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α-Oxosulfines Part 1: Reactivity of α-Oxosulfines Obtained From Retro Diels-Alder Reaction of 1,4-Oxathiin-*S*-Oxides.

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Abstract: Oxidation of 1,4-oxathiin derivatives **10-16** affords the corresponding sulfoxides **17-26** in high yield and good stereoselectivity. The oxathiin-*S*-oxides undergo a Retro Diels-Alder (RDA) reaction to form α-oxosulfines under very mild conditions. These reactive intermediates can be successfully trapped as dienophiles or as electron poor dienes in Inverse Electron Demand Diels-Alder reaction (IEDDA). The relationship between the structure of the starting sulfoxide, the geometry of the intermediate sulfine and the stereochemistry of the final cycloadduct have been tentatively correlated.

The chemistry of sulfines has attracted the interest of many authors because of the various synthetic possibilities offered by the carbon-sulfur and sulfur-oxygen non linear cumulated double bonds. Nucleophilic attack at sulfur, nucleophilic displacement at carbon, and the cycloaddition with 1,3-dipoles and dienes have been the main topics of the sulfine chemistry.[1-3] Despite their promising synthetic value α-oxo and α,α'-dioxo-functionalised sulfines have so far received relatively little attention. These reactive species have been synthesised by reaction of carbonyl compounds[4] or silyl enol ether with thionyl chloride,[5,6,7] or thermally generated from 1,4,3-oxathiazin-*S*-oxides[8] or anthracene derived thiopyran-*S*-oxides[9] and trapped by a Diels-Alder reaction with electron rich dienes.

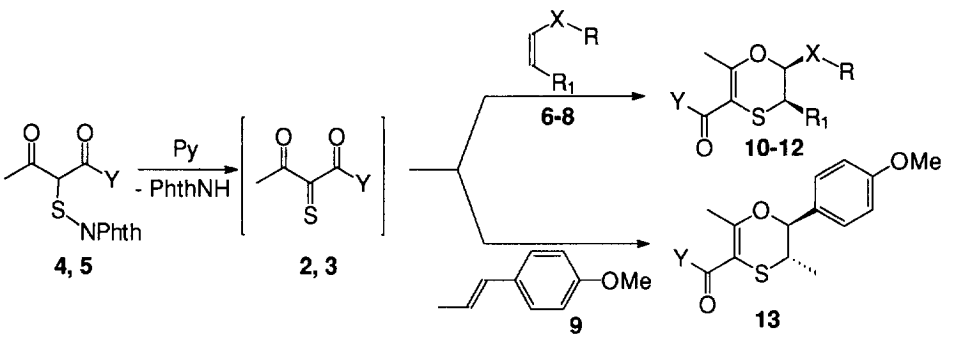
Zwanenburg and co-workers have reported the reaction of two stable α-oxosulfines with ethyl vinyl ether in an IEDDA[6] reaction but the other examples regarding the use of acyl sulfines as electron poor dienes gave controversial results.[7]

In a preliminary communication we have recently reported[10] a new method for the formation of α,α'-dioxosulfines "via" a RDA process from oxathiin-*S*-oxides which occurs in very mild conditions. The functionalised sulfines obtained can be easily trapped as dienophiles or as electron poor.

In this paper we report the study of the reactivity of various α-oxosulfines generated following this new procedure.

RESULTS AND DISCUSSION

We developed a simple and general method for the synthesis of 1,4-oxathiin[11] heterocyclic systems based on the IEDDA reaction of α,α'-dioxothiones with various electron rich alkenes. The reactive thione intermediates are formed by addition of a weak base to suitable thiophthalimide derivatives which in turn can be prepared by the reaction of the phthalimidesulfenyl chloride **1** (PhthN-SCl, Phth = phthaloyl) with β-dicarbonyls[11]. Thus thiones **2** and **3,** obtained by treatment of phthalimido derivatives **4** and **5** with pyridine in chloroform, react with vinyl ethers **6** and **7**, phenyl vinyl sulfide (**8**) and anethole (**9**) to give the corresponding oxathiinic cycloadducts **10-13** in good yields (SCHEME 1). The cycloaddition reaction is completely regio-selective, in that the oxygen of the bis-heterodiene links to the hetero or aryl substituted olefinic carbon, and chemo-selective since α,α'-dioxothiones derived from β-ketoesters participate in the cycloaddition only with the ketonic carbonyl. The reaction is also stereoselective, in fact when 1,2-disubstituted alkenes are used as dienophile (for example **7** or **9**) the geometry of the double bond is retained in the cycloadduct.

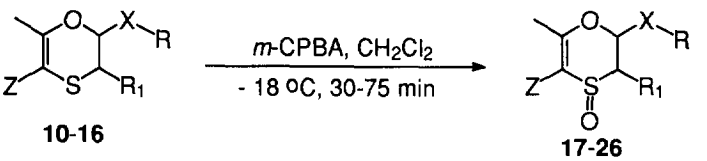


2, **4**, **13a**: Y=Me
3, **5**, **13b**: Y=OEt
6: X=O, R=Et, R_1=H
7: X=O, R,R_1= -$(CH_2)_3$-
8: X=S, R=Ph, R_1=H
10a: Y=Me, X=O, R=Et, R_1=H
10b: Y=OEt, X=O, R=Et, R_1=H
11a: Y=Me, X=O, R,R_1= -$(CH_2)_3$-
11b: Y=OEt, X=O, R,R_1= -$(CH_2)_3$-
12: Y=Me, X=S, R=Ph, R_1=H

SCHEME 1

The oxathiin derivatives **10-13** and compounds **14-16**, prepared from **10b** and **11b** by $LiAlH_4$ reduction of the ester group and protection of the formed hydroxy group as acetate or methoxymethyl ether, can be oxidised to the corresponding sulfoxides **17-26** using various oxidising agents.[12] In our hands the best results have been obtained using one equivalent of *meta*-chloroperoxybenzoic acid (*m*-CPBA) in dichloromethane (Scheme 2).

The results reported in Scheme 2 deserve some comments. The oxidation of derivatives **10-16** to the corresponding sulfoxides should give a mixture of diastereoisomers, we actually observed the formation of two diastereoisomers in the oxidation of cycloadducts **10a**, **10b**, **13b** and **14** (Entries 1, 2, 7 and 8).[13] On the contrary the oxidation of the other derivatives gave a single sulfoxide. It is noteworthy that oxidation of **12** (Entry 5) afforded the oxathiin-*S*-oxide **21** in 85% isolated yield as single stereo and regioisomer. No trace of oxidation at the exo-cyclic phenyl substituted sulfur was detected in the crude reaction mixture.



10-16 **17-26**

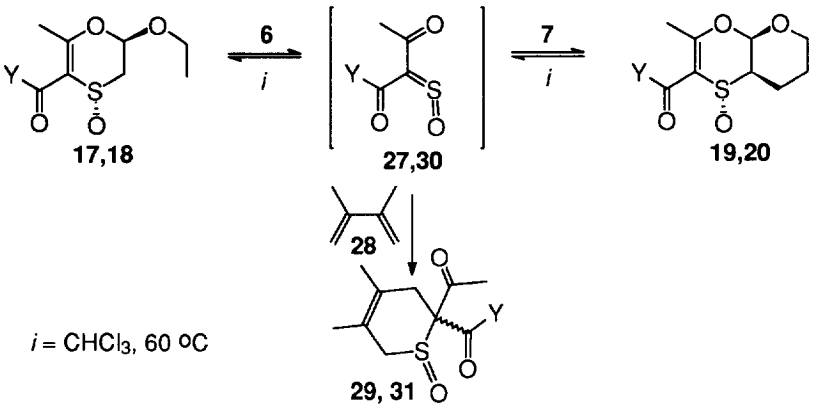
Entry	Product	X	R	R_1	Z	Sulfoxide	Yield (%)	E/Z
1	**10a**	O	Et	H	COMe	**17**	70	94/6
2	**10b**	O	Et	H	COOEt	**18**	84	85/15
3	**11a**	O	$-(CH_2)_3-$		COMe	**19**	71	>98/2
4	**11b**	O	$-(CH_2)_3-$		COOEt	**20**	74	>98/2
5	**12**	S	Ph	H	COMe	**21**	85	>98/2
6	**13a**	4-OMe-Ph		Me	COMe	**22**	62	>98/2
7	**13b**	4-OMe-Ph		Me	COOEt	**23**	75	67/33
8	**14**	O	Et	H	CH_2OMOM	**24**	67	81/19
9	**15**	O	$-(CH_2)_3-$		CH_2OMOM	**25**	76	>98/2
10	**16**	O	$-(CH_2)_3-$		CH_2OAc	**26**	98	>98/2

SCHEME 2

The high stereoselectivity observed in the oxidation suggests that one face of the oxathiin systems is hindered to the approach of the peroxydic oxygen. By means of ^1H nmr spectra and taking in consideration the values of J^2 coupling constants and the deshielding effect of the sulfoxyllic oxygen on adjacent protons[14] we attribute to the major isomers an (4-6)*E* geometry (i.e. an *anti* relationship between the sulfoxyllic oxygen and the substituent at C_6 with the former in pseudo-axial position. See experimental).[15] We also verified that the carbonyl group in position 3 in **10** or **11** has a minor effect in directing the oxidation reaction. In fact the oxidation of oxathiins **14-16** (Entries 8-10), gave results quite similar to those obtained for the oxidation of derivatives **10a,b** and **11b** where the ester group might have some effect in the control of the stereoselectivity.

Having in hands these polyfunctionalised sulfoxides we started the study of some aspects of their reactivity. With the aim of using the α,β-unsaturated carbonyl moiety of such oxathiin-*S*-oxides as an electron poor diene,[16] we heated **17** in chloroform at 60 °C in the presence of 2 equivalents of pyrane **7** as potential dienophile. After 45h at 60 °C we observed by ^1H nmr the complete disappearance of **17**, with formation of the sulfoxide **19** which was isolated in 54% yield. A rationalisation of this result involves the formation of the α,α'-dioxosulfine **27** (Y = Me) by thermal RDA reaction of sulfoxide **17**. The sulfine **27** then acts as electron poor diene in an IEDDA process with the dienophile **7** affording **19** as unique cycloadduct (SCHEME 3). On the other hand when **19** was heated at 60 °C for 22 h in chloroform in the presence of a four fold excess of **6** the sulfoxide *E*-**17** was isolated in 98% yield, clearly indicating that the sulfine **27** is the common intermediate in

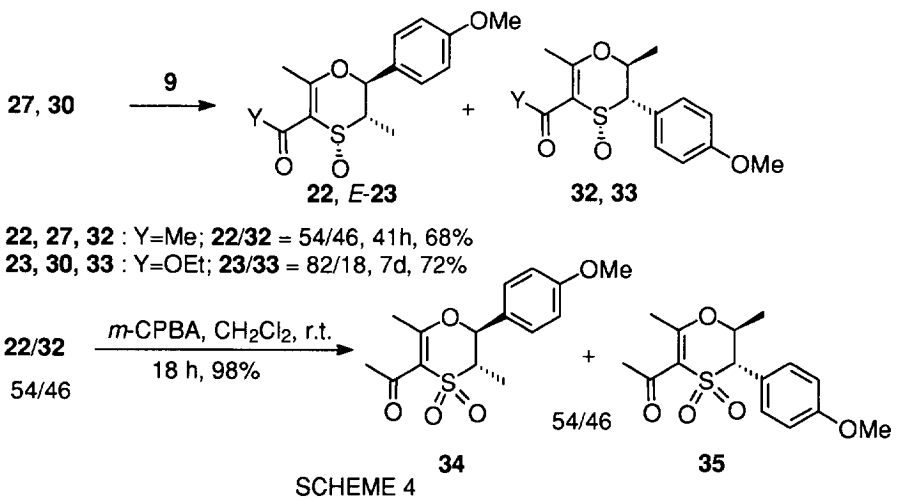
both processes (SCHEME 3). Moreover when sulfine **27** is generated in the presence of 2,3-dimethyl-1,3-butadiene **28** a direct Diels-Alder reaction occurs and the dihydrothiopyran cycloadduct **29** (Y = Me) was isolated in almost quantitative yield (SCHEME 3).



SCHEME 3

Similarly the α-keto-α'-carboethoxysulfine **30** (Y = OEt) has been generated from sulfoxide *E*-**18** at 60 °C and trapped with dihydropyrane **7** or diene **28** to give sulfoxides **20** and **31** respectively (SCHEME 3). However as general trend we observed an higher reaction time required to generate α-keto-α'-carboethoxysulfines than the corresponding dichetosulfines.

When **27** and **30** reacted with anethole **9**, mixtures of regioisomeric sulfoxides **22**, **32** and *E*-**23**, **33** were obtained (SCHEME 4).

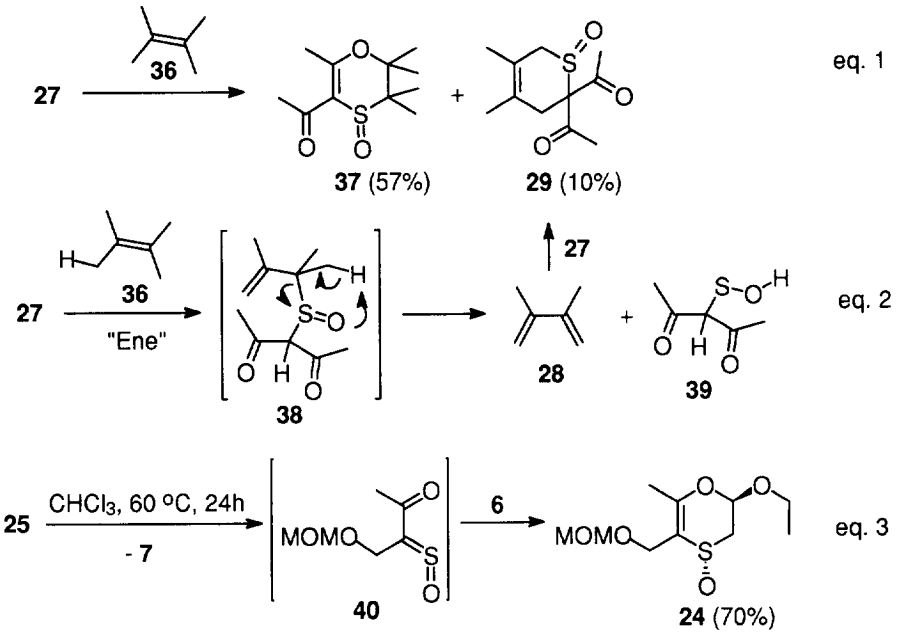


SCHEME 4

The regioisomeric relationship of the mixture of sulfoxides has been confirmed by ^{1}H nmr data (*Z*-**23** vs. **33**) and by oxidation of the mixture of **22** and **32**, as obtained from the cycloaddition reaction, which gave the

corresponding sulfones **34** and **35** in the same ratio of the starting sulfoxides, while a single sulfone would be expected if **22** and **32** were stereoisomers at sulfoxyllic sulfur (SCHEME 4).

The high dienic reactivity of α-acyl sulfines is shown by the following experiments. When **27** reacted with of 2,3-dimethyl-2-butene **36** we observed the formation of cycloadduct **37**, isolated in 57% yield (SCHEME 5 eq. 1).



SCHEME 5

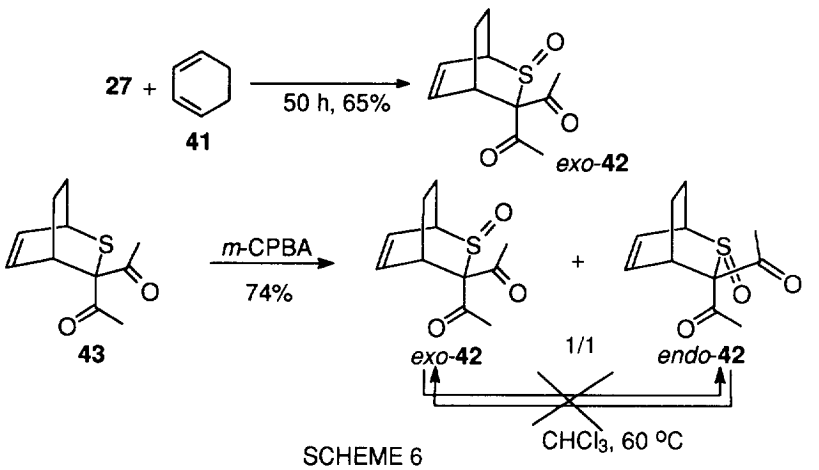
From this reaction we also isolated small amounts of the dihydrothiopyran-*S*-oxides **29** (about 10%). A reasonable explanation for this result foresees an "ene" reaction of **27** with **36** to give sulfoxide **38**. Thermal elimination of sulfenic acid **39** affords diene **28** which reacts with **27** in a classical [4+2] cycloaddition reaction (see SCHEME 3) to give **29**. However the formation of cycloadduct **37** shows that oxosulfine **27** is able to react as diene with relatively poor activated dienophiles, while for example thione **2** reacts with alkene **36** to give a thiophilic "ene" adduct as the exclusive reaction product.[11] Moreover when 1,4-oxathiin-*S*-oxide **25** was treated under standard conditions ($CHCl_3$, 60 °C) with ethyl vinyl ether **6**, the sulfoxide *E*-**24** was isolated in 70% yield, showing that sulfine **40** is an efficient diene despite the lack of electron withdrawing groups in α' position (SCHEME 5 eq. 3).

Thus, together with the possibility to use an extended range of alkenes as efficient dienophiles, also simple α-oxosulfines, with alkyl group in α' position, can be used as efficient dienes.

Another interesting result arose when sulfine **27** was generated in the presence of cyclohexadiene **41**. In this case we observed the formation of dihydrothiopyran-*S*-oxide **42** as single isomer which was isolated in

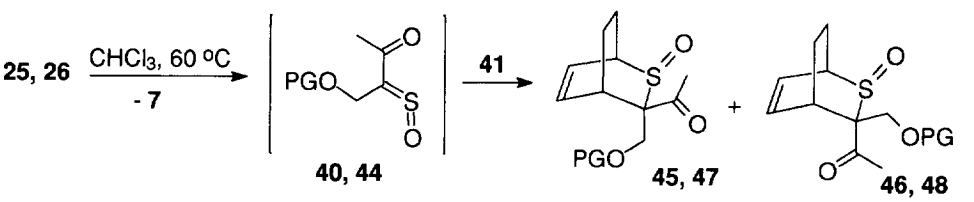
65% yield, ^{1}H and ^{13}C nmr of this compound indicated, in accordance with the literature data,[1,9] an *exo* geometry (SCHEME 6).

We verified that the formation of a single diastereoisomer was not the result of a sulfine mediated thermal riequilibration between *exo-* and *endo-***42**. In fact oxidation of sulfide **43**, which is the product of the cycloaddition of **2** with **41**,[17] affords a 1/1 mixture of both the stereoisomers of **42** which were separated by flash chromatography and independently treated in chloroform at 60 °C with no formation of any equilibration product even after prolonged reaction times (SCHEME 6).



SCHEME 6

The preferred formation of *exo*-adducts was further demonstrated in the reaction with cyclohexadiene **41** of sulfines **40** and **44**, generated from **25** and **26**. In these cases we obtained two stereoisomeric mixtures of cycloadducts (**45, 46** and **47, 48**) whose spectroscopic data showed that the sulfoxyllic oxygen was *exo* in every case[18] (see experimental) (SCHEME 7).



25, 40, 45, 46 : PG=MOM; **45/46**=82/18, (26 h, 83%)

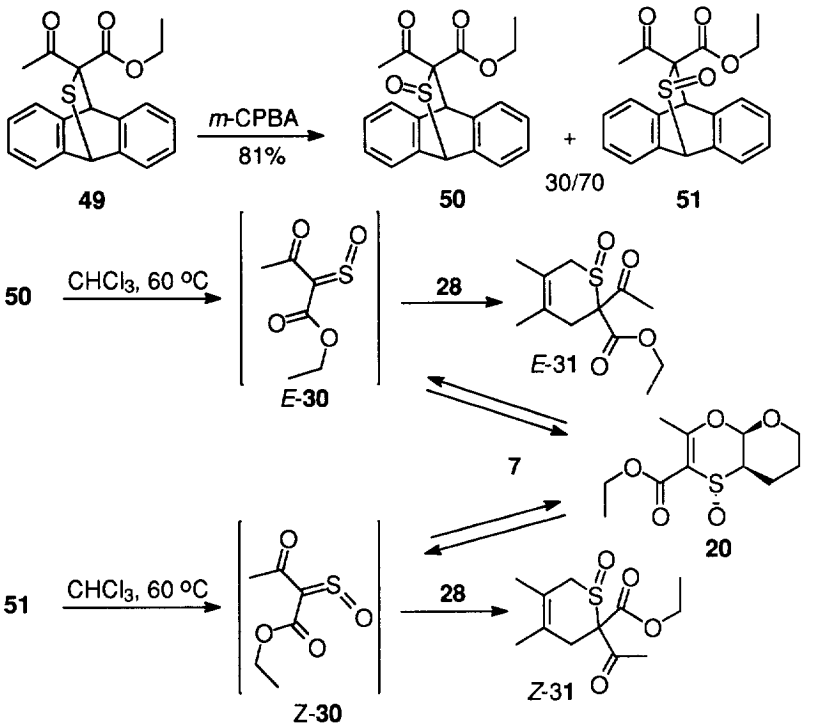
26, 44, 47, 48 : PG=Ac; **47/48**=80/20, (22 h, 90%)

SCHEME 7

In several cases it has been reported that unsymmetrical substituted sulfines retain their geometry during the cycloaddition reaction when they act as dienophiles.[9,19]

It was of interest to verify whether this was also true for α,α'-dioxothiones when they participate to cycloaddition reactions both as dienes or as dienophiles. With this aim the sulfide **49,** obtained from

cycloaddition of **3** with anthracene, was oxidised with *m*-CPBA to give a 30/70 mixture of two stereoisomeric sulfoxides **50** and **51** which were separated by flash chromatography[20] (SCHEME 8).



SCHEME 8

Since anthracene cycloadducts are known to undergo RDA reaction in very mild conditions with retention of the sulfine geometry,[9,21] we decided to use this approach to verify the geometrical stability of the sulfine **30**. When **50** and **51** were independently heated at 60 °C in $CHCl_3$ they generated sulfines *E*-**30** and *Z*-**30** respectively which, in turn, react with diene **28** to give *E* and *Z* thiopyrans **31** with retention of the sulfine geometry.[22]

However when the *E* and *Z*-**30** were trapped using dihydropyran **7** we observed, in both processes, the formation of the single sulfoxide *E*-**20** (SCHEME 8). This can be alternatively explained assuming that both *E* and *Z*-**30** react with **7** to give *E*-**20** or, more likely, assuming that the initially formed *E* and *Z* stereoisomers equilibrate to the thermodynamic more stable *E*-1,4-oxathiin-*S*-oxide **20**.[23] These hypotheses can also justify the streoconvergency observed in the cycloadditions of oxosulfines when they are involved as electron poor dienes. However it should be pointed out that oxathiin-*S*-oxides generate mixtures of *E* and *Z* acylsulfines. In fact when sulfine **30** was generated from **18** or **20** (both as single *E* diastereoisomers) and trapped with 2,3-dimethyl-1,3-butadiene mixtures of 1:1 *E* and *Z*-**31** were obtained (see SCHEME 3).

CONCLUSIONS

In conclusion we have shown a new and simple method for the formation of various α-oxosulfines by RDA reactions of 1,4-oxathiin-*S*-oxides which occur in very mild conditions. These acylsulfines behave as efficient electron poor dienes as well as dienophiles in inverse or direct electron demand Diels-Alder reactions which afford new oxathiin or thiopyran heterocyclic systems in good yield. It has been possible to correlate the geometry of the starting sulfoxides with that of the final products.

The simplicity of the synthesis of oxathiin-*S*-oxides systems and the easy access to the intermediate sulfines make this new approach an effective tool for the study and the possible synthetic applications of these particular and interesting α-acyl thiosubstituted heterocumulenes.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded (when not specified) in $CDCl_3$ at 200 and 50 MHz respectively, using residual $CHCl_3$ at 7.26 ppm for ^1H and central peak of $CDCl_3$ at 77 ppm for ^{13}C as reference lines. Mass spectra and GC-MS analysis were obtained using a gaschromatograph, equipped with a OV101 30 m. capillary column, interfaced on a mass spectrometer. Melting point are uncorrected. $CHCl_3$, CH_2Cl_2, and THF were dried following standard procedures, all commercial reagents were used without further purification as obtained from freshly opened containers. Lithium aluminium hydride reduction of oxathiin **10b** and **11b** to the corresponding alcohols have been achieved as described elsewhere,[11] the protection of the hydroxy group has been performed following standard literature procedures.[24] Phthalimidesulfenyl chloride **1**, oxothiophthalimides **4** and **5**, oxathiines **10a**, **11a**, **12** and **13a** and dihydrothiopyran **43** have been described elsewhere.[11,17] Derivatives **10b**, **11b**, **13b**, and **49** have been similarly prepared, spectroscopic data are as follows:

1,4-oxathiin **10b.** Yellow oil, 82%. ^1H NMR δ 1.18 (t, 3H, J = 7.0 Hz); 1.22 (t, 3H, J = 7.0 Hz); 2.25 (s, 3H); 2.69÷2.87 (m, 2H, AB part of an ABX system, J_{AB} = 13.0 Hz); 3.54÷3.69 (m, 1H); 3.78÷3.93 (m, 1H); 4.12 (q, 2H, J = 7.0 Hz); 5.18 (dd, 1H, X part of an ABX system, J = 2.6 and 4.8 Hz).^{13}C NMR δ 14.0 (q); 14.8 (q); 21.1 (q); 28.4 (t); 60.6 (t); 64.5 (t); 96.2 (d); 96.6 (s); 158.4 (s); 165.0 (s). MS *m/z* (rel. int.) 232 (24); 187 (18); 160 (5); 72 (44); 43 (100). Anal. Calcd. for $C_{10}H_{16}O_4S$: C, 51.71; H, 6.95. Found: C, 51.69; H, 7.18.

1,4-oxathiin **11b.** Oil, 91%. ^1H NMR δ 1.30 (t, 3H, J = 6.6 Hz); 1.65÷2.00 (m, 4H); 2.37 (s, 3H); 3.00÷3.10 (m, 1H); 3.62÷3.98 (m, 2H); 4.13÷4.28 (m, 2H); 5.48 (d, 1H, J = 2.6 Hz). ^{13}C NMR δ 14.1 (q); 20.9 (q); 24.88 and 24.93 (t); 35.6 (d); 60.6 and 60.8 (t); 93.9 (s); 95.1 (d); 158.8 (s); 165.3 (s). MS *m/z* (rel. int.) 244 (25); 198 (31); 160 (20); 84 (100). Anal. Calcd. for $C_{11}H_{16}O_4S$. C, 54.08; H, 6.60. Found: C, 54.06; H, 6.87.

1,4-oxathiin **13b.** Oil, 60%. IR cm^{-1} 3010; 2979; 1707; 1593; 1513; 1232. ^1H NMR δ 1.04 (d, 3H, J = 6.6 Hz); 1.32 (t, 3H, J = 7.0 Hz); 2.36 (s, 3H); 3.13 (dq, 1H, J = 8.4 and 6.6 Hz); 3.82 (s, 3H); 4.26 (q, 2H, J = 7.0 Hz); 4.64 (d, 1H, J = 8.4 Hz); 6.85÷6.97 (m, 2H Arom.); 7.16÷7.23 (m, 2H Arom.). ^{13}C NMR δ 14.3 (q); 16.8 (q); 21.4 (q); 37.2 (d); 55.2 (q); 60.8 (t); 84.0 (d); 97.2 (s); 114.1 (d); 128.3 (d); 129.9 (s); 159.9 (s); 161.2 (s); 165.5 (s). MS *m/z* (rel. int.) 308 (21); 263 (20); 148 (100). Anal. Calcd. for $C_{16}H_{20}O_4S$. C, 62.32; H, 6.54. Found: C, 62.12; H, 6.79.

Anthracene adduct **49.** White solid, m.p. 65-68 °C, 78%. ^{1}H NMR δ 1.11 (s, 3H, J = 7.2 Hz); 1.80 (s, 3H); 3.85÷4.18 (m, 2H); 5.16 (s, 1H); 5.31 (s, 1H); 7.05÷7.22 (m, 4H Arom.); 7.27÷7.39 (m, 3H Arom.); 7.44÷7.52 (m, 1H Arom.). ^{13}C NMR δ 13.7 (q); 29.0 (q); 46.7 (d); 50.7 (d); 62.1 (t); 73.4 (s); 121.7, 122.1, 125.9, 126.2, 126.7, 126.8, 126.9 and 127.4 (d.); 138.6, 139.1, 142.7, 143.2 (s); 168.5 (s); 204.0 (s). MS *m/z* (rel. int.) 338 (6); 296 (13); 178 (100); 160 (5). Anal. Calcd. for $C_{13}H_{14}O_3S_2$. C, 70.98; H, 5.36. Found: C, 70.82; H, 5.26.

General Procedure for the oxidation of oxathiin and thiopyran systems to the corresponding sulfoxides.

To a solution of the heterocycle in dichlometane kept at -18 °C *meta*-chloroperoxybenzoic acid (1.05 equivalents) in dichloromethane is added and the reaction manteined at this temperature until a tlc showed the complete disappearance of the starting sulfide (30-75 min). The reaction mixture is then diluted with dichloromethane (20-40 mL), washed with 10% sodium metabisulfite (1x30 mL), with saturated sodium carbonate (3x30 mL) and dryed over anhydrous sodium sulfate. Evaporation of the afforded the crude sulfoxides which were purified by flash chromatography. *E/Z* ratios have been measured by integration of the ^{1}H NMR peacks on the crude reaction mixtures.

1,4-oxathiin-S-Oxides **17.** White solid, m.p. 68-71 °C (dichloromethane/methanol = 20/1), 70%, (*E/Z* = 94/6) only major isomer was isolated by flash chromatography. IR cm^{-1} 2984; 2934; 1671; 1528; 1248; 1019 (S=O stret.). ^{1}H NMR δ 1.23 (t, 3H, J = 7.2 Hz); 2.35 (s, 3H); 2.47 (s, 3H); 2.58 (dd, 1H, A part of an AMX system, J = 10.6 and 14.0 Hz); 3.19 (dd, 1H, M part of an AMX system, J = 2.0 and 14.0 Hz); 3.63÷3.79 (m, 1H); 3.94÷4.10 (m, 1H); 5.41 (dd, 1H, X part of an AMX system, J = 10.6 and 2.0 Hz). ^{13}C NMR δ 14.8 (q); 22.7 (q); 29.1 (q); 46.2 (t); 66.6 (t); 94.3 (d); 116.7 (s); 170.4 (s); 193.7 (s). MS *m/z* (rel. int.) 218 (1); 201 (10); 176 (31); 146 (20); 72 (100). Anal. Calcd. for $C_9H_{14}O_4S$. C, 49.53; H, 6.47. Found: C, 49.32; H, 6.40.

1,4-oxathiin-S-Oxides **18.** 84% (dichloromethane/methanol = 30/1), (*E/Z* = 85/15):

E isomer, oil. IR cm^{-1} 2981; 1710; 1562; 1249; 1031 (S=O stret.). ^{1}H NMR δ 1.30 (t, 3H, J = 7.2 Hz); 1.34 (t, 3H, J = 7.2 Hz); 2.47 (s, 3H); 2.58 (dd, 1H, A part of an AMX system, J = 10.6 and 13.8 Hz); 3.19 (dd, 1H, M part of an AMX system, J = 1.4 and 13.8 Hz); 3.70÷3.85 (m, 1H); 4.01÷4.16 (m, 1H); 4.18÷4.42 (m, 2H); 5.52 (dd, 1H, X part of an AMX system, J = 10.6 and 1.4 Hz). ^{13}C NMR δ 14.2 (q); 15.0 (q); 22.0 (q); 46.7 (t); 61.5 (t); 66.8 (t); 94.9 (d); 109.1 (s); 164.3 (s); 170.9 (s). MS *m/z* (rel. int.) 248 (11); 203 (30); 200 (98); 72 (100). Anal. Calcd. for $C_{10}H_{16}O_5S$. C, 48.37; H, 6.50. Found: C, 48.43; H, 6.16.

Z isomer, white solid m.p. 60 °C dec. IR cm^{-1} 2979; 1709; 1577; 1249; 1031 (S=O stret.). ^{1}H NMR δ 1.26 (t, 3H, J = 7.1 Hz); 1.34 (t, 3H, J = 7.1 Hz); 2.46 (s, 3H); 2.84 (dd, 1H, A part of an AMX system, J = 2.6 and 14.6 Hz); 3.50 (dd, 1H, M part of an AMX system, J = 2.9 and 14.6 Hz); 3.62÷3.94 (m, 2H); 4.20÷4.46 (m, 2H); 5.60 (dd, 1H, X part of an AMX system, J = 2.6 and 2.9 Hz). MS *m/z* (rel. int.) 248 (2); 203 (5); 200 (17); 72 (100).

1,4-oxathiin-S-Oxide **19.** Oil , 71% (petroleum ether/ethyl acetate = 3/1). IR cm^{-1} 2924; 1674; 1534; 1261; 1026 (S=O stret.). ^{1}H NMR δ 1.00÷1.26 and 1.69÷2.01 (m, 4H); 2.49 (s, 3H); 2.55 (s, 3H); 3.24 (ddd, 1H, J = 2.8, 3.7 and 4.0 Hz); 3.89÷4.04 (m, 2H); 5.79 (d, 1H, J = 2.8 Hz). ^{13}C NMR δ 17.7 and 23.8 (t); 22.8 (q); 29.4 (q); 51.6 (d); 61.5 (t); 90.9 (d); 114.2 (s); 171.0 (s); 194.3 (s). MS *m/z* (rel. int.) 128 (M^+-102, 10); 84 (38); 43 (100). Anal. Calcd. for $C_{10}H_{14}O_4S$. C, 52.16; H, 6.13. Found: C, 51.69; H, 6.59.

1,4-oxathiin-S-Oxide **20.** Oil, 74% (dichloromethane/methanol = 30/1). ^{1}H NMR δ 1.34 (t, 3H, J = 7.3 Hz); 1.41÷1.93 (m, 4H); 2.52 (s, 3H); 3.10÷3.22 (m, 1H); 3.83÷4.00 (m, 2H); 4.11÷4.18 (m, 2H); 5.80 (d, 1H, J = 2.6 Hz). Anal. Calcd. for $C_{11}H_{16}O_5S$. C, 50.76; H, 6.20. Found: C, 50.59; H, 6.45

1,4-oxathiin-S-Oxide **21.** Yellow solid, m.p. 80-83 °C , 85% (petroether/ethyl acetate = 2/1). IR cm^{-1} 3080; 2922; 1674; 1525; 1239; 1021 (S=O stret.). ^1H NMR δ 2.45 (s, 3H); 2.54 (s); 2.62 (dd, 1H, A part of an AMX system, J = 12.6 and 14.0 Hz); 3.36 (dd, 1H, M part of an AMX system, J = 1.4 and 14.0 Hz); 5.78 (dd, 1H, X part of an AMX system, J = 12.6 and 1.4 Hz); 7.28÷7.40 (m, 3H Arom); 7.52 ÷7.60 (m, 2H Arom). ^{13}C NMR δ 23.0 (q); 29.1 (q); 47.0 (t); 75.6 (d); 117.0 (s); 129.3 and 129.5 (d); 129.4 (s); 134.4 (d); 172.1 (s); 193.9 (s). MS *m/z* (rel. int.) 282 (4); 136 (67); 135 (100). Anal. Calcd. for $C_{13}H_{14}O_3S_2$. C, 55.30; H, 5.00. Found: C, 55.39; H, 4.89.

1,4-oxathiin-S-Oxide **22.** Glassy solid, 62% (dichloromethane/methanol = 30/1). IR cm^{-1} 3008; 2934; 1668; 1611; 1513; 1246; 1028 (S=O stret.). ^1H NMR δ 1.14 (d, 3H, J = 7.0 Hz); 2.43 (s, 3H); 2.61 (s, 3H); 2.83 (dq, 1H, J = 11.0 and 7.0 Hz); 3.83 (s, 3H); 5.18 (d, 1H, J = 11.0 Hz); 6.90÷7.00 (m, 2H Arom); 7.22÷7.32 (m, 2H Arom). ^{13}C NMR δ 11.7 (q); 23.0 (q); 29.2 (q); 50.6 (d); 55.3 (q); 74.3 (d); 114.4 (d); 117.32 (s); 127.24 (s); 129.0 (d); 160.4 (s); 171.8 (s); 194.4 (s). MS *m/z* (rel. int.) 294 (1); 147 (100). Anal. Calcd. for $C_{15}H_{18}O_4S$. C, 61.20; H, 6.16. Found: C, 61.50; H, 6.20.

1,4-oxathiin-S-Oxides **23.** 75% (ethyl acetate/petroleum ether = 2/1), (*E*/*Z* = 67/33):

E isomer, white solid, m.p. 132-134 °C. IR cm^{-1} 2978; 1706; 1239; 1042 (S=O stret.). ^1H NMR δ 1.11 (d, 3H, J = 7.3 Hz); 1.36 (t, 3H, J = 7.0 Hz); 2.45 (s, 3H); 2.78 (dq, 1H, J = 7.3 and 11.0 Hz); 3.82 (s, 3H); 4.22÷4.31 (m, 2H); 5.22 (d, 1H, J = 11.0 Hz); 6.82÷7.01 (m, 2H Arom); 7.23÷7.34 (m, 2H Arom). ^{13}C NMR δ 11.8, 14.2 and 22.0 (q); 50.6 (d); 55.3 (q); 61.3 (t); 74.6 (d); 109.6 (s); 114.3, 127.6 and 129.0 (d); 160.3, 164.6 and 172.0 (s). Anal. Calcd. for $C_{16}H_{20}O_5S$. C, 59.24; H, 6.21. Found: C, 59.55; H, 6.12.

Z isomer, oil. IR cm^{-1} 2935; 1709; 1236; 1051 (S=O stret.). ^1H NMR δ 1.18 (d, 3H, J = 7.0 Hz); 1.37 (t, 3H, J = 7.0 Hz); 2.42 (s, 3H); 3.22 (dq, 1H, J = 7.0 and 11.0 Hz); 3.83 (s, 3H); 4.34 (q, 2H, J = 7.0 Hz); 4.78 (d, 1H, J = 11.0 Hz); 6.92÷6.97 (m, 2H Arom); 7.20÷7.28 (m, 2H Arom).

1,4-oxathiin-S-Oxides **24.** Oil, 67% (dichloromethane/methanol = 10/1), (*E*/*Z* = 81/19) only major *E* isomer was isolated by flash chromatography. ^1H NMR δ 1.29 (t, 3H, J = 7.2 Hz); 2.10 (s, 3H); 2.66 (dd, 1H, A part of an AMX system, J = 10.3 and = 14.0 Hz); 3.17 (dd, 1H, M part of an AMX system, J_X = 1.4 and = 14.0); 3.39 (s, 3H); 3.66÷3.81 (m, 1H); 3.97÷4.12 (m, 1H); 4.37 (bs, 2H); 4.66 (bs, 2H); 5.36 (dd, 1H, M part of an AMX system, J = 10.3 and 1.4 Hz). ^{13}C NMR δ 15.04 (q); 18.3 (q); 48.0 (t); 55.5 (q); 63.7 (t); 66.30 (t); 93.7 (d); 95.4 (t); 109.26 (s); 158.9 (s). MS *m/z* (rel. int.) 202 (1); 189 (23); 72 (100).

1,4-oxathiin-S-Oxide **25:** Oil, 76% (dichloromethane/methanol = 20/1). ^1H NMR δ 1.67÷2.00 (m, 4H); 2.14 (s, 3H); 3.07÷3.17 (m, 1H); 3.39 (s, 3H); 3.74÷4.04 (m, 2H); 4.39 (bs, 2H,); 4.66 (bs, 2H); 5.65 (d, 1H, J = 2.6 Hz). ^{13}C NMR δ 17.6 (q); 18.3 (t); 24.1 (t); 53.4 (q); 55.4 (d); 61.3 (t); 63.8 (t); 89.9 (t); 95.3 (d); 106.8 (s); 158.9 (s). MS *m/z* (rel. int.) 262 (2); 201 (5); 84 (100).

1,4-oxathiin-S-Oxide **26.** Oil, 98% (dichloromethane/methanol = 10/1). ^1H NMR δ 1.07÷1.30 (m, 1H); 1.70÷2.00 (m, 3H); 2.07 (s, 3H); 2.15 (s, 3H); 3.07÷3.18 (m, 1H); 3.73÷4.03 (m, 2H); 4.93 (bs, 2H); 5.68 (d, 1H, J = 2.2 Hz). Anal. Calcd. for $C_{11}H_{16}O_5S$. C, 59.99; H, 5.03. Found: C, 59.59; H, 5.21

Dihydrothiopyran-S-oxides **42.** 74% (petroleum ether/ethyl acetate = 1/1), (*exo*/*endo* = 1:1).

Exo isomer, white solid m.p. 84÷87 °C. IR cm^{-1} 2944; 1697; 1460; 1031 (S=O stret.). ^1H NMR δ 1.26÷1.50 (m, 2H,); 2.15 (s, 3H); 2.23÷2.67 (m, 2H); 2.36 (s, 3H); 3.62÷3.67 (m, 1H); 4.12÷4.16 (m, 1H); 6.23 (bt, 1H,); 6.39 (bt,

1H). ^{13}C NMR δ 13.4 and 18.6 (t); 27.8 and 30.3 (q); 34.6 (d); 54.3 (d); 89.1 (s); 128.2 and 137.0 (d); 197.6 and 200.64 (s). MS *m/z* (rel. int.) 209 (M^{+}-17, 6); 77 (100). Anal. Calcd. for $C_{11}H_{14}O_3S$. C, 58.39; H, 6.24. Found: C, 58.00; H, 6.31.

Endo isomer, white solid m.p. 91÷96 °C. IR cm^{-1} 2955; 1697; 1464; 1029 (S=O stret.). ^{1}H NMR δ 1.10÷1.21 (m, 2H); 1.20÷1.59 (m, 2H); 2.23 (s, 3H); 2.24 (s, 3H); 3.50÷3.55 (m, 1H); 4.19÷4.26 (m, 1H); 6.10 (bt, 1H, J = 7.4 Hz); 6.99 (bdd, 1H, J = 8.0 and 7.4 Hz). ^{13}C NMR δ 15.8 and 20.0 (t); 28.3 and 31.7 (q); 34.4 (d); 53.2 (d); 95.5 (s); 123.1 and 137.3 (d); 196.8 and 201.7 (s). MS *m/z* (rel. int.) 226 (3); 123 (100).

Oxidation of Anthracene adduct **49.** 81%, (ethyl acetate/petroleum ether = 1/2), (*E*/*Z* = 30/70).

E sulfoxide **50**. IR cm^{-1} 3040; 2984; 1719; 1223; 1066(S=O stretc.). ^{1}H NMR δ 1.12 (t, 3H, J = 6.8 Hz); 2.22 (s, 3H); 3.92÷4.08 (m, 2H); 5.27 (s, 1H); 5.79 (s, 1H); 7.20÷7.55 (m, 7H Arom.); 7.75÷7.80 (m, 1H Arom.).

Z sulfoxide **51**. IR cm^{-1} 3041; 2983; 1747; 1714; 1227; 1066(S=O stretc.). ^{1}H NMR δ 1.18 (t, 3H, J = 7.0 Hz); 1.99 (s, 3H); 4.00÷5.27 (m, 2H); 5.25 (s, 1H); 5.81 (s, 1H); 7.20÷7.57 (m, 7H Arom.); 7.70÷7.78 (m, 1H Arom.). ^{13}C NMR δ 13.8 and 30.0 (q); 49.3 (d); 62.6 (t); 67.9 (d); 88.2 (s); 126.0, 127.3, 127.4, 127.7, 127.9, 128.3, 128.7 and 128.8 (d); 132.4, 132.8, 136.3 and 138.4 (s); 163.2 and 199.5 (s). Anal. Calcd. for $C_{20}H_{18}O_4S$. C, 67.78; H, 5.12. Found: C, 68.00; H, 5.13.

General procedure for the generation and trapping of α-acylsulfines.

A solution of the sulfoxide and the trapping agent (usually 2 equivalents) in $CHCl_3$ or $CDCl_3$ were heated at 60 °C until by ^{1}H nmr the complete disappearance of the starting sulfoxides was observed (see general part). Evaporation of the solvent and flash chromatography afforded the products of sulfine trapping. Spectroscopical data of sulfoxides obtained following this procedure (if not yet described) are as follow.

Reaction of sulfine **27** *with 2,3-dimehyl-1,3-butadiene: dihydrothiopyran-S-oxides* **29**. Oil, 98% (ethyl acetate/petroleum ether = 1/4). IR cm^{-1} 2922; 1697; 1046 (S=O stret.). ^{1}H NMR δ 1.69 (bs, 3H); 1.82 (bs, 3H); 2.15 (s, 3H); 2.44 (s, 3H); 2.68 (1H, A part of an AB system, J_{AB} = 18.0 Hz); 3.02÷3.20 (m); 3.47 (1H, X part of an XY system, J_{XY} = 17.4 Hz). MS *m/z* (rel. int) 228 (2); 186 (73); 180 (2); 95 (100).). Anal. Calcd. for $C_{11}H_{16}O_3S$. C, 57.87; H, 7.06. Found: C, 57.90; H, 7.12.

Reaction of sulfine **27** *with anethole*: 68%, **22/32** = 54/46 (ethyl acetate/petroleum ether/methanol = 3/1/0.01). *1,4-oxathiin-S-Oxides* **32**. Oil, IR cm^{-1} 3010; 2934; 1668; 1609; 1513; 1026 (S=O stret.) cm^{-1}. ^{1}H NMR δ 1.36 (d, 3H, J = 6.6 Hz); 2.44 (s, 3H); 2.53 (s, 3H); 3.55 (d, 1H, J = 11.0 Hz); 3.81 (s, 3H); 5.10 (dq, 1H, J = 11.0 and 6.6 Hz); 6.90÷7.00 (m, 2H Arom); 7.22÷7.32 (m, 2H Arom). ^{13}C NMR δ 18.4 (q); 23.1 (q); 29.1 (q); 55.3 (q); 61.0 (d); 67.8 (d); 114.5 (d); 117.8 (s); 123.3 (s); 130.9 (d); 160.2 (s); 171.6 (s); 194.4 (s). MS *m/z* (rel. int.) 252 (M^{+}-42, 1); 148 (100). Anal. Calcd. for $C_{15}H_{18}O_4S$. C, 61.20; H, 6.16. Found: C, 61.45; H, 6.26.

In the reaction of sulfine **30** with anethole, which afforded a mixture of regioisomeric sulfoxides **23** and **33** in 82/18 ratio (72% yield), only the major regioisomer *E*-**23** was isolated from the crude reaction mixture.

Reaction of sulfine **27** *with 2,3-dimehyl-2-butene: 1,4-oxathiin-S-Oxides* **37.** Oil, 57% (ethyl acetate/petroleum ether = 3/1). IR cm^{-1} 2925; 1671; 1530; 1241; 1045 (S=O stret.). ^{1}H NMR δ 1.11 (s, 3H); 1.45 (s, 3H); 1.51 (s, 3H); 1.63 (s, 3H); 2.35 (s, 3H); 2.59 (s, 3H). MS *m/z* (rel. int.) 230 (2); 146 (2); 84 (146). Anal. Calcd. for $C_{11}H_{18}O_3S$. C, 57.36; H, 7.88. Found: C, 57.00; H, 8.20.

Reaction of sulfine **40** *with cyclohexadiene: dihydrothiopyran-S-oxides* **45** and **46** (**45/46** = 82/18), 83% (ethyl acetate/petroleum ether = 4/1). Major isomer **45**: ^{1}H NMR δ 1.24÷1.61 (m, 2H); 1.84÷1.99 (m,1H); 2.36 (s, 3H); 2.42÷2.60 (m, 1H); 3.25÷3.29 (m, 1H); 3.33 (s, 3H); 3.91÷4.01 (m, 1H); 3.98 (2H, AB system, J = 11.0 Hz); 4.60 (2H, XY system, J = 6.6 Hz); 5.92 (bt, 1H); 6.68 (bt, 1H). ^{13}C NMR δ 12.1 and 19.8 (t); 27.2 (q); 32.3 (d); 53.2 (q); 55.7 (d); 66.6 (t); 71.2 (t); 96.8 (s); 122.1 and 142.1 (d); 205.1 (s). MS *m/z* (rel. int.) 258 (12); 215 (43); 210 (24); 197 (3); 79 (100). Anal. Calcd. for $C_{11}H_{14}O_3S$. C, 55.79; H, 7.02. Found: C, 55.42; H, 7.38.

Minor isomer **46**: ^{1}H NMR δ 1.03÷1.17 (m, 1H); 1.31÷1.45 (m,1H); 1.53÷1.67 (m, 2H); 2.43 (s, 3H); 3.16÷3.22 (m, 1H); 3.33 (s, 3H); 3.85 (2H, AB system, J = 10.6 Hz); 4.13÷4.19 (m, 1H); 4.54 (2H, XY system, J = 6.6 Hz); 6.25 (bt, 1H); 6.60 (bt, 1H). MS *m/z* (rel. int.) 258 (3); 215 (3); 210 (55); 197 (2); 79 (100).

Reaction of sulfine **44** *with cyclohexadiene: dihydrothiopyran-S-oxides* **47** and **48** (**47/48** = 80/20), 90% (ethyl acetate/petroleum ether = 4/1). Major isomer **47**: ^{1}H NMR δ 1.38÷1.63 (m, 2H); 1.86÷1.98 (m,1H); 2.04 (s, 3H); 2.37 (s, 3H); 2.43÷2.61 (m, 1H); 3.19÷3.23 (m, 1H); 3.95÷3.99 (m, 1H); 4.57 (2H, AB system, J = 12.7 Hz); 5.94 (bt, 1H); 6.66 (bt, 1H). ^{13}C NMR δ 11.9 and 19.9 (t); 20.7 (q); 27.2 (q); 32.2 (d); 53.3 (d); 62.7 (t); 70.3 (s); 122.1 and 142.0 (d); 170.1 and 204.3 (s). MS *m/z* (rel. int.) 256 (2.); 213 (2); 208 (10); 148 (100).

Minor isomer **48**: ^{1}H NMR δ 1.09÷1.70 (m, 4H); 2.02 (s, 3H); 2.41 (s, 3H); 3.15÷3.23 (m, 1H); 4.16÷4.21 (m, 1H); 4.41 (2H, AB system, J = 11.8 Hz); 6.29 (bt, 1H); 6.64 (bt, 1H). MS *m/z* (rel. int.) 256 (1); 213 (5); 208 (5); 105 (100).

*Reaction of sulfine E-***30** *with 2,3-dimehyl-1,3-butadiene: Dihydrothiopyran-S-oxide E-***31**. In this case the sulfine was generated from sulfoxide **50** heated in chloroform at 60 °C for 2 hours. Evaporation of the solvent and flash chromatography (ethyl acetate/petroleum ether = 1/3) afforded compound *E*-**31** (54%) as an oil. ^{1}H NMR δ 1.25 (t, 3H, J = 7.4 Hz); 1.70 (bs, 3H); 1.78 (bs, 3H); 2.43 (s, 3H); 2.56÷2.70 (1H, A part of an AB system, J = 17.6 Hz); 2.92÷3.08 (m, 1H, B part of an AB system, J = 17.6 Hz); 3.12÷3.28 (1H, X part of an XY system, J = 17.4 Hz); 3.44÷3.61 (1H, Y part of an XY system, J = 17.4 Hz); 4.14÷4.32 (m, 2H). MS *m/z* (rel. int.) 258 (100); 216 (22).

*Reaction of sulfine Z-***30** *with 2,3-dimehyl-1,3-butadiene Dihydrothiopyran-S-oxide Z-***31**. In this case the sulfine was generated from sulfoxide **51** heated in chloroform at 60 °C for 2 hours. Evaporation of the solvent and flash chromatography (ethyl acetate/petroleum ether = 1/3) afforded compound *Z*-**31** (41%) as an oil. ^{1}H NMR δ 1.31 (t, 3H, J = 6.8 Hz); 1.67 (bs, 3H); 1.80 (bs, 3H); 2.20 (s, 3H); 2.61÷2.74 (1H, X part of an XY system, J = 18.4 Hz); 3.09÷3.24 (m, 2H); 3.39÷3.53 (1H, B part of an AB system, J = 19.2 Hz); 4.32 (q, 2H, J = 6.8 Hz). Anal. Calcd. for $C_{12}H_{18}O_4S$. C, 55.79; H, 7.02. Found: C, 55.62; H, 7.14.

Oxidation of a mixture of 1,4-oxathiin-S-oxides **22** *and* **32** *to the corresponding S,S-Dioxides* **34** *and* **35**. The reaction was carried out using a mixture of sulfoxides **22** and **32**, as obtained from the reaction of sulfine **27** with anethole, using two equivalents of *meta*-chloroperoxybenzoic acid for 22 hours at room temperature. ^{1}H NMR of the crude reaction mixture showed the presence of sulfones regioisomer **34** and **35** in 54/46 ratio (100% overall yield). Major sulfone **34** was obtained pure by flash chromatography (eluent ethyl acetate/petroleum ether = 1/2.5) as a white solid m.p. 120÷124 °C. IR cm^{-1} 3010; 2936; 1681; 1612; 1514; 1250 (SO_2 stret.); 1130 (SO_2 stret.). ^{1}H NMR δ 1.13 (d, 3H, J = 7.0 Hz); 2.33 (s, 3H); 2.64 (s, 3H); 3.52 (dq, 1H, J = 11.8 and 7.0 Hz); 3.84 (s, 3H); 5.32 (d, 1H, J = 11.8 Hz); 6.90÷7.00 (m, 2H Arom); 7.20÷7.30 (m, 2H Arom.). ^{13}C NMR δ 6.4 (q); 22.1 (q); 31.8 (q); 55.4 (q); 57.6 (d); 83.1 (d); 114.6 (d); 119.04 (s); 126.1 (s); 128.8 (d); 160.86 (s); 170.9 (s); 191.6 (s). MS *m/z* (rel. int.) 310 (3); 160 (3); 148 (100). Anal. Calcd. for $C_{15}H_{18}O_5S$. C, 58.05; H, 5.85. Found: C, 57.84; H, 5.87.

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18. Oxidation of a mixture of **45** and **46** afforded a mixture of the corresponding two sulfones in this case too. However since a further strereogenic centre remains on the molecule the sole does not allow to

discriminate between *exo-exo* and *endo-endo* or *exo-endo* and *endo-exo* isomers. Attempts to obtain further indications reducing the sulfoxides to sulfides with $(Me_3Si)_2S$ and $(EtO)_3P$ were unsuccessful.

19. Zwanenburg, B.; Thijis, L.; Broens, J. B.; Strating, J. *Recl. Trav. Chim. Pays Bas,* **1972**, *91*, 443-446.
20. Attribution of the relative geometry of **50** and **51** (and then to *E* and *Z*-**31**) has been tentatively obtained assuming an higher deshielding effect for the methyl group when it is adjacent to the sulfoxyllic oxygen (*E* isomers).
21. Hasserodt, J.; Pritzkow, H.; Sundermeyer, W. *Liebigs Ann.,* **1995**, 95-104.
22. Traces of the other stereoisomers (less than 5% by ^1H nmr) were observed in these reactions.
23. The formation of *Z* isomers in the cycloaddition of acyl sulfines acting as dienes has never been detected even checking "via" ^1H nmr the reaction mixtures after few minutes at 60 °C.
24. Greene, T. W.; Wuts, P. G. M. In *Protective Groups in Organic Synthesis*; John Wiley and Sons, Inc.: New York, 1991; pp. 10-147.

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