Stereochemical Course of the Reaction between Thiocarbonyl Compounds and Oxiranes: Reaction with *cis*- and *trans*-2,3-Dimethyloxirane

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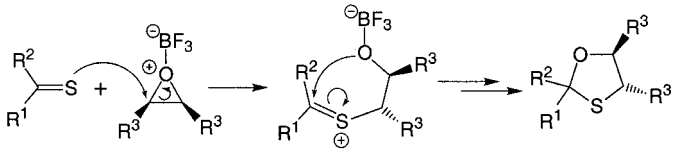
The reactions of thiocarbonyl compounds with *cis*-2,3-dimethyloxirane (**1a**) in CH_2Cl_2 in the presence of $BF_3 \cdot Et_2O$ or $SnCl_4$ led to *trans*-4,5-dimethyl-1,3-oxathiolanes, whereas with *trans*-2,3-dimethyloxirane (**1b**) *cis*-4,5-dimethyl-1,3-oxathiolanes were formed. With the stronger *Lewis* acid $SnCl_4$, the formation of side-products was also observed. In the case of 1,3-thiazole-5(4*H*)-thione **2**, these side-products are the corresponding 1,3-thiazol-5(4*H*)-one **5** and the 1:2 adduct **8** (*Schemes 2–4*). Their formation can be rationalized by the decomposition of the initially formed spirocyclic 1,3-oxathiolane and by a second addition onto the C=N bond of the 1:1 adduct, respectively. The secondary epimerization by inversion of the configuration of the spiro-C-atom (*Schemes 5–7*) can be explained by a *Lewis*-acid-catalyzed ring opening of the 1,3-oxathiolane ring and subsequent ring closure to the thermodynamically more stable isomer (*Scheme 12*). In the case of 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**20**), apart from the expected spirocyclic 1,3-oxathiolanes **21** and **23**, dispirocyclic 1:2 adducts were formed by a secondary addition onto the C=O group of the four-membered ring (*Schemes 9* and *10*).

1. Introduction. – The reaction of oxo compounds with oxiranes in the presence of a *Lewis* acid is one of the common methods for preparing 1,3-dioxolanes, which are well-known as protecting groups [3]. Its mechanism with different catalysts has been carefully studied [4][5]. The observed inversion of the configuration of one oxirane C-atom indicates an S_N2-type mechanism, involving an attack of the oxo compound onto the activated oxirane. For the reaction between thiocarbonyl compounds and oxiranes under similar conditions, we have proposed an analogous mechanism in our previous work [1][2] (*cf.* also [6][7]) (*Scheme 1*).

Scheme 1



A'

In the present paper, we report on the investigations of the stereochemical course of this reaction, providing evidence that supports the proposed mechanism. Thus, the stereochemically defined *cis*- and *trans*-2,3-dimethyloxiranes (**1a** and **1b**, resp.) were reacted with different types of thiocarbonyl compounds.

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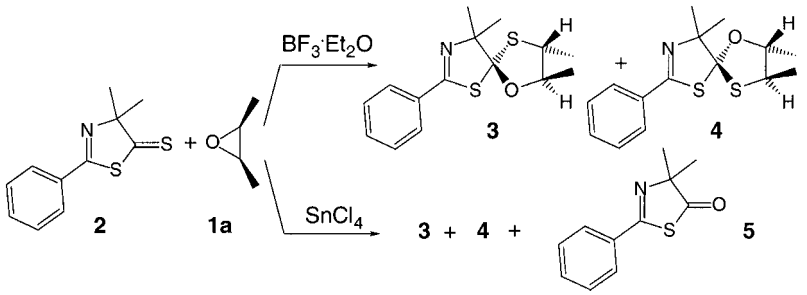
[1]) Part III of the planned Ph.D. thesis of *M.B.*, University of Zurich. For Part I, see [1]; for Part II see [2].

2. Results. – 2.1. *Reactions of 4,4-Dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione* (**2**). 2.1.1. *Reaction with* cis*-2,3-Dimethyloxirane* (**1a**). The reaction of **1a** and **2** was carried out in dry CH_2Cl_2 under N_2 atmosphere in the presence of $BF_3 \cdot Et_2O$ as the source of BF_3 as *Lewis* acid. In the first experiments, 5 equiv. of **1a** were added to the solution of **2** at $-30°$, and the reaction mixture was allowed to warm to 0°. Its color, as well as TLC control, indicated that thiazole-thione **2** was still present. Therefore, at this temperature, another 2 equiv. of **1a** were added, and the mixture was allowed to warm to room temperature overnight. After workup and chromatographic separation, the addition products **3** and **4** were obtained in 49 and 10% yield, respectively (*Scheme 2*)[2]). Apart from that, 39% of the starting material **2** was recovered. The structures of **3** and **4** were assigned on the basis of NMR experiments (NOESY and DQF-COSY). A strong indication of the configuration was provided by the ^3J values of 9.3 and 8.0 Hz, respectively, between the two H-atoms of the 1,3-oxathiolane ring. These values are in the range observed in our previous work with *cis*-fused bicyclic oxiranes (*cf.* [1][2]), and they are also in good agreement with the data reported for differently substituted di- and trimethyl-1,3-oxathiolanes [8].

Scheme 2



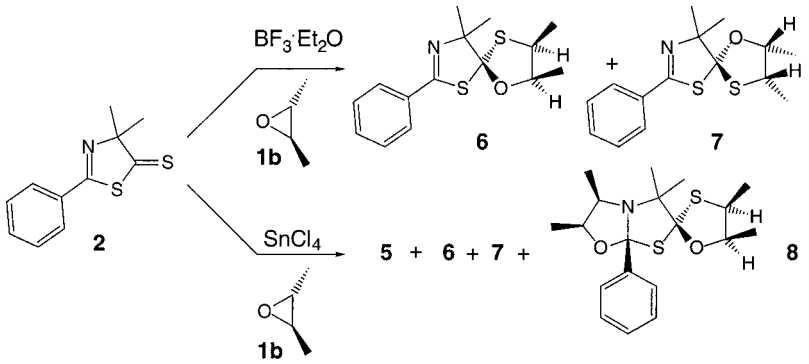
The reaction at room temperature led to the same products **3** and **4**, in 65 and 15% yield, respectively, and 17% of **2** was recovered. As a significant amount of thiazole-thione **2** was left unconsumed, we decided to vary the catalyst. Therefore, a $SnCl_4$ solution was used in the next set of reactions, and, at room temperature after only *ca.* 20 min, the mixture was almost colorless. The reaction was terminated after 30 min to yield, after chromatographic separation, **3** and **4** (63 and 12%, resp.), and *ca.* 5% of the 1,3-thiazol-5(4*H*)-one **5**. The reaction at 0° for 1.5 h led to **3**, **4**, and **5** in 82, 13, and 4% yield, respectively.

2.1.2. *Reaction with* trans*-2,3-Dimethyloxirane* (**1b**). Because of the experience mentioned above, the reaction of **2** with 5 equiv. of **1b** in the presence of $BF_3 \cdot Et_2O$ was performed at room temperature. The TLC monitoring of the reaction showed no further changes after 3–4 h, although **2** was still present. To consume **2** completely, another portion of $BF_3 \cdot Et_2O$ was added, followed by another 5 equiv. of **1b**. After stirring the mixture overnight and chromatographic separation, **6** and **7** were isolated in 76 and 11% yield, respectively, and 11% of **2** was recovered (*Scheme 3*). The structures of the products were again assigned on the basis of the above mentioned NMR

[2]) All chiral substances are racemates, but only one enantiomer is shown in the schemes for the sake of clarity.

experiments. In this case, the ^3J values for the 1,3-oxathiolane H-atoms were 4.6 and 4.3 Hz, respectively, indicating, in contrast to the values found for **3** and **4**, a *cis*-relationship of the Me groups, and are again in accordance with the data from the literature [8]. The relative configuration of **6** was confirmed by X-ray crystallography (see *Fig. 1*).

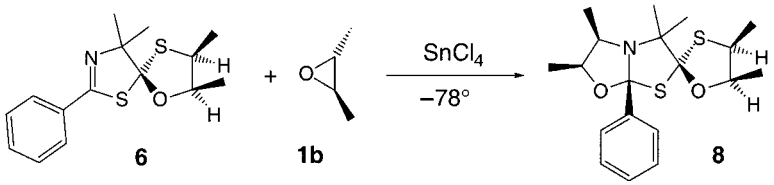
Scheme 3



The reaction of **1b** and **2** at room temperature with $SnCl_4$ as catalyst led to a surprising result. The color of the reaction mixture changed rapidly, the solution being almost colorless after *ca.* 15 min. After stirring for 30 min, separation of the products by column chromatography gave, apart from the 1:1 adducts **6** and **7**, the 1:2 addition product **8**. The yields were 60, 5, and 14%, respectively. The analogous reaction at 0° gave the same products in 67, 7, and 9% yield, respectively. Additionally, thiazolone **5** (16%) was also formed. The structure of **8** was also confirmed by X-ray crystallography (*Fig. 1*). The relative configuration of the substituents of the 1,3-oxazolidine ring is again *cis*. Due to a slightly different geometry, the coupling between the *cis*-oriented H-atoms in the oxazolidine ring is larger: they appear as *quintuplets*, with ^3J values in the range of 6.4–6.9 Hz.

The 1:2 adduct **8** is the result of addition of a second molecule of **1b** to the C=N bond of the 1,3-thiazole ring of **6**. Apparently, the more powerful *Lewis* acid $SnCl_4$ enables an addition to this bond. To confirm this proposal, we reacted the main 1:1 adduct **6** with **1b** under analogous conditions. The reaction at room temperature led to 37% of 1,3-thiazolone **5**, and 30% of starting material **6** was recovered. Starting the same reaction at −78° and stirring the mixture for 15 h, allowing it to warm to r.t., led to the expected product **8** in 30% yield, apart from 63% of recovered **6** (*Scheme 4*).

Scheme 4



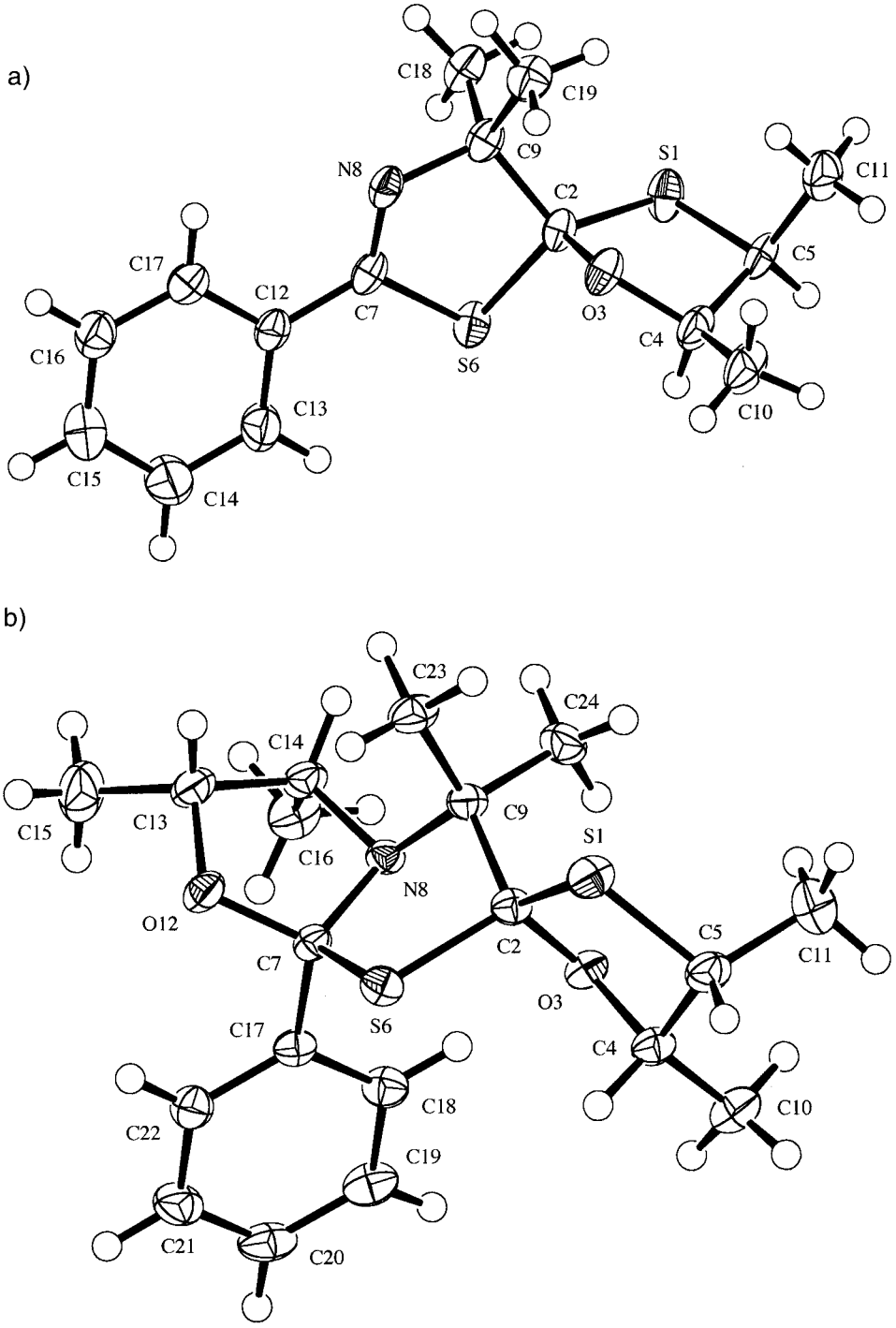
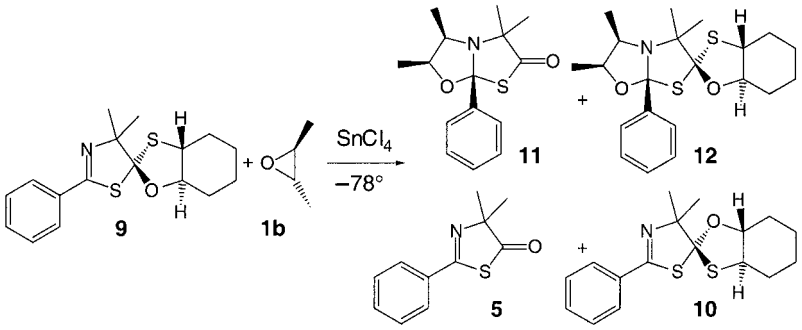


Fig. 1. *ORTEP Plot* [9] *of the molecular structure of* a) **6** *and* b) **8** (arbitrary numbering of the atoms; 50% probability ellipsoids)

2.1.3. *Reaction of the Derivatives of* **2**. To expand the scope of the reaction of **6** with **1b** to give the 1:2 adduct, we tried to perform it with analogous compounds, *i.e.*, with the pair of diastereoisomers **9** and **10** (*cf. Schemes 5* and *6*), obtained in our previous work [1]. The compounds were carefully purified and allowed to react with **1b** under the conditions described above (– 78° – r.t., $SnCl_4$ (1.1 equiv.), **1b** (7 equiv.)).

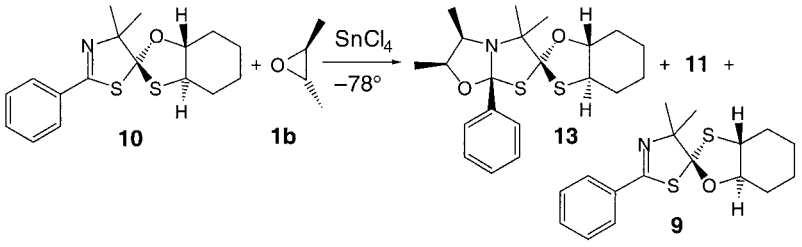
In the case of **9**, the reaction was performed for 30 and 50 h. After a reaction time of *ca.* 50 h, only traces (*ca.* 1%) of the addition product **12** were detected, but 1,3-thiazolone **5** (18%) and the unexpected perhydro-1,3-oxazolo[2,3-*b*]-1,3-thiazole **11** (23%) were isolated, as well as 39% of the starting material **9**. After the shorter reaction time of 30 h, **12** was obtained in 12% and **11** in 13% yield, while 38% of **9** was recovered. In each reaction, small amounts (2 and 4%, resp.) of **10**, a diastereoisomer of the starting material **9**, were also detected (*Scheme 5*).

Scheme 5



The reaction of the other diastereoisomer **10** with **1b** led to even more surprising results. After a reaction time of 30 h, the two main products were the adduct **13** and **11**, which could be regarded as a decomposition product of **13**. They were isolated in 22 and 14% yield, respectively. Quite surprisingly, only 3% of the starting **10** and a much larger amount of its diastereoisomer **9** (45%) were isolated (*Scheme 6*).

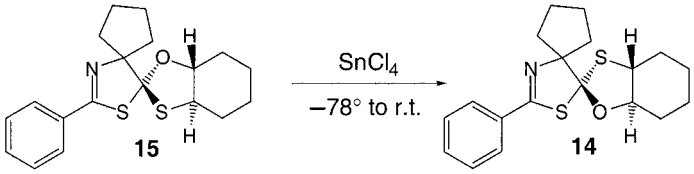
Scheme 6



Apparently, under the chosen reaction conditions one diastereoisomer predominantly undergoes rearrangement to the other thermodynamically more stable one (*i.e.*, **10** → **9**). The existence of an equilibrium is indicated by the fact that, in the reaction with **9**, small amounts of **10** were found.

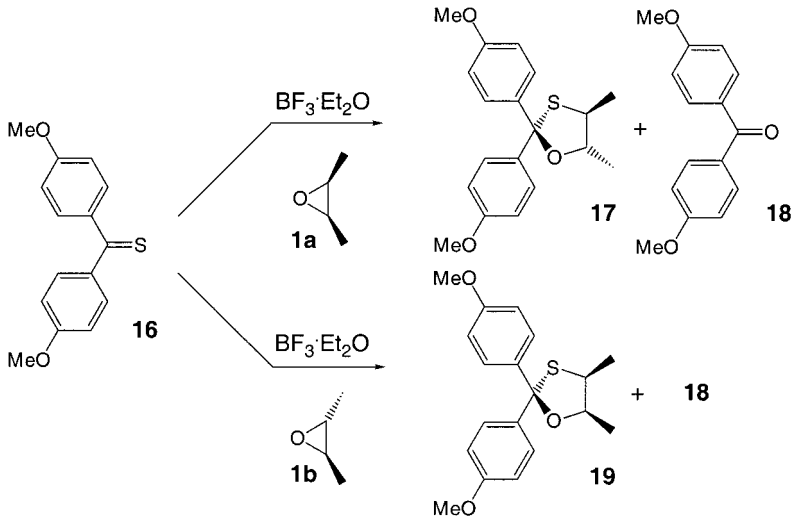
The presence of the *Lewis* acid $SnCl_4$ obviously catalyzed the epimerization of the 1:1 adducts. To verify that, control experiments with another pair of diastereoisomers, **14** and **15** (*cf.* [1]), were carried out (*Scheme 7*). To CH_2Cl_2 solutions of equal amounts of them, 1.1 equiv. of $SnCl_4$ were added at $-78°$, and the stirred mixtures were allowed to warm to room temperature. Workup of both mixtures gave exclusively one product, namely **14**, isolated in 90 and 95% yield, respectively.

Scheme 7



2.2. *Reactions of Bis(4-methoxyphenyl)methanethione* (**16**). 2.2.1. *Reaction with* cis-*2,3-Dimethyloxirane* (**1a**). The addition of $BF_3 \cdot Et_2O$ to a solution of **16** in CH_2Cl_2 at $-78°$ led to a change of the color from blue to violet. Then, 5 equiv. of **1a** were added at once, and within 20–30 s the color of the mixture changed to orange-yellow. The reaction was quenched with H_2O, and the workup gave 1,3-oxathiolane **17** and ketone **18** in 31 and 57% yield, respectively (*Scheme 8*). Repeating the reaction at $-90°$ led to an increased yield of **17** (61%), and a decreased amount of the decomposition product **18** (39%). The relative configuration of **17** was again deduced from the ^3J value of 9.0 Hz between the 1,3-oxathiolane H-atoms.

Scheme 8

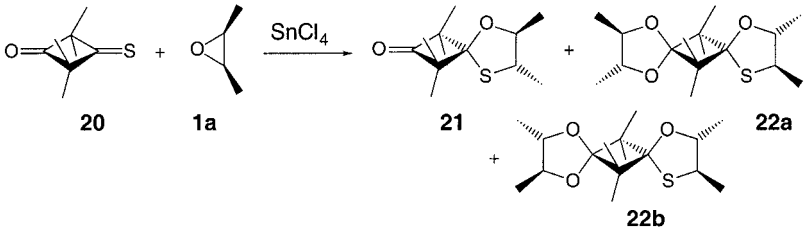


2.2.2. *Reaction with* trans-*2,3-Dimethyloxirane* (**1b**). Due to the better yields in the case of **1a** at lower temperatures, the reaction with **1b** was performed at $-90°$ under similar conditions. The reaction was terminated after *ca.* 30-s stirring, and 88% of

product **19** with a *cis*-configuration of the substituents (^3J(H–C(4), H–C(5)) = 4.9 Hz) was isolated, as well as 10% of **18**.

2.3. *Reactions of 2,2,4,4-Tetramethyl-3-thioxocyclobutanone* (**20**). 2.3.1. *Reaction with* cis-*2,3-Dimethyloxirane* (**1a**). Preliminary experiments established that $BF_3 \cdot Et_2O$ is not an appropriate catalyst for this reaction. The consumption of the thioxo ketone **20** was relatively low, despite a longer reaction time (*ca.* 24 h), and additional amounts of the catalyst and of **1a**. The mixture of products was complex, and the products were difficult to separate. Accordingly, $SnCl_4$ was used as *Lewis* acid in the reaction at 0°. After the addition of 5 equiv. of **1a**, the red color of the solution disappeared within 30 min. The separation of the products gave the 1:1 adduct **21**, as well as a mixture of the 1:2 adducts **22a** and **22b** in 27 and 8% yield, respectively. In the ^{1}H-NMR spectra of each product the ^3J values of 8.7 and 8.8 Hz between the H-atoms of the five-membered rings indicated a *trans*-relationship of the Me groups of the 1,3-oxathiolane ring (*Scheme 9*).

Scheme 9



The formation of **22** can be explained by the addition of **1a** to the strained cyclobutanone C=O bond of **21**. NMR Experiments (DQF-COSY, NOESY) revealed that two compounds are present in a ratio of *ca.* 1:1. Unfortunately, it was not possible to distinguish between the diastereoisomers **22a** and **22b**, and to separate them. After crystallization from CH_2Cl_2, the X-ray crystal-structure analysis of **22a** (*Fig. 2*) confirmed the *trans*-relationship of the Me groups at the five-membered rings[3]).

2.3.2. *Reaction with* trans-*2,3-Dimethyloxirane* (**1b**). The reaction was performed as with **1a**. Again, a 1:1 addition product **23** and a dispiro compound **24** were isolated in 28 and 6% yield, respectively (*Scheme 10*). In contrast to the reaction with **1a**, only one 1:2 adduct was present according to the NMR spectra. The ^3J value of 4.2 Hz between the H-atoms of the five-membered rings indicates that the relative configuration of the substituents of the five-membered rings of both products is *cis*. Unfortunately, all additional NMR experiments could not provide a differentiation between the structures of the two possible diastereoisomers **24a** and **24b**. The structure of **23** has been independently confirmed by X-ray crystal-structure analysis (*Fig. 3*).

Products derived from **20** were generally obtained in lower yields than in the cases of **2** and **16**. This can be explained by their relatively high volatility, which reduces the

[3]) Crystallization of the mixture **22a**/**22b** from CH_2Cl_2 gave single crystals of **22a** suitable for the X-ray crystal-structure analysis.

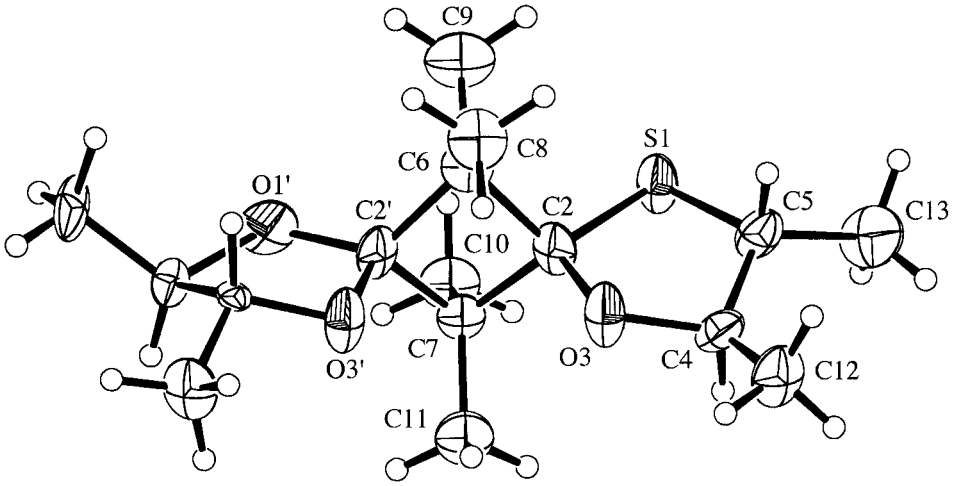


Fig. 2. *ORTEP Plot* [9] *of the molecular structure of* **22a** (arbitrary numbering of the atoms; 50% probability ellipsoids)

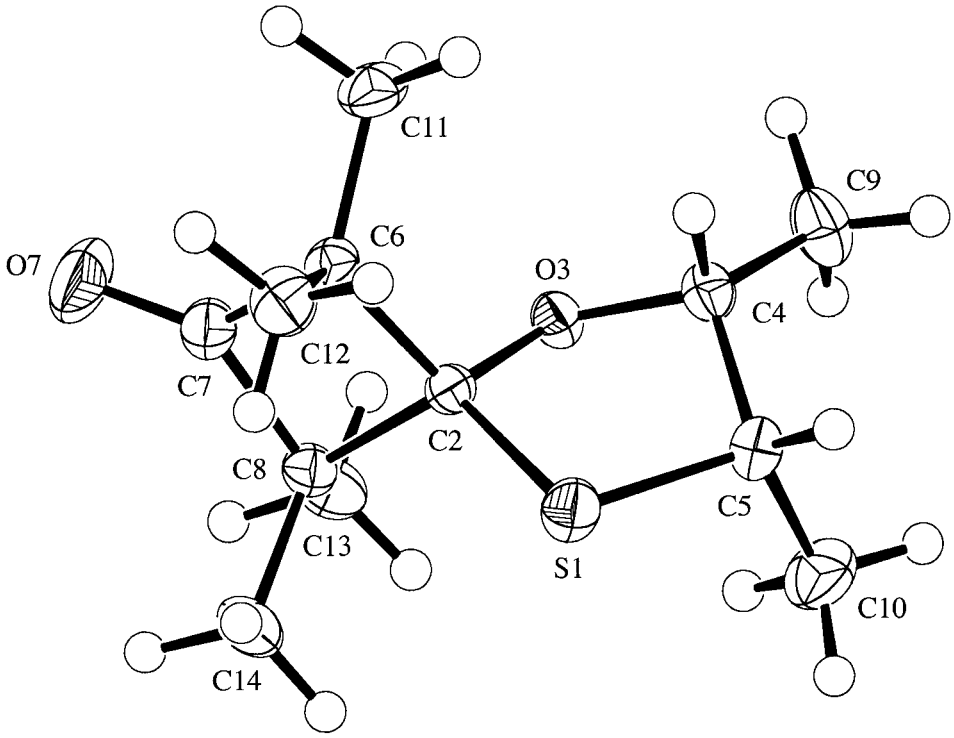
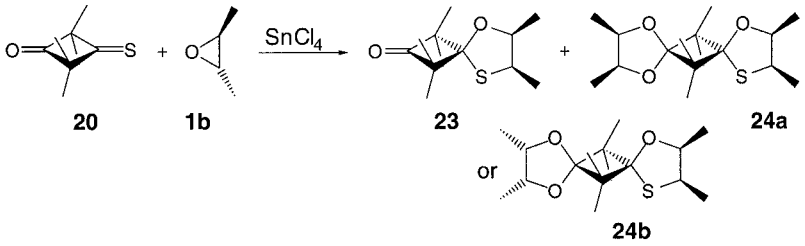


Fig. 3. *ORTEP Plot* [9] *of the molecular structure of* **23** (arbitrary numbering of the atoms; 50% probability ellipsoids)

Scheme 10



amounts of isolated products[4]). The decomposition product 2,2,4,4-tetramethylcyclobutane-1,3-dione is also volatile and thus difficult to isolate.

3. Discussion. – Oxiranes are valuable intermediates in organic synthesis partly because the nucleophilic ring-opening leads to 1,2-difunctionalized C-skeletons or heterocycles, and partly because such cleavages usually occur stereospecifically in a *trans*-fashion. In general, these reactions require the presence of a catalyst that could range from *Lewis* acids [10][11], anhydrous $CuSO_4$ [12], Al_2O_3 [13], and organometallic compounds [14], to tetracyanoethylene [15] or even bentonitic clay [16]. These reactions make oxiranes important synthons for the stereoselective preparation of O-containing heterocycles (*e.g.*, [17][18]), as well as carbocyclic compounds, *e.g.*, cyclopropanes [19]. In the reaction with thiocarbonyl compounds to give 1,3-oxathiolanes, the *Lewis* acids BF_3 as its etherate, $SnCl_4$, and $Mg(ClO_4)_2$ proved to be most convenient [1][2][6][7].

The results reported in the present paper confirm the previously proposed mechanism shown in *Scheme 1*. In all cases investigated, the *cis*-substituted oxirane **1a** led to *trans*-substituted 1,3-oxathiolanes, and the *trans*-substituted oxirane **1b** was transformed into *cis*-substituted 1,3-oxathiolanes, *i.e.*, the nucleophilic ring opening occurs with inversion of the configuration of one C-atom. This was confirmed by X-ray crystal-structure determination, as well as by the ^3J values between the H-atoms of the five-membered ring, which are in the range of 4.2–4.9 Hz for the *cis*-substituted oxathiolanes and 8.0–9.3 Hz for the *trans*-substituted ones, consistent with the literature data [8]. This mechanism is in accordance with earlier reported results, which indicated that *cis*-oxiranes were selectively opened to *threo*-compounds, and *trans*-oxiranes provided *erythro* derivatives [12][20].

Based on the described results, we postulate that the reaction of thiocarbonyl compounds and oxiranes proceeds by activation of the oxirane *via* complexation with the *Lewis* acid, followed by an S_N2-type ring opening, leading to zwitterions of type **A′** or **A″** (*Scheme 1* or *Scheme 11*, corresponding to the used oxirane and/or *Lewis* acid). The latter then cyclize to give the correspondingly substituted 1,3-oxathiolane.

The reactivity of the two stereoisomeric oxiranes **1a** and **1b** is comparable, but in some cases **1a** seems to be slightly more reactive, which is reflected in shorter reaction times. This higher reactivity (*cf.* also [17][18]) could have resulted in the faster

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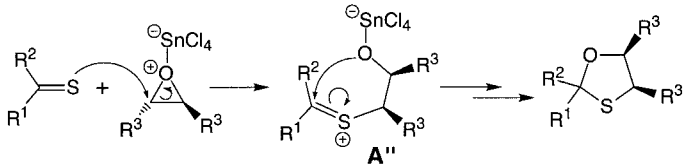
[4]) For instance, keeping **23** under h.v. (*ca.* 3×10^{-5} Torr) for a period of two days led to its complete disappearance.

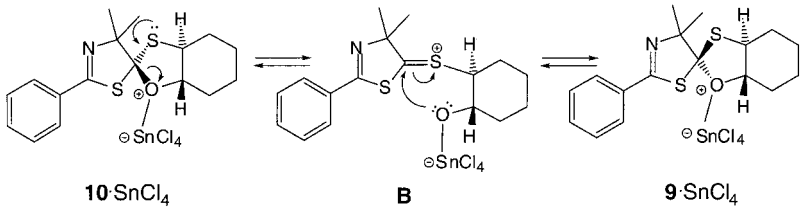
Scheme 11



consumption of **1a**, thus preventing a second addition with the less reactive C=N bond of the thiazole ring of **2**. Therefore, no 1:2 adduct of type **8** was detected. A possible explanation of the generally observed lower reactivity of the *trans*-oxirane **1b** is the different ground-state energy compared with the *cis*-isomer **1a**: we assume that the difference in their enthalpies of formation ($\Delta\Delta H_f^\circ$) is similar to that of *trans*- and *cis*-1,2-dimethylcyclopropane, which has been determined to be -1.06 kcal/mol [21]. The energetically less favored (*i.e.*, more strained) *cis*-isomer undergoes ring-opening reactions more easily. In addition, **1b** leads to the formation of the sterically more crowded *cis*-4,5-dimethyl-1,3-oxathiolanes and the corresponding transition states, whereas the reaction of **1a** leading to *trans*-substituted 1,3-oxathiolanes proceeds with release of steric strain.

The observed epimerization in the cases of **9**/**10** and **14**/**15** could be explained by the opening of the oxathiolane ring induced by the stronger *Lewis* acid $SnCl_4$. The formed zwitterion **B** can undergo ring closure again by nucleophilic attack from the opposite side, thus shifting the equilibrium towards the thermodynamically more stable epimer (*Scheme 12*).

Scheme 12



10·$SnCl_4$ **B** **9**·$SnCl_4$

In the 1:2 adducts **8**, **22**, and **24**, the relative configuration of the substituents in the additional ring is always the same as in the oxathiolane, which is formed first, indicating an analogous mechanism for the reaction of the oxiranes with different types of double bonds.

We thank the analytical units of our institute for spectra and analyses, Mr. *J. Tödtli* for his assistance with the determination of the crystal structures, and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for financial support.

Experimental Part

1. *General*. See [22].

2. *Reaction of Thiocarbonyl Compounds with 2,3-Dimethyloxiranes. General Procedure.* To a soln. of a thiocarbonyl compound (*ca.* 1 mmol) in dry CH_2Cl_2 (10–15 ml) under N_2, 1.1 equiv. of a *Lewis* acid ($BF_3 \cdot Et_2O$ or $SnCl_4$) was added. In general, this leads to a more or less pronounced change in the color of the soln. Then, the mixture was stirred for *ca.* 30 min, and 6–13 equiv. of *cis*- and *trans*-2,3-dimethyloxirane (**1a** and **1b**, resp.) were

added dropwise at different temp. (from $-90°$ up to r.t.), depending on the reactivity of the starting materials. The reaction time was varied from 15 s to more than 2 d, regarding the reactivity of the starting materials, as well as the stability of the products. The reaction course has been monitored by TLC. When the reaction was terminated, the mixture was washed with sat. aq. NaCl soln. The combined org. layers were dried ($MgSO_4$) and evaporated *i.v.* The products were separated by chromatography (SiO_2; CC or prep. TLC (PLC)).

2.1. *Reactions of 4,4-Dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione* (**2**). 2.1.1. *Reaction with* **1a**. *a*) Reaction of **2** (221 mg, 1 mmol) with **1a** (514 mg, 7.14 mmol) and $BF_3 \cdot Et_2O$ (160 mg, 1.13 mmol) (20 h, $-30°$ to r.t., CC (hexane/AcOEt 30:1)) yielded 87 mg (39%) of **2**, 144 mg (49%) of *(5*RS*,7*SR*,8*SR*)-4,4,7,8-tetramethyl-2-phenyl-6-oxa-1,9-dithia-3-azaspiro[4.4]non-2-ene* (**3**), and 30 mg (10%) of *(5*RS*,7*RS*,8*RS*)-4,4,7,8-tetramethyl-2-phenyl-6-oxa-1,9-dithia-3-azaspiro[4.4]non-2-ene* (**4**).

b) Reaction of **2** (220 mg, 1 mmol) with **1a** (602 mg, 8.36 mmol) and $BF_3 \cdot Et_2O$ (156 mg, 1.1 mmol) (30 h, r.t., CC (hexane/AcOEt 30:1)) yielded 38 mg (17%) of **2**, 189 mg (65%) of **3**, and 44 mg (15%) of **4**.

c) Reaction of **2** (111 mg, 0.5 mmol) with **1a** (353 mg, 4.9 mmol) and $SnCl_4$ (*ca.* 1M soln., 0.6 ml) (0.5 h, r.t., CC (hexane/AcOEt 33:1)) gave 93 mg (63%) of **3**, 18 mg (12%) of **4**, and 5 mg (4%) of *4,4-dimethyl-2-phenyl-1,3-thiazol-5(4*H*)-one* (**5**) [23].

d) Reaction of **2** (111 mg, 0.5 mmol) with **1a** (504 mg, 7 mmol) and $SnCl_4$ (*ca.* 1M soln., 0.6 ml) (1.5 h, $0°$, CC (hexane/AcOEt 33:1)) gave 120 mg (82%) of **3**, 19 mg (13%) of **4**, and 4 mg (4%) of **5**.

Data of **3**: Colorless oil. IR ($CHCl_3$): 2980*m*, 2932*m*, 2870*w*, 1592*m*, 1576*m*, 1491*w*, 1448*m*, 1380*m*, 1361*w*, 1263*s*, 1215*m*, 1207*s*, 1154*w*, 1094*m*, 1008*m*, 955*s*. ^{1}H-NMR: 7.81–7.77 (*m*, 2 arom. H); 7.46–7.36 (*m*, 3 arom. H); 3.97 (*dq*, $^3J = 9.3$, 6.0, H–C(7)); 3.13 (*dq*, $^3J = 9.3$, 6.4, H–C(8)); 1.58, 1.43 (2*s*, 2 Me); 1.36 (*d*, $^3J = 6.0$, Me–C(7)); 1.35 (*d*, $^3J = 6.4$, Me–C(8)). ^{13}C-NMR: 165.1 (*s*, C=N); 133.7 (*s*, 1 arom. C); 131.0, 128.3, 127.9 (3*d*, 5 arom. CH); 116.1 (*s*, spiro-C); 84.9 (*d*, C(7)); 81.3 (*s*, Me_2C); 49.2 (*d*, C(8)); 24.9, 20.6 (2*q*, 2 Me); 16.4 (*q*, 2 Me). CI-MS: 294 (100, $[M+1]^+$). Anal. calc. for $C_{15}H_{19}NOS_2$ (293.45): C 61.39, H 6.53, N 4.77, S 21.85; found: C 61.45, H 6.56, N 4.71, S 21.49.

Data of **4**: Colorless oil. IR ($CHCl_3$): 2978*s*, 2932*s*, 2872*m*, 1723*w*, 1593*m*, 1576*m*, 1490*w*, 1448*s*, 1379*m*, 1360*m*, 1313*w*, 1263*s*, 1225*s*, 1158*w*, 1091*m*, 1060*s*, 1038*s*, 1003*m*, 955*s*. ^{1}H-NMR: 7.80–7.76 (*m*, 2 arom. H); 7.46–7.35 (*m*, 3 arom. H); 3.96 (*dq*, $^3J = 8.0$, 6.2, H–C(7)); 3.38 (*dq*, $^3J = 8.0$, 6.6, H–C(8)); 1.63, 1.40 (2*s*, 2 Me); 1.38 (*d*, $^3J = 6.2$, Me–C(7)); 1.35 (*d*, $^3J = 6.6$, Me–C(8)). ^{13}C-NMR: 164.2 (*s*, C=N); 133.8 (*s*, 1 arom. C); 131.0, 128.3, 128.1 (3*d*, 5 arom. CH); 117.5 (*s*, spiro-C); 88.4 (*d*, C(7)); 83.0 (*s*, Me_2C); 50.7 (*d*, C(8)); 24.5, 20.4 (2*q*, 2 Me); 18.3, 16.4 (2*q*, 2 Me). CI-MS: 294 (100, $[M+1]^+$), 145 (5). Anal. calc. for $C_{15}H_{19}NOS_2$ (293.45): C 61.39, H 6.53, N 4.77, S 21.85; found: C 61.29, H 6.36, N 4.83, S 21.58.

2.1.2. *Reaction with* **1b**. *a*) Reaction of **2** (111 mg, 0.5 mmol) with **1b** (2×240 mg, 6.67 mmol) and $BF_3 \cdot Et_2O$ (2×78 mg, 1.1 mmol) (20 h, r.t., CC (hexane/AcOEt 33:1)) yielded 12 mg (11%) of **2**, 111 mg (76%) of *(5*RS*,7*SR*,8*RS*)-4,4,7,8-tetramethyl-2-phenyl-6-oxa-1,9-dithia-3-azaspiro[4.4]non-2-ene* (**6**), and 16 mg (11%) of *(5*RS*,7*RS*,8*SR*)-4,4,7,8-tetramethyl-2-phenyl-6-oxa-1,9-dithia-3-azaspiro[4.4]non-2-ene* (**7**).

b) Reaction of **2** (112 mg, 0.5 mmol) with **1b** (247 mg, 3.43 mmol) and $SnCl_4$ (*ca.* 1M soln., 0.6 ml) (0.5 h, r.t., CC (hexane/AcOEt 33:1)) yielded 88 mg (60%) of **6**, 8 mg (5%) of **7**, and 26 mg (14%) of *(2*RS*,3*SR*,4′*RS*,5*SR*,5′*SR*)-2,3,4′,5′,8,8-hexamethyl-5-phenylspiro[4-oxa-6-thia-1-azabicyclo[3.3.0]octane-7,2′-[1,3]oxathiolane]* (**8**).

c) Reaction of **2** (111 mg, 0.5 mmol) with **1b** (504 mg, 7 mmol) and $SnCl_4$ (*ca.* 1M soln., 1 ml) (2 h, $0°$, CC (hexane/AcOEt 33:1)) gave 98 mg (67%) of **6**, 10 mg (7%) of **7**, 16 mg (9%) of **8**, and 16 mg (16%) of **5**.

Data of **6**: Colorless crystals. M.p. 71–72°. IR (KBr): 3065*w*, 2971*s*, 2931*s*, 2874*m*, 1594*s*, 1575*m*, 1490*w*, 1458*m*, 1448*s*, 1383*m*, 1357*m*, 1331*w*, 1314*w*, 1263*s*, 1213*m*, 1179*w*, 1153*m*, 1075*s*, 1060*s*, 1013*s*, 967*m*, 951*s*. ^{1}H-NMR: 7.80–7.77 (*m*, 2 arom. H); 7.44–7.35 (*m*, 3 arom. H); 4.46 (*dq*, $^3J = 6.3$, 4.6, H–C(7)); 3.43 (*dq*, $^3J = 6.9$, 4.6, H–C(8)); 1.63, 1.44 (2*s*, 2 Me); 1.33 (*d*, $^3J = 6.3$, Me–C(7)); 1.22 (*d*, $^3J = 6.9$, Me–C(8)). ^{13}C-NMR: 165.2 (*s*, C=N); 133.7 (*s*, 1 arom. C); 131.0, 128.3, 127.9 (3*d*, 5 arom. CH); 116.7 (*s*, spiro-C); 81.0 (*d*, C(7)); 80.8 (*s*, Me_2C); 45.3 (*d*, C(8)); 25.1, 20.3 (2*q*, 2 Me); 18.1, 15.0 (2*q*, 2 Me). CI-MS: 294 (100, $[M+1]^+$), 206 (14). Anal. calc. for $C_{15}H_{19}NOS_2$ (293.45): C 61.39, H 6.53, N 4.77, S 21.85; found: C 61.28, H 6.34, N 4.74, S 21.90.

Crystals of **6** suitable for the X-ray crystal-structure analysis were grown from hexane/CH_2Cl_2.

Data of **7**: Colorless oil. IR ($CHCl_3$): 2968*s*, 2930*s*, 2857*m*, 1722*m*, 1593*m*, 1576*m*, 1490*w*, 1457*m*, 1448*m*, 1380*s*, 1360*w*, 1263*s*, 1153*w*, 1077*s*, 1059*s*, 1013*m*, 955*s*. ^{1}H-NMR: 7.81–7.77 (*m*, 2 arom. H); 7.46–7.35 (*m*, 3 arom. H); 4.44 (*dq*, $^3J = 6.4$, 4.3, H–C(7)); 3.44 (*dq*, $^3J = 6.9$, 4.3, H–C(8)); 1.61, 1.39 (2*s*, 2 Me); 1.37 (*d*, $^3J = 6.9$, Me–C(8)); 1.32 (*d*, $^3J = 6.4$, Me–C(7)). ^{13}C-NMR: 164.6 (*s*, C=N); 133.8 (*s*, 1 arom. C); 131.0, 128.3, 128.1 (3*d*, 5 arom. CH); 116.9 (*s*, spiro-C); 85.2 (*d*, C(7)); 83.8 (*s*, Me_2C); 47.3 (*d*, C(8)); 29.7, 24.2 (2*q*, 2 Me); 16.3, 15.9 (2*q*, 2 Me). CI-MS: 294 (100, $[M+1]^+$). Anal. calc. for $C_{15}H_{19}NOS_2$ (293.45): C 61.39, H 6.53, N 4.77, S 21.85; found: C 61.44, H 6.55, N 5.05, S 21.64.

Data of **8**: Colorless crystals. M.p. 161–162°. IR (KBr): 2975*s*, 2962*s*, 2928*s*, 2899*m*, 1726*w*, 1485*w*, 1450*m*, 1378*s*, 1359*m*, 1311*w*, 1288*w*, 1223*m*, 1191*m*, 1157*m*, 1121*m*, 1076*s*, 1052*s*, 1013*m*, 990*m*, 967*s*, 928*w*. ^{1}H-NMR: 7.71–7.67 (*m*, 2 arom. H); 7.29–7.17 (*m*, 3 arom. H); 4.56 (*quint.*, ^3J = 6.4, H–C(3)); 4.25 (*dq*, ^3J = 6.3, 4.5, H–C(5′)); 3.70 (*quint.* ^3J = 6.9, H–C(2)); 3.42 (*dq*, ^3J = 6.9, 4.5, H–C(4′)); 1.54, 1.31 (2*s*, 2 Me); 1.25 (*d*, ^3J = 6.3, Me–C(5′)); 1.18 (*d*, ^3J = 6.4, Me–C(3)); 1.17, 0.91 (2*d*, ^3J = 6.9, Me–C(2), Me–C(4′)). ^{13}C-NMR: 147.3 (*s*, 1 arom. C); 127.4, 127.3, 126.3 (3*d*, 5 arom. CH); 116.1 (*s*, C(5)); 113.6 (*s*, spiro-C); 81.0 (*d*, C(3)); 76.9 (*d*, C(5′)); 72.3 (*s*, Me_2C); 56.2 (*d*, C(2)); 46.1 (*d*, C(4′)); 25.3, 24.1, 17.7, 17.6, 15.5, 15.0 (6*q*, 6 Me). CI-MS: 366 (25, $[M+1]^+$), 278 (100). Anal. calc. for $C_{19}H_{27}NO_2S_2$ (365.56): C 62.43, H 7.44, N 3.83, S 17.54; found: C 62.53, H 7.40, N 3.76, S 17.33.

In a control experiment, **8** was independently synthesized: reaction of **6** (51 mg, 0.17 mmol) with **1b** (75 mg, 1.04 mmol) and $SnCl_4$ (*ca.* 1M soln., 0.2 ml), (15 h, −78° to r.t., CC (hexane/AcOEt 33:1)), yielded 32 mg (63%) of **6** and 19 mg (30%) of **8**.

Crystals of **8** suitable for the X-ray crystal-structure analysis were grown from hexane/AcOEt.

2.1.3. *Reactions of (1*RS,*6*RS,*8*SR*)- and (1*RS,*6*RS,*8*RS*)-4′,5′-Dihydro-4′,4′-dimethyl-2′-phenylspiro[7-oxa-9-thiabicyclo[4.3.0]nonane-8,5′-[1,3]thiazole]* (**9** and **10**, resp.). *a*) Reaction of **9** (90 mg, 0.28 mmol) with **1b** (145 mg, 2.01 mmol) and $SnCl_4$ (*ca.* 1M soln., 0.35 ml) (50 h, −78° to r.t., CC (hexane/AcOEt 40:1)) yielded 10 mg (18%) of **5**, 18 mg (23%) of *(2*RS,*3*SR*)-2,3,8,8-tetramethyl-5-phenyl-4-oxa-6-thia-1-azabicyclo[3.3.0]octan-7-one* (**11**), 1.5 mg (1%) of *(1′*RS,*2*RS,*3*SR,*5*SR,*6′*RS,*7*SR*)-2,3,8,8-tetramethyl-5-phenylspiro[4-oxa-6-thia-1-azabicyclo[3.3.0]octane-7,8′-[7]oxa[9]thiabicyclo[4.3.0]nonane]* (**12**), 35 mg (39%) of **9**, and 2 mg (2%) of **10**.

b) Reaction of **9** (53 mg, 0.17 mmol) with **1b** (84 mg, 1.17 mmol) and $SnCl_4$ (*ca.* 1M soln., 0.2 ml) (30 h, −78° to r.t., CC (hexane/AcOEt 50:1)) yielded 6 mg (13%) of **11**, 8 mg (12%) of **12**, 20 mg (38%) of **9**, and 2 mg (4%) of **10**.

c) Reaction of **10** (40 mg, 0.12 mmol) with **1b** (65 mg, 0.90 mmol) and $SnCl_4$ (*ca.* 1M soln., 0.15 ml) (30 h, −78° to r.t., CC (hexane/AcOEt 50:1)) yielded 5 mg (14%) of **11**, 10 mg (22%) of *(1′*RS,*2*RS,*3*SR,*5*SR,*6′*RS,*7*RS*)-2,3,8,8-tetramethyl-5-phenylspiro[4-oxa-6-thia-1-azabicyclo[3.3.0]octane-7,8′-[7]oxa[9]thiabicyclo[4.3.0]nonane]* (**13**), 18 mg (45%) of **9**, and 1 mg (3%) of **10**.

Data of **11**: Colorless crystals. M.p. 65–67°. IR (KBr): 2982*s*, 2927*s*, 2899*m*, 2856*m*, 1697*s*, 1492*w*, 1461*m*, 1449*m*, 1388*m*, 1377*m*, 1310*w*, 1260*s*, 1202*m*, 1180*m*, 1120*s*, 1075*s*, 1025*s*, 968*m*, 923*w*, 905*m*. ^{1}H-NMR: 7.75–7.71 (*m*, 2 arom. H); 7.40–7.36 (*m*, 3 arom. H); 4.69–4.60 (*m*, H–C(3)); 3.63 (*quint.*, ^3J = 6.7, H–C(2)); 1.53 (*s*, 1 Me); 1.29 (*d*, ^3J = 6.5, Me–C(3)); 1.23 (*d*, ^3J = 6.7, Me–C(2)); 1.03 (*s*, 1 Me). ^{13}C-NMR: 211.9 (*s*, C=O); 142.7 (*s*, 1 arom. C); 129.4, 128.1, 127.2 (3*d*, 5 arom. CH); 118.9 (*s*, C(5)); 75.6 (*d*, C(3)); 75.2 (*s*, Me_2C); 56.7 (*d*, C(2)); 29.3, 22.5 (2*q*, 2 Me); 18.5, 14.4 (2*q*, 2 Me). CI-MS: 278 (100, $[M+1]^+$), 217 (5). Anal. calc. for $C_{15}H_{19}NO_2S$ (277.39): C 64.95, H 6.90, N 5.05, S 11.56; found: C 64.99, H 7.12, N 4.75, S 11.57.

Data of **12**: Colorless oil. IR ($CHCl_3$): 2931*s*, 2859*m*, 1718*m*, 1602*w*, 1453*m*, 1380*m*, 1315*w*, 1262*s*, 1177*w*, 1098*s*, 1071*m*, 1011*m*. ^{1}H-NMR: 7.70–7.67 (*m*, 2 arom. H); 7.30–7.22 (*m*, 3 arom. H); 4.58 (*quint.*, ^3J = 6.5, H–C(3)); 3.88 (*quint.*, ^3J = 6.8, H–C(2)); 3.53–3.45 (*m*, H–C(6′)); 2.77 (*ddd*, ^3J = 11.8, 9.7, 3.6, H–C(1′)); 2.20–2.05, 1.89–1.76 (2*m*, 2 CH_2); 1.54, 1.26 (2*s*, 2 Me); 1.51–1.21 (*m*, 2 CH_2); 1.20 (*d*, ^3J = 6.5, Me–C(3)); 0.99 (*d*, ^3J = 6.8, Me–C(2)). ^{13}C-NMR: 146.1 (*s*, 1 arom. C); 127.8, 127.5, 126.5 (3*d*, 5 arom. CH); 117.1 (*s*, C(5)); 116.3 (*s*, spiro-C); 87.8 (*d*, C(3)); 76.2 (*d*, C(6′)); 72.7 (*s*, Me_2C); 55.8 (*d*, C(2)); 54.1 (*d*, C(1′)); 30.1, 28.9 (2*t*, 2 CH_2); 27.1, 22.9 (2*q*, 2 Me); 25.4, 23.9 (2*t*, 2 CH_2); 18.1, 15.0 (2*q*, 2 Me). CI-MS: 392 (16, $[M+1]^+$), 278 (100), 176 (19).

Data of **13**: Colorless oil. IR ($CHCl_3$): 2939*s*, 2862*m*, 1720*m*, 1602*w*, 1491*w*, 1448*m*, 1380*m*, 1262*s*, 1177*w*, 1099*s*, 1066*m*, 1008*m*, 946*w*. ^{1}H-NMR: 7.71–7.67 (*m*, 2 arom. H); 7.30–7.22 (*m*, 3 arom. H); 4.74 (*quint.*, ^3J = 6.5, H–C(3)); 3.72 (*quint.*, ^3J = 6.7, H–C(2)); 3.49–3.40 (*m*, H–C(6′)); 3.15 (*ddd*, ^3J = 11.5, 9.9, 3.5, H–C(1′)); 2.24–2.13, 1.89–1.81 (2*m*, 2 CH_2); 1.52, 1.22 (2*s*, 2 Me); 1.45–1.07 (*m*, 2 CH_2); 1.20 (*d*, ^3J = 6.5, Me–C(3)); 1.05 (*d*, ^3J = 6.7, Me–C(2)). ^{13}C-NMR: 145.5 (*s*, 1 arom. C); 128.0, 127.6, 126.6 (3*d*, 5 arom. CH); 121.1 (*s*, C(5)); 115.9 (*s*, spiro-C); 89.2 (*d*, C(3)); 75.4 (*d*, C(6′)); 72.8 (*s*, Me_2C); 55.9 (*d*, C(2)); 53.7 (*d*, C(1′)); 30.7, 28.3 (2*t*, 2 CH_2); 28.2, 24.5 (2*q*, 2 Me); 25.3, 23.9 (2*t*, 2 CH_2); 18.2, 14.7 (2*q*, 2 Me). CI-MS: 392 (100, $[M+1]^+$), 278 (88), 176 (22).

2.1.4. *Isomerization of (1″*RS,*6″*RS,*8″*SR*)- and (1″*RS,*6″*RS,*8″*RS*)-4′,5′-Dihydro-2′-phenyldispiro[cyclopentane-1,4′-[1,3]thiazole-5′,8″-[7]oxa[9]thiabicyclo[4.3.0]nonane]* (**14** and **15**, resp.). *a*) Reaction of **14** (20 mg, 0.058 mmol) with $SnCl_4$ (*ca.* 1M soln., 0.1 ml) (15 h, −78° to r.t., CC (hexane/AcOEt 30:1)) yielded 18 mg (90%) of **14**.

b) Reaction of **15** (20 mg, 0.058 mmol) with $SnCl_4$ (*ca.* 1M soln., 0.1 ml) (15 h, −78° to r.t., CC (hexane/AcOEt 30:1)) yielded 19 mg (95%) of **14**.

2.2. *Reactions of Bis(4-methoxyphenyl)methanethione* (**16**). 2.2.1. *Reactions with* **1a**. *a*) Reaction of **16** (258 mg, 1 mmol) with **1a** (360 mg, 5 mmol) and $BF_3 \cdot Et_2O$ (170 mg, 1.19 mmol) (30 s, −78°, CC (hexane/AcOEt 20:1)) yielded 103 mg (31%) of *(4*RS,*5*RS*)-4,5-dimethyl-2,2-bis(4-methoxyphenyl)-1,3-oxathiolane* (**17**) and 139 mg (57%) of *bis(4-methoxyphenyl)methanone* (**18**).

b) Reaction of **16** (258 mg, 1 mmol) with **1a** (360 mg, 5 mmol) and $BF_3 \cdot Et_2O$ (161 mg, 1.13 mmol) (15 s, −90°, CC (hexane/AcOEt 20:1)) yielded 201 mg (61%) of **17** and 95 mg (39%) of **18**.

Data of **17**: Colorless oil. IR ($CHCl_3$): 3008*m*, 2978*m*, 2934*m*, 2910*m*, 2871*w*, 2839*w*, 1608*s*, 1584*w*, 1509*s*, 1465*m*, 1443*m*, 1414*w*, 1377*w*, 1303*m*, 1250*s*, 1173*s*, 1112*w*, 1095*m*, 1035*s*, 925*w*. ^{1}H-NMR: 7.57–7.53 (*m*, 2 arom. H); 7.34–7.30 (*m*, 2 arom. H); 6.91–6.87 (*m*, 2 arom. H); 6.82–6.79 (*m*, 2 arom. H); 3.83, 3.78 (2*s*, 2 MeO); 3.77 (*dq*, ^3J = 9.0, 6.0, H–C(5)); 3.49 (*dq*, ^3J = 9.0, 6.5, H–C(4)); 1.45 (*d*, ^3J = 6.0, Me–C(5)); 1.29 (*d*, ^3J = 6.5, Me–C(4)). ^{13}C-NMR: 158.9, 158.8, 138.2, 138.0 (4*s*, 4 arom. C); 128.6, 127.8, 113.1 (3*d*, 8 arom. CH); 97.0 (*s*, C(2)); 84.1 (*d*, C(5)); 55.2 (*q*, 2 MeO); 52.5 (*d*, C(4)); 17.4, 17.0 (2*q*, 2 Me). CI-MS: 331 (100, $[M+1]^+$), 289 (14), 243 (82). Anal. calc. for $C_{19}H_{22}O_3S$ (330.45): C 69.06, H 6.71, S 9.70; found: C 69.12, H 6.79, S 9.82.

2.2.2. *Reaction with* **1b**. Reaction of **16** (258 mg, 1 mmol) with **1b** (360 mg, 5 mmol) and $BF_3 \cdot Et_2O$ (170 mg, 1.19 mmol) (30 s, −90°, CC (hexane/AcOEt 20:1)) yielded 291 mg (88%) of *(4*RS,*5*SR*)-4,5-dimethyl-2,2-bis(4-methoxyphenyl)-1,3-oxathiolane* (**19**) and 25 mg (10%) of **18**.

Data of **19**: Colorless oil. IR ($CHCl_3$): 3005*w*, 2963*m*, 2936*m*, 2911*w*, 2839*w*, 1608*m*, 1584*w*, 1509*s*, 1465*m*, 1442*w*, 1414*w*, 1380*w*, 1303*m*, 1251*s*, 1172*s*, 1097*m*, 1078*s*, 1035*s*, 1010*s*, 923*w*. ^{1}H-NMR: 7.57–7.52 (*m*, 2 arom. H); 7.35–7.30 (*m*, 2 arom. H); 6.92–6.87 (*m*, 2 arom. H); 6.83–6.78 (*m*, 2 arom. H); 4.23 (*dq*, ^3J = 6.3, 4.9, H–C(5)); 3.83, 3.78 (2*s*, 2 MeO) 3.56 (*dq*, ^3J = 6.9, 4.9, H–C(4)); 1.40 (*d*, ^3J = 6.3, Me–C(5)); 1.37 (*d*, ^3J = 6.9, Me–C(4)). ^{13}C-NMR: 158.9, 158.7, 138.0, 137.9 (4*s*, 4 arom. C); 128.5, 128.0, 113.2, 113.1 (4*d*, 8 arom. CH); 97.0 (*s*, C(2)); 79.8 (*d*, C(5)); 55.3, 55.2 (2*q*, 2 MeO); 49.0 (*d*, C(4)); 18.2, 15.6 (2*q*, 2 Me). CI-MS: 331 (95, $[M+1]^+$), 243 (100). Anal. calc. for $C_{19}H_{22}O_3S$ (330.45): C 69.06, H 6.71, S 9.70; found: C 69.00, H 6.76, S 9.78.

2.3. *Reactions of 2,2,4,4-Tetramethyl-3-thioxocyclobutanone* (**20**). 2.3.1. *Reactions with* **1a**. Reaction of **20** (156 mg, 1 mmol) with **1a** (360 mg, 5 mmol) and $SnCl_4$ (*ca.* 1M soln., 2.2 ml) (0.5 h, 0°, CC (hexane/AcOEt 40:1) and PLC (hexane/AcOEt 30:1)) yielded 62 mg (27%) of *(6*RS,*7*RS*)-1,1,3,3,6,7-hexamethyl-5-oxa-8-thiaspiro[3.4]octan-2-one* (**21**) and 24 mg (8%) of a *ca.* 1:1 mixture of *(2*RS,*3*RS,*9*RS,*10*RS*)-* and *(2*RS,*3*RS,*9*SR,*10*SR*)-2,3,6,6,9,10,12,12-octamethyl-1,4,8-trioxa-11-thiadispiro[4.1.4.1]dodecane* (**22a** and **22b**, resp.).

Data of **21**: Colorless oil. IR ($CHCl_3$): 2971*s*, 2932*s*, 2870*m*, 1772*s*, 1462*s*, 1380*s*, 1364*m*, 1290*w*, 1227*m*, 1212*m*, 1156*w*, 1097*s*, 1076*m*, 1029*s*, 952*m*, 911*w*. ^{1}H-NMR: 3.52 (*dq*, ^3J = 8.7, 6.0, H–C(6)); 3.03 (*dq*, ^3J = 8.7, 6.5, H–C(7)); 1.29 (*d*, ^3J = 6.0, Me–C(6)); 1.26 (*d*, ^3J = 6.5, Me–C(7)); 1.23, 1.22, 1.16, 1.12 (4*s*, 4 Me). ^{13}C-NMR: 221.4 (*s*, C=O); 97.8 (*s*, spiro-C); 85.7 (*d*, C(6)); 66.2, 64.6 (2*s*, 2 Me_2C); 49.8 (*d*, C(7)); 24.2, 23.9, 18.3, 17.2, 17.0, 16.9 (6*q*, 6 Me). CI-MS: 229 (75, $[M+1]^+$), 158 (100). Anal. calc. for $C_{12}H_{20}O_2S$ (228.36): C 63.12, H 8.83, S 14.04; found: C 63.08, H 8.80, S 13.84.

Data of **22a** *and* **22b** (*ca.* 1:1 mixture): Colorless crystals. M.p. 56–58°. IR (KBr): 2970*s*, 2930*s*, 2870*m*, 1467*m*, 1443*m*, 1375*m*, 1288*w*, 1276*w*, 1241*m*, 1224*m*, 1153*w*, 1120*m*, 1092*s*, 1062*m*, 1034*s*, 1019*s*, 986*m*, 936*m*, 916*w*. ^{1}H-NMR: 3.52–3.35 (*m*, 2 × H–C(2), H–C(3), H–C(9)); 2.89 (*dq*, ^3J = 8.8, 6.7, 2 H–C(10)); 1.27 (*d*, ^3J = 5.7, 2 Me); 1.220 (*d*, ^3J = 5.7, 1 Me); 1.215 (*d*, ^3J = 6.7, 2 Me–C(10)); 1.210 (*d*, ^3J = 5.7, 1 Me); 1.19 (*d*, ^3J = 5.7, 1 Me); 1.18 (*d*, ^3J = 5.6, 1 Me); 1.16, 1.15, 1.14, 1.03, 1.02, 0.99, 0.98 (7*s*, 8 Me). ^{13}C-NMR: 110.4, 99.4 (2*s*, 2 × 2 spiro-C); 85.3, 85.2, 78.8, 78.7, 78.4 (5*d*, 2 × C(2), C(3), C(9)); 55.2, 53.7 (2*s*, 2 × 2 Me_2C); 49.0 (*d*, 2 C(10)); 25.1, 25.0, 24.1, 24.0, 19.5, 18.3, 18.0, 17.3, 16.8, 16.7 (10*q*, 2 × 8 Me). CI-MS: 301 (100, $[M+1]^+$), 213 (18), 142 (11). Anal. calc. for $C_{16}H_{28}O_3S$ (300.46): C 63.96, H 9.39, S 10.67; found: C 64.46, H 9.48, S 10.60.

Crystals of **22a** suitable for the X-ray crystal-structure analysis were grown from CH_2Cl_2.

2.3.2. *Reaction with* **1b**. Reaction of **20** (156 mg, 1 mmol) with **1b** (370 mg, 5.14 mmol) and $SnCl_4$ (*ca.* 1M soln., 2.2 ml) (0.5 h, 0°, CC (hexane/AcOEt 40:1) and PLC (hexane/AcOEt 30:1)) yielded 64 mg (28%) of *(6*RS,*7*SR*)-1,1,3,3,6,7-hexamethyl-5-oxa-8-thiaspiro[3.4]octan-2-one* (**23**) and 19 mg (6%) of *(2*RS,*3*SR,*9*SR,*10*RS*)- or (2*RS,*3*SR,*9*RS,*10*SR*)-2,3,6,6,9,10,12,12-octamethyl-1,4,8-trioxa-11-thiadispiro[4.1.4.1]dodecane* (**24a** or **24b**, resp.).

Data of **23**: Colorless crystals. M.p. 50–51°. IR (KBr): 2971*s*, 2929*m*, 2892*m*, 2865*m*, 1785*s*, 1765*s*, 1458*s*, 1445*m*, 1378*s*, 1363*m*, 1336*w*, 1312*w*, 1253*m*, 1198*m*, 1158*m*, 1096*s*, 1040*m*, 1017*s*, 949*m*, 905*w*. ^{1}H-NMR: 4.05 (*dq*, ^3J = 6.3, 4.2, H–C(6)); 3.25 (*dq*, ^3J = 6.8, 4.2, H–C(7)); 1.26 (*d*, ^3J = 6.3, Me–C(6)); 1.23 (*d*, ^3J = 6.8, Me–C(7)); 1.17, 1.15, 1.12 (3*s*, 1:2:1, 4 Me). ^{13}C-NMR: 221.6 (*s*, C=O); 97.6 (*s*, spiro-C); 82.0 (*d*, C(6)); 66.4, 64.3 (2*s*, 2 Me_2C); 46.1 (*d*, C(7)); 24.7, 23.7, 17.6, 17.6, 17.2, 15.4 (6*q*, 6 Me). ESI-MS: 251 (100, $[M+Na]^+$). Anal. calc. for $C_{12}H_{20}O_2S$ (228.36): C 63.12, H 8.83, S 14.04; found: C 62.83, H 8.77, S 14.12.

Crystals of **23** suitable for the X-ray crystal-structure analysis were grown from CH_2Cl_2.

Data of **24a** *or* **24b**: Colorless oil. IR ($CHCl_3$): 2980*s*, 2933*s*, 2872*m*, 1769*w*, 1467*s*, 1456*m*, 1442*m*, 1380*s*, 1366*w*, 1338*w*, 1298*w*, 1275*m*, 1262*w*, 1238*m*, 1148*m*, 1083*s*, 1042*s*, 1018*s*, 983*w*, 933*w*. ^{1}H-NMR: 4.12–3.96 (*m*, H–C(2), H–C(3), H–C(9)); 3.10 (*dq*, ^3J = 6.8, 4.2, H–C(10)); 1.24 (*d*, ^3J = 6.3, 1 Me); 1.17, 1.16 (2*s*, 2 Me); 1.11 (*d*, ^3J = 6.8, Me–C(10)); 1.10, 1.07 (2*d*, ^3J = 6.2, 2 Me); 1.01, 1.00 (2*s*, 2 Me). ^{13}C-NMR: 110.1, 99.3 (2*s*, 2 spiro-C); 81.4, 74.3, 73.9 (3*d*, C(2), C(3), C(9)); 54.6, 54.3 (2*s*, 2 Me_2C); 45.3 (*d*, C(10)); 25.1, 24.2, 18.0, 17.7, 17.5, 15.7, 15.0, 14.9 (8*q*, 8 Me). CI-MS: 301 (100, $[M+1]^+$), 213 (21). Anal. calc. for $C_{16}H_{28}O_3S$ (300.46): C 63.96, H 9.39, S 10.67; found: C 63.83, H 9.49, S 10.91.

3. *X-Ray Crystal-Structure Determination of* **6**, **8**, **22a**, *and* **23** (see *Table* and *Figs. 1–3*)[5]). All measurements were made on a *Rigaku AFC5R* diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71069 Å) and a 12-kW rotating anode generator. The $\omega/2\theta$ scan mode was employed for data collection. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Data collection and refinement parameters are given in the *Table*, views of the molecules are shown in *Figs. 1–3*. The structures were

Table. *Crystallographic Data of Compounds* **6**, **8**, **22a**, *and* **23**

	6	**8**	**22a**	**23**
Crystallized from	hexane/CH_2Cl_2	hexane/AcOEt	CH_2Cl_2	CH_2Cl_2
Empirical formula	$C_{15}H_{19}NOS_2$	$C_{19}H_{27}NO_2S_2$	$C_{16}H_{28}O_3S$	$C_{12}H_{20}O_2S$
Formula weight [g·mol^{-1}]	293.44	365.55	300.45	228.35
Crystal color, habit	colorless, prism	colorless, prism	colorless, prism	colorless, prism
Crystal dimensions [mm]	0.15 × 0.40 × 0.43	0.35 × 0.38 × 0.50	0.20 × 0.20 × 0.50	0.45 × 0.45 × 0.48
Temp. [K]	173(1)	173(1)	173(1)	173(1)
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic
Space group	*C*2/*c*	$P2_1/n$	$Cmc2_1$	$P\bar{1}$
Z	8	4	4	2
Reflections for cell determination	25	25	25	25
2θ Range for cell determination [°]	26–35	39–40	23–34	39–40
Unit cell parameters *a* [Å]	32.617(9)	13.009(8)	13.630(2)	9.095(1)
b [Å]	10.573(7)	7.263(6)	11.503(5)	12.319(2)
c [Å]	9.125(6)	20.732(6)	10.843(4)	6.126(1)
α [°]	90	90	90	100.56(1)
β [°]	102.20(5)	102.98(3)	90	109.27(1)
γ [°]	90	90	90	86.25(1)
V [Å^3]	3075(3)	1909(2)	1700.0(8)	637.0(2)
D_x [g cm^{-3}]	1.268	1.272	1.174	1.190
μ(MoK_α) [mm^{-1}]	0.338	0.290	0.195	0.235
$2\theta_{(max)}$ [°]	55	60	55	55
Total reflections measured	3778	6211	1321	3107
Symmetry independent reflections	3522	5563	1170	2923
Reflections used [$I > 2\sigma(I)$]	2330	4225	1170 [634 > 2σ (*I*)]	2559
Parameters refined	172	326	138	216
Final *R*	0.0754	0.0400	0.0580	0.0318
wR ($w = [\sigma^2(F_o) + (0.005F_o))^2]^{-1}$)	0.0736	0.0365	0.1871[a])	0.0329
Goodness of fit	3.056	1.925	1.044	2.405
Secondary extinction coefficient	–	$1.2(5)\cdot10^{-7}$	–	–
Final Δ_{max}/σ	0.0004	0.0005	0.003	0.0004
$\Delta\rho$ (max; min) [e·Å^{-3}]	0.80; −0.44	0.39; −0.26	0.18; −0.24	0.34; −0.18

[a]) $w = [\sigma^2(F_o^2) + (0.1008P)^2]^{-1}$, where $P = 1/3\ (F_o^2 + 2\ F_c^2)$

[5]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC – 145101 – 145104 for **6**, **8**, **22a**, and **23**, resp. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

solved by direct methods using *SIR92* [24]. For each structure, all non-H-atoms were refined anisotropically and the H-atoms were treated as described below.

Refinement of each structure was carried out on F (F^2 for **22a**) using full-matrix least-squares procedures. A correction for secondary extinction was applied in the case of **8**. In the case of **22a**, reflection 200 was omitted from the final refinement because of suspected extinction effects. Neutral-atom-scattering factors for non-H-atoms were taken from [25a] and the scattering factors for H-atoms from [26]. Anomalous dispersion effects were included in F_c [27]. The values for f' and f'' were those of [25b]. The values of the mass-attenuation coefficients are those of [25c]. All calculations were performed using the *teXsan* crystallographic software package [28], as well as *SHELXL97* for **22a** [29].

In the case of **6**, all of the H-atoms were fixed in geometrically calculated positions with $d(C-H) = 0.95$ Å and each was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom. For **8** and **23**, all of the H-atoms were located in difference-electron-density maps, and their positions were allowed to refine together with individual isotropic displacement parameters. In compound **22a**, the molecule sits across a crystallographic mirror plane which passes through the four Me groups of the four-membered ring. As the molecule itself cannot possess such mirror symmetry, the model has to be defined such that the S-atom in one five-membered ring and the corresponding O-atom in the other five-membered ring occupy overlapping disordered sites with 50% site occupation. These two atoms could successfully be refined individually. In addition, the two Me-substituted C-atoms are disordered over two alternate twist arrangements of the five-membered ring and one of the Me C-atoms is also disordered. These disordered sites could be resolved and refined satisfactorily with 50% site occupation factors. All of the H-atoms were fixed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom ($1.5U_{eq}$ for the Me groups).

The space groups of compounds **6**, **8**, and **23** are centrosymmetric and, therefore, the crystals are racemic. In **6**, the Me groups of the 1,3-oxathiolane ring are *cis*-configured, and the ring has an envelope conformation with C(4)[6]) as the flap. The 4,5-dihydro-1,3-thiazole ring also has an envelope conformation, but in this case the spiro atom C(2) acts as the envelope flap. In compound **8**, the vicinal Me groups of the 1,3-oxathiolane ring, as well as of the 1,3-oxazolidine ring, are *cis*-configured, and the Ph ring at C(7)[6]) is in a *cis*-relationship to the Me groups at C(13) and C(14). The 1,3-oxathiolane ring has an envelope conformation with C(4) as the envelope flap, the central 1,3-thiazolidine ring has a half-chair conformation twisted on the C(2)–C(9) bond, and the 1,3-oxazolidine ring has an envelope conformation with N(8) as the envelope flap. The Me groups in the five-membered ring of **23** are also *cis*-configured. The 1,3-oxathiolane ring has an envelope conformation with C(4)[6]) as the envelope flap. The space group of **22a** is non-centrosymmetric; however, the crystals are racemic. The absolute direction of the polar axis has been chosen arbitrarily as the quality of the data did not permit a reliable determination of the absolute structure. The molecule sits across a crystallographic mirror plane. By consideration of the bond lengths in the disordered region (see above), one can select the sets of atoms which constitute each conformation of the molecule and thereby deduce that the adjacent Me substituents must be *trans* to one another. However, it is more difficult to determine the relative configuration of the Me groups at opposite ends of the molecule, and the diagram represents only one possibility. From geometrical considerations, it is likely that this diagram represents the true overall relative configuration, but the alternative possibility also has feasible, but slightly less ideal geometry.

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