**3**, PhthNSCl, Phth = phthaloyl) (Scheme 1). The simplicity and mildness of this methodology allowed a detailed study of the reactivity of α-acylthiocarbonyl compounds, which proved to be efficient electron-poor dienophiles,[1] bis(heterodienes),[2] as well as enophiles[2] capable of reacting with appropriate unsaturated counterparts to give dihydrothiopyrans, 1,4-oxathiins, and thiophilic ene adducts, respectively (Scheme 1).

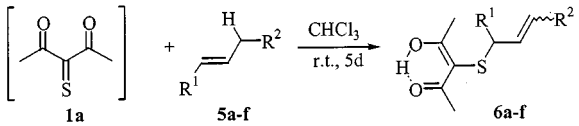


Scheme 1. Generation and reactivity of α,α′-dioxothiones

Several examples of "ene" reactions of thiocarbonyl compounds have been reported,[3] most of which furnish a mixture of thiophilic and carbophilic adducts. However, it has been demonstrated that the presence of electron-withdrawing groups on the thiocarbonyl compound favours formation of the thiophilic adduct.[4] In agreement with this trend, α,α′-dioxothiones have been found to show complete regioselectivity in favour of the creation of a new carbon−sulfur bond.[2]

In this paper, we report the reactions of thione **1a** with a number of allyl derivatives, including hetero-substituted species, with a view to evaluating the application, scope, and stereochemical features of the ene reactions of α,α′-dioxothiones.

In a first set of experiments, thione **1a**, generated from the corresponding thiophthalimide **2a** (R = Me; Y = Me) and 2 equiv. of pyridine, was treated with 2 equiv. of alkenes **5a−f**[5] in chloroform at room temperature. A rather slow[6] ene reaction took place leading to the thiophilic adducts **6a−f**, which were obtained as single regioisomers in all cases.



	R^1	R^2	Yield (%)	*E*/*Z* ratio
5a, 6a	H	*n*-Pr	56	12/1
5b, 6b	Et	Me	46	9/1
5c, 6c	H	*n*-Hex	62	11/1
5d, 6d	H	4-Meo-C_6H_4	49	> 50/1
5e, 6e	H	2-OH-C_6H_4	68	>50/1
5f, 6f	H	$SiMe_3$	61	4/1

Scheme 2. Regio- and stereoselective ene reactions of thione **1a**

As shown in Scheme 2, the formation of the new carbon−carbon double bond in **6** occurs with high (*E*) stereoselectivity.

Identification of the geometry of the major isomers was possible in several cases by ^{1}H-NMR spectroscopy. Thus, the single ene adducts **6d** and **6e**[7] showed a vinylic coupling constant ^3J = 15.8 Hz indicating an (*E*) geometry. Similarly, for the vinyl sulfide **6f**,[8] the major and the minor

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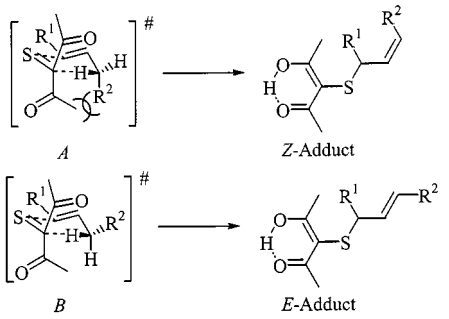
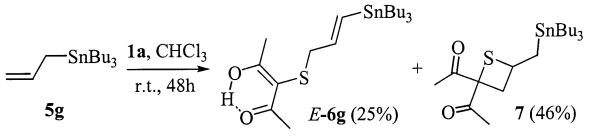
isomer showed vinylic coupling constants ^3J = 18.0 and 14.0 Hz, respectively.

For derivatives **6a−c**, spectroscopic data were not useful in assigning the relative geometries of the ene adducts. In fact, irrespective of the solvent used ($CDCl_3$ or C_6D_6), the small difference in the chemical shifts of the vinylic protons did not allow measurement of the ^3J coupling constants. We assume that these derivatives also show a preference for (*E*) geometry based on a comparison with the other results presented here as well as with previous findings.[4] Moreover, considering literature data dealing with the ene reaction,[9] a higher activation energy for transition state *A* leading to *Z* isomers compared to that for transition state *B* leading to *E* isomers can be expected, owing to steric hindrance between the R^2 group of the alkene and one of the two acetyl groups in **1a** (Scheme 3).



Scheme 3. A rational for the observed (*E*) stereoselectivity in the ene reactions of thione **1a**

An anomalous result was obtained upon treating **1** with allyltributylstannane (**5g**). In this case, the expected thiophilic ene adduct (*E*)-**6g** was found in the crude reaction mixture only as a minor component,[10] while the major product was the [2+2] cycloadduct **7**, isolated in 46% yield (Scheme 4). The structure of **7** was established on the basis of its spectroscopic data. For example, the identification of two different acetyl groups (δ = 2.32 and 2.17, and δ = 206.4, 202.1, 28.8 and 27.5 for the ^{1}H- and ^{13}C-NMR signals of the two CH_3CO groups, respectively) allowed us to rule out the formation of either a different ene adduct or a 1,4-oxathiin ring system, while being perfectly consistent with a [2+2] cycloadduct of type **7**. On the basis of similar considerations, we also tentatively attributed the regiochemistry of the single compound obtained (see Experimental Section).

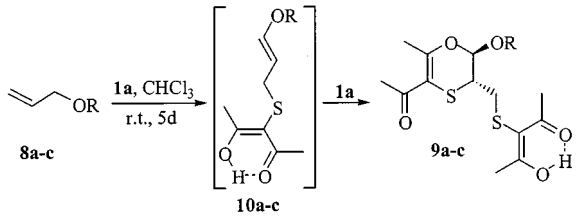


Scheme 4. The first example of a [2+2] cycloaddition reaction of α,α′-dioxothiones

Relatively few [2+2] cycloadditions have been reported for electron-poor thiones[11] and that depicted in Scheme 4 represents the only example of such a reaction for α,α′-dioxothiones.

The reaction of thione **1a** with other hetero-substituted allyl derivatives was subsequently investigated.[12]

The result obtained upon reaction of **1a** with allyl ethyl ether **8a** was rather interesting. After 5 d at room temperature, we isolated a single product which was assigned the oxathiin structure **9a** depicted in Scheme 5.



8a, **9a**, **10a**: R = Et, 85% (10 eq. of **8a**)
8b, **9b**, **10b**: R = *t*-$BuMe_2Si$, 39%
8c, **9c**, **10c**: R = Allyl, 36%

Scheme 5. Tandem "ene-(4π+2π) cycloaddition" of thione **1a**

A possible rationalization of this result involves the initial formation of the expected ene adduct (*E*)-**10a** followed by an inverse electron demand Diels−Alder reaction of heterodiene **1a** with the enol ether (*E*)-**10a** affording the final product **9a** with retention of the stereochemistry of the intermediate enol ether (Scheme 5). The cycloaddition reaction is evidently faster than the initial ene reaction since, on monitoring the reaction by ^{1}H-NMR spectroscopy, the ene adduct (*E*)-**10a** was never detected. Moreover, on carrying out the reaction using a tenfold excess of allyl ether **8a**, we observed an increase in the overall reaction rate, as well as in the yield of **9a** (85%),[5] still without evidence of the intermediate enol ether (*E*)-**10a**.

A similar tandem "ene-(4π + 2π) cycloaddition" occurred in the reaction of thione **1a** with allyl *tert*-butyldimethylsilyl ether (**8b**) and diallyl ether (**8c**), which allowed the isolation of the bis(adducts) **9b** and **9c** as single isomers (Scheme 5).

When thione **1a** was treated with the electron-rich styrene **6d**, a very slow cycloaddition reaction took place and derivative **11** was isolated in 22% yield after 8 d at room temperature (Figure 1). This slow cycloaddition rate reasonably accounts for the fact that no appreciable amounts of cycloadduct **11** were detected in the reaction of **1a** with allylanisole **5d**[13] (see Scheme 2).

The above results represent the first examples of tandem "ene-cycloaddition" reactions of an α,α′-dioxothione that acts sequentially as an enophile and as an electron-poor diene, providing further evidence of the versatility of acylthiones in the stereoselective construction of sulfur-containing heterocyclic systems.

We have verified the feasibility of running a similar tandem reaction using thione **1a** first as an enophile and then as an electron-poor dienophile. Consequently, the ene reaction should form a dienic system capable of reacting further with the carbon−sulfur double bond of **1a**. A similar versatility is offered by the reaction of α-acylthiones with allenes.[2][14]

The reaction of **1a** with tetramethylallene afforded the ene adduct **12** as a single product in 56% yield. The pres-

ence in **12** of an enolic β-dicarbonyl group, linked through sulfur to a 1,1,2,3-tetrasubstituted 1,3-diene, was readily established from the ^{1}H- and ^{13}C-NMR spectra, allowing the assignment of the structure shown in Figure 1.

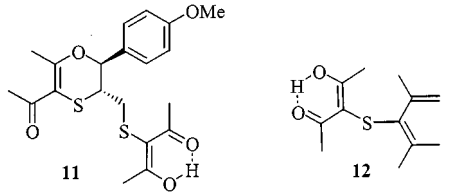
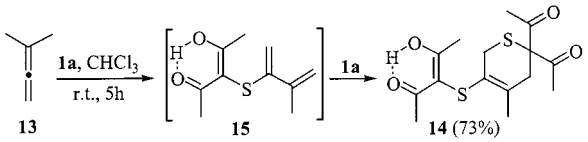


Figure 1. The products of the reaction of **1a** with styrene **6d** and with tetramethylallene

Although **12** contains a diene moiety, no trace of any dihydrothiopyran ring system, which might conceivably have been derived from the reaction of **1a** with **12**, was detected in the reaction mixture. We attribute this lack of reactivity to the high steric hindrance about the tetrasubstituted diene **12**. In fact, when dioxothione **1a** was treated with 1,1-dimethylallene (**13**), the cycloadduct **14** was isolated as the only reaction product in 73% yield. Therefore, in this case, the proposed intermediate ene adduct **15** reacted as a diene with the carbon−sulfur double bond of **1a** affording the thiopyran cycloadduct **14** (Scheme 6), which was obtained by a tandem "ene-(2π + 4π) cycloaddition" reaction of thione **1a**.



Scheme 6. Tandem "ene-(2π+4π) cycloaddition" of thione **1a**

Monitoring of the reaction by ^{1}H-NMR spectroscopy did not show the presence of any detectable amount of the intermediate ene adduct **15**, indicating that the cycloaddition is faster than the ene reaction. In fact, **14** was obtained as a 10:1 mixture of two regioisomers and spectroscopic data were not sufficient for the assignment of their relative regiochemistries. However, the major isomer gave crystals suitable for an X-ray structure analysis, from which it could be concluded that this derivative has the structure shown in Scheme 6 (Figure 2).

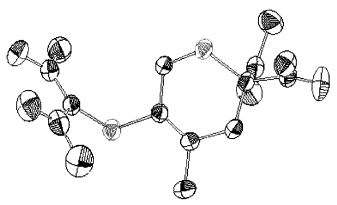


Figure 2. ORTEP view of compound **14**

In conclusion, we have shown that α,α′-dioxothione **1a** behaves as an efficient enophile towards a number of different allyl derivatives. In all cases, the ene reaction affords single thiophilic ene adducts, and the formation of the new carbon−carbon double bond occurs with high (*E*) stereoselectivity.

Using allyl ethers **8a−c** or allene **13** as ene counterparts, the initially formed ene adduct represents a suitable dienophile or diene for reaction with a second equivalent of thione **1a**, which leads to oxathiin or thiopyran ring systems, respectively. Both the reactions of these tandem "ene-cycloaddition" sequences occur with remarkable stereo- and regioselectivity. Further aspects of the reactivity of α,α′-dioxothiones are currently under investigation in this laboratory.

Experimental Section

NMR: Varian Gemini-200 (200 and 50 MHz, for ^{1}H and ^{13}C, respectively). For ^{1}H and ^{13}C NMR, $CDCl_3$ as solvent, $\delta_H = 7.26$ and $\delta_C = 77.0$ as reference standards. − MS: Carlo Erba QMD100 (70 eV). − IR: Perkin−Elmer 4800. X-ray: Philips PW 1100. − Melting points are uncorrected. − $CHCl_3$, CH_2Cl_2 and pyridine were dried according to standard procedures; all commercial reagents were used without further purification as obtained from freshly opened containers. Thiophthalimide **2a**[2] and phthalimidesulfenyl chloride **1**[1] were prepared as described elsewhere. − Derivatives **6**, **7**, **9**, **11**, **12** and **14** were obtained by adding two equiv. of pyridine to a solution of **2a** and two equiv. of the corresponding ene counterparts in ethanol-free chloroform. The mixtures were kept at room temperature until the complete consumption of the thiophthalimide **2a** and/or of the dimer of thione **1a**, as monitored by ^{1}H-NMR spectroscopy.[1] Evaporation of the solvent, followed by silica gel flash chromatography (hexanes/ethyl acetate as eluent) gave the ene adducts as pure compounds. (*E*/*Z*) ratios of derivatives **6a−f** were assessed by ^{1}H-NMR analysis of the crude reaction mixtures. Unless specified otherwise, the following data refer to the major (*E*) isomers. In the Experimental Section, the names of the compounds refer to their keto forms.

(2*E*)-3-(Hex-2-enylthio)pentane-2,4-dione (6a): Colourless oil (hexane/ethyl acetate, 30:1). − ^{1}H NMR: δ = 17.17 (s, 1 H, enol OH), 5.48−5.26 (m, 2 H, vinylic H), 3.05 (d, J = 6.2 Hz, 2 H, CH_2−S), 2.37 (s, 6 H, CH_3C=O), 2.00−1.90 (m, 2 H, allylic CH_2), 1.43−1.24 (m, 2 H, CH_2CH$_3$) 0.86 (t, J = 7.8 Hz, 3 H, CH_3CH$_2$). − ^{13}C NMR: δ = 198.4 (s, C=O), 135.0 (d), 125.2 (d), 103.9 (s), 39.5 (t), 34.9 (t), 25.1 (q), 22.7 (t), 14.1 (q). − MS; *m*/*z* (%): 214 (19) [M$^+$], 153 (2), 132 (23), 55 (100). − $C_{11}H_{18}O_2S$ (214.3): calcd. C 61.65, H 8.47; found C 61.48, H 8.63.

(2*E*)-3-(1-Ethylbut-2-enylthio)pentane-2,4-dione (6b): Colourless oil (hexane/ethyl acetate, 30:1). − ^{1}H NMR: δ = 17.23 (s, 1 H, enol OH), 5.22−5.18 (m, 2 H, vinylic H), 2.99−2.87 (m, 1 H, CHS), 2.34 (s, 6 H, CH_3C=O), 1.73−1.44 (m, 5 H), 0.97 (t, J = 7.4 Hz, 3 H, CH_3CH$_2$). − ^{13}C NMR: δ = 198.1 (s, C=O), 131.2 (d), 127.1 (d), 104.0 (s), 55.3 (d), 27.2 (t), 24.6 (q), 17.1 (q), 12.0 (q). − $C_{11}H_{18}O_2S$ (214.3): calcd. C 61.65, H 8.47; found C 61.54, H 8.33.

(2*E*)-3-(Non-2-enylthio)pentane-2,4-dione (6c): Colourless oil (hexane/ethyl acetate, 30:1). − ^{1}H NMR: δ = 17.17 (s, 1 H, enol OH), 5.38−5.35 (m, 2 H, vinylic H), 3.05 (d, J = 5.8 Hz, 2 H, SCH_2), 2.37 (s, 6 H, CH_3C=O), 2.02−1.90 (m, 2 H, allylic H), 1.25−0.93 (m, 8 H, aliphatic H), 0.86 (t, J = 6.6 Hz, 3 H, CH_3CH$_2$). − ^{13}C NMR: δ = 198.2 (s, C=O), 135.1 (d), 125.1 (d), 103.8 (s), 39.4 (t), 32.8 (t), 32.1 (t), 29.5 (t), 29.3 (t), 25.0 (q), 23.0 (t), 14.5 (q). − MS; *m*/*z* (%): 256 (6) [M$^+$], 156 (2), 132 (72), 117 (10), 69 (100). − $C_{14}H_{24}O_2S$ (256.1): calcd. C 65.58, H 9.43; found C 65.38, H 9.39.

(2*E*)-3-[3-(4-Methoxyphenyl)prop-2-enylthio]pentane-2,4-dione (6d): Colourless oil (hexane/ethyl acetate, 6:1). − ^{1}H NMR: δ =

17.24 (s, 1 H, enolic OH), 7.28−7.21 (AA′ part of an AA′XX′ system, 2 H, aromatic H), 6.88−6.80 (XX′ part of an AA′XX′ system, 2 H, aromatic H), 6.20 (d, J = 15.8 Hz, 1 H, vinylic H), 6.01 (dt, J = 15.8 and 7.4 Hz, 1 H, vinylic H), 3.80 (s, 3 H, OCH_3), 3.24 (d, J = 7.4 Hz, 2 H, SCH_2), 2.38 (s, 6 H, CH_3C=O). − ^{13}C NMR: δ = 198.0 (s, C=O), 159.2 (s), 132.2 (d), 129.3 (s), 127.3 (d), 122.2 (d), 114.0 (d), 103.3 (s), 55.2 (q), 39.62 (t), 24.54 (q). − MS; *m/z* (%): 278 (0.1) [M^+], 178 (3), 148 (12), 147 (100). − $C_{15}H_{18}O_3S$ (278.4): calcd. C 64.72, H 6.52; found. C 64.61, H 6.50.

(2*E*)-3-[3-(2-Hydroxyphenyl)prop-2-enylthio]pentane-2,4-dione (6e): Colourless oil (hexane/ethyl acetate, 4:1). − ^{1}H NMR: δ = 17.21 (s, 1 H, enolic OH), 7.32−7.27 (m, 1 H, aromatic H), 7.15−7.07 (m, 1 H, aromatic H), 6.93−6.73 (m, 2 H, aromatic H), 6.50 (d, J = 15.8 Hz, 1 H, vinylic H), 6.22 (dt, J = 15.8 and 7.6 Hz, 1 H, vinylic H), 5.21 (s, 1 H, phenolic OH), 3.34 (d, J = 7.6 Hz, 2 H, CH_2S), 2.42 (s, 6 H, CH_3C=O). − MS; *m/z* (%): 264 (55) [M^+], 222 (12), 179 (33), 134 (100). − $C_{14}H_{16}O_3S$ (264.3): calcd. C 63.61, H 6.10; found. C 63.46, H 6.24.

3-(4,4-Dimethyl-4-silapent-2-enylthio)pentane-2,4-dione (6f):

(*E*) Isomer: Colourless oil (hexane/ethyl acetate, 20:1). ^{1}H NMR: δ = 17.18 (s, 1 H, enolic OH), 5.95 (dt, 1 H, J = 18.0 and 6.8 Hz, vinylic H), 5.52 (d, J = 18.0 Hz, 1 H, vinylic H), 3.13 (d, J = 6.8 Hz, 2 H, CH_2S), 2.38 (s, 6 H, CH_3C=O), 0.03 (s, 9 H, CH_3Si). − MS; *m/z* (%): 244 (24) [M^+], 203 (42), 189 (20), 157 (11), 131 (14), 73 (75), 59 (100). − $C_{11}H_{20}O_2SSi$ (244.4): calcd. C 54.05, H 8.25; found C 53.70, H 8.36.

(*Z*) Isomer: ^{1}H NMR: δ = 17.08 (s, 1 H, enolic OH), 6.31 (dt, 1 H, J = 14.0 and 8.0 Hz, vinylic H), 5.59 (d, J = 14.0 Hz, 1 H, vinylic H), 3.03 (d, J = 8.0 Hz, 2 H, CH_2S), 2.43 (s, 6 H, CH_3C=O), 0.08 (s, 9 H, CH_3Si).

3-[2-Methyl-1-(methylethylidene)prop-2-enylthio]pentane-2,4-dione (12): Colourless oil (hexane/ethyl acetate, 20:1). − ^{1}H NMR: δ = 17.21 (s, 1 H, enolic OH), 4.95 (br. s, 1 H, vinylic H), 4.40 (br. s, 1 H, vinylic H), 2.32 (s, 6 H, CH_3CO), 1.99 (s, 3 H, CH_3C=), 1.82 (s, 3 H, CH_3C=), 1.77 (s, 3 H, CH_3CH=). − ^{13}C NMR: δ = 197.0 (s, C=O), 142.2 (s), 131.9 (s), 130.7 (s), 116.1 (t), 103.8 (s), 24.5 (q), 22.6 (q), 22.2 (q), 20.9 (q). − MS; *m/z* (%): 226 (9) [M^+], 141 (20), 84 (100). − $C_{12}H_{18}O_2S$ (226.3): calcd. C 63.68, H 8.02; found C 64.02, H 7.69.

1-[2-Acetyl-4-(2,2-dibutyl-2-stannahexyl)thietan-2-yl]ethan-1-one (7): Colourless oil (hexane/ethyl acetate, 20:1). − ^{1}H NMR: δ = 3.33−3.25 (m, 1 H, CHS), 3.15−2.98 (m, 2 H, CH_2C), 2.32 (s, 3 H, CH_3C=O), 2.17 (s, 3 H, CH_3C=O), 1.7−1.2 (m, 14 H, aliphatic H), 1.0−0.6 (m, 15 H, aliphatic H). − ^{13}C NMR: δ = 206.4 (s, C=O), 202.1 (s, C=O), 80.1 (s), 41.8 (d), 41.6 (t), 29.1 (t), 28.8 (q), 27.5 (q), 27.4 (t), 25.8 (t), 13.6 (t), 8.8 (q). − MS; *m/z* (%): 405 (100) [M^+ − Bu], 363 (35), 291 (10), 249 (31), 121 (47), 43 (44). − $C_{20}H_{38}O_2SSn$ (461.3): calcd. C 52.08, H 8.30; found C 52.43, H 8.17.

(2*R*,3*R*)-[3-(5-Acetyl-2-ethoxy-6-methyl-2*H*,3*H*-1,4-oxathiin-3-yl)-methylthio]pentane-2,4-dione (9a): Pale-yellow oil (hexane/ethyl acetate, 4:1). − ^{1}H NMR: δ = 17.10 (s, 1 H, enolic OH), 5.24 (d, J = 4.0 Hz, 1 H, OCHO), 4.00−3.60 (m, 2 H, OCH_2CH_3), 3.06−2.97 (m, 1 H, SCH), 2.80−2.56 (m, 2 H, SCH_2), 2.43 (s, 6 H, CH_3C=O), 2.30 (s, 3 H, CH_3CO), 2.27 (s, 3 H, CH_3C=), 1.89 (t, J = 6.0 Hz, 3 H, OCH_2CH_3). − ^{13}C NMR: δ = 197.4 (s, C=O), 195.5 (s, C=O), 156.2 (s), 104.8 (s), 103.7 (s), 96.5 (d), 65.0 (t), 40.3 (d), 38.3 (t), 29.6 (q), 24.5 (q), 21.7 (q), 15.0 (q). − MS; *m/z* (%): 346 (0.3) [M^+], 291 (1), 169 (10), 127 (100). − $C_{15}H_{22}O_5S_2$ (346.4): calcd. C 52.00, H 6.40; found. C 51.96, H 6.05.

(2*S*,3*R*)-3-{[5-Acetyl-6-methyl-2-(1,1,2,2-tetramethyl-1-silapropyl-oxy)-2*H*,3*H*-1,4-oxathiin-3-yl]methylthio}pentane-2,4-dione (9b): Yellow oil (hexane/ethyl acetate, 10:1). − ^{1}H NMR: δ = 17.12 (s, 1 H, enolic OH), 5.43 (d, J = 4.4 Hz, 1 H, OCHO), 2.99−2.52 (m, 3 H, $SCHCH_2S$), 2.45 (s, 6 H, CH_3C=O), 2.31 (s, 3 H, CH_3C=O), 2.25 (s, 3 H, CH_3C=C), 0.90 [s, 9 H, $(CH_3)_3C$], 0.16 (s, 3 H, CH_3Si), 0.14 (s, 3 H, CH_3Si). − ^{13}C NMR: δ = 197.4 (s, C=O), 195.5 (s, C=O), 156.6 (s), 104.9 (s), 103.8 (s), 92.9 (d), 42.7 (d), 37.8 (t), 29.7 (s), 25.5 (q), 24.5 (q), 21.8 (q), 17.8 (q), −4.2 (q), −5.1 (q). − MS; *m/z* (%): 432 (0.7) [M^+], 415 (1), 373 (2), 301 (12), 241 (5), 73 (100). − $C_{19}H_{32}O_5S_2Si$ (432.7): calcd. C 52.74, H 7.45; found. C 52.56, H 7.32.

(2*R*,3*R*)-3-[(5-Acetyl-6-methyl-2-prop-2-enyloxy-2*H*,3*H*-1,4-oxathiin-3-yl)methylthio]pentane-2,4-dione (9c): Yellow oil (hexane/ethyl acetate, 10:1). − ^{1}H NMR: δ = 17.09 (s, 1 H, enolic OH), 5.98−5.21 (m, 4 H, vinylic H + OCHO), 4.38−4.12 (m, 2 H, OCH_2), 3.07−2.98 (m, 1 H, SCH), 2.78−2.55 (m, 2 H, CH_2S), 2.41 (s, 6 H, CH_3C=O), 2.28 (s, 3 H, CH_3C=O), 2.26 (s, 3 H, CH_3C=). − ^{13}C NMR: δ = 197.3 (s, C=O), 195.4 (s, C=O), 155.9 (s), 133.0 (d), 118.7 (t), 104.9 (s), 103.7 (s), 95.1 (d), 69.6 (t), 40.2 (d), 38.4 (t), 29.5 (q), 24.5 (q), 21.7 (q). − $C_{16}H_{22}O_5S_2$ (358.5): calcd. C 53.61, H 6.19; found C 53.83, H 6.33.

(2*S*,3*R*)-3-{[5-Acetyl-2-(4-methoxyphenyl)-6-methyl-2*H*,3*H*-1,4-oxathiin-3-yl]methylthio}pentane-2,4-dione (11): Colourless oil (hexane/ethyl acetate, 4:1). − ^{1}H NMR: δ = 17.09 (s, 1 H, enolic OH), 7.27−7.18 (AA′ part of an AA′MM′ system, 2 H, aromatic H), 6.95−6.91 (MM′ part of an AA′MM′ system, 2 H, aromatic H), 4.97 (d, J = 6.8 Hz, 1 H, OCH), 3.83 (s, 3 H, OCH_3), 3.25−3.18 (m, 1 H, SCH), 2.68−2.38 (m, 2 H, CH_2S), 2.35 (s, 6 H, CH_3C=O), 2.34 (s, 3 H, CH_3C=O), 2.33 (s, 3 H, CH_3C=C). − $C_{20}H_{24}O_5S_2$ (408.5): calcd. C 58.80, H 5.92; found C 58.92, H 6.11.

3-(2,2-Diacetyl-4-methyl-3*H*,6*H*-thiin-5-ylthio)pentane-2,4-dione (14): White solid; m.p. 131−132°C (hexane/ethyl acetate, 4:1). − ^{1}H NMR: δ = 17.05 (s, 1 H, enolic OH), 2.88 (br. q, J = 1.8 Hz., 2 H, CH_2S), 2.62 (br. s, 2 H, allylic CH_2), 2.31 (s, 6 H, CH_3C=O), 2.25 (s, 6 H, CH_3C=O), 2.04 (br. s, 3 H, CH_3C=). − ^{13}C NMR: δ = 201.17 (s, C=O), 197.4 (s, C=O), 131.9 (s), 121.8 (s), 101.4 (s), 69.9 (s), 36.4 (t), 26.7 (t), 25.8 (q), 24.8 (q), 21.3 (q). − MS; *m/z* (%): 328 (9) [M^+], 285 (50), 197 (31), 155 (90), 111 (100). − $C_{15}H_{20}O_4S_2$ (328.4): calcd. C 54.85, H 6.14; found C 54.56, H 6.19.

Crystal Data and Structure Refinement for Compound 14: Empirical formula: $C_{15}H_{20}O_4S_2$; molecular mass: 328.43; temperature: 293(2) K; wavelength: 0.71070 Å; crystal system: monoclinic; space group: $P21/a$ (no. 14); unit cell dimensions: a = 7.4990(10) Å, b = 28.814(2) Å, c = 7.7820(10) Å, β = 106.20(10)°; volume: 1614.7(3) Å^3; Z = 4; density (calculated): 1.351 Mg/m^3; absorption coefficient: 0.342 mm^{-1}; F(000): 696; crystal dimensions: 0.4 × 0.4 × 0.8 mm; θ range for data collection: 2.73° to 28.01°; index ranges: $-9 \le h \le 9$, $0 \le k \le 38$, $0 \le l \le 10$; reflections collected: 4153; independent reflections: 3891 [R(int) = 0.0309]; refinement method: full-matrix least squares on F^2; data/restraints/parameter: 3891/0/270; goodness-of-fit on F^2: 1.033; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0371, $wR2$ = 0.1039; R indices (all data): $R1$ = 0.0532, $wR2$ = 0.1244; largest diff. peak and hole: 0.247 and −0.348 eÅ^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-106501. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[5] Using large excesses (10−20 equiv.) of the allyl derivative, we observed an appreciable increase in the reaction rate as well as in the yield of the ene adduct.
[6] α,α′-Dioxothiones are reactive intermediates which are subject to a base-catalysed reversible formation of dimeric species in solution. This phenomenon made it possible to carry out very slow reactions with these thiones, giving acceptable yields.[1]
[7] The reaction of **1a** with **5e** also led to the isolation (25%) of a by-product derived from electrophilic aromatic substitution of the sulfur atom of **1a** at the 5-position of phenol **5e**: G. Capozzi, S. Menichetti, C. Nativi, unpublished results.
[8] In the crude reaction mixture obtained by treating **1a** with **5f**, it was possible to detect about 10% of the 1,4-oxathiin derived from [4 + 2] cycloaddition of the dienic acylthione to the double bond of the allylsilane.
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[13] In this case, an "ene-cycloaddition" tandem process would probably have been possible by carrying out the reaction of **1a** with **5d** in a 2:1 ratio. Due to the very low rates of both these reactions, such an experiment was not performed.
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