Reaction of 1,3-Thiazole-5(4*H*)-thiones with 1,2-Epoxycycloalkanes: Formation of Spirocyclic 1,3-Oxathiolanes

by **Milen Blagoev**[1]**, Anthony Linden**, and **Heinz Heimgartner***

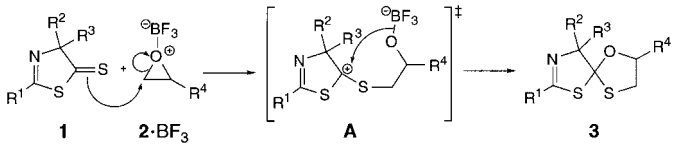
Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

Treatment of solutions of 1,3-thiazole-5(4*H*)-thiones **1** in CH_2Cl_2 at room temperature with $BF_3 \cdot Et_2O$ and 1,2-epoxycyclohexane (7-oxabicyclo[4.1.0]heptane; **2a**) or 1,2-epoxycyclopentane (6-oxabicyclo[3.1.0]hexane; **2b**) yielded mixtures of diastereoisomeric spirocyclic 1,3-oxathiolanes (**3**/**4** and **8**/**9**, respectively). In addition, the corresponding 1,3-dithiolane **6** was formed as a minor product in the reaction of 4,4-dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione (**1a**) with **2a**. The structures of the different types of products have been established by X-ray crystal-structure analysis. An ionic two-step mechanism *via* nucleophilic ring-opening of the complexed oxirane by the attack of the thiocarbonyl S-atom is proposed. This proposal is supported by the formation of the propellane **10** with a *Wagner-Meerwein* rearrangement as the key step.

1. Introduction. – Most conveniently, 1,3-oxathiolanes are prepared by acid-catalyzed condensation of 2-sulfanylalkan-1-oles or their derivatives with carbonyl compounds to form the mixed cyclic O,S-acetal [1][2]. They have become important as radioprotectants, and they are biologically active [2] and known as useful carbonyl protecting groups, because the hemithioketal group can be removed under neutral conditions with *Raney*-Ni [3].

A completely different synthetic strategy for the formation of 1,3-oxathiolanes is based on the *Lewis*-acid-catalyzed reaction of thiocarbonyl compounds with oxiranes [4][5][2]). This direct condensation has some advantages, because oxiranes and thiocarbonyl derivatives are easily accessible, and it does not require procedures involving H_2O removal to shift the equilibrium towards the products, as is necessary in the other methodology. Recently, the synthesis of spirocyclic 1,3-oxathiolanes, resulting from the reaction of oxiranes with 1,3-thiazole-5(4*H*)-thiones and trithiocarbonates, respectively, has been reported [4][5]. As the presence of a *Lewis* acid proved to be essential, the mechanism in *Scheme 1* has been proposed.

Scheme 1



[1]) Part of the planned Ph.D. thesis of *M.B.*, University of Zürich.

[2]) Recently, this reaction has been used for converting 1,3-dithiolane-2-thiones into 1,3-dithiolan-2-ones *via* the formation of an intermediate 1-oxa-4,6,9-trithiaspiro[4.4]nonane [6].

With the aim of generalizing this method for the synthesis of spirocyclic oxathiolanes, we extended the study to bicyclic oxiranes. Here, we describe the reactions of 1,3-thiazole-5(4*H*)-thiones **1a**–**c** with 1,2-epoxycyclohexane (**2a**) and 1,2-epoxycyclopentane (**2b**).

2. Results. – 2.1. *Reactions with 1,2-Epoxycyclohexane* (*7-Oxabicyclo[4.1.0]heptane*; **2a**). As a first example, 4,4-dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione (**1a**) was chosen. After the addition of $BF_3 \cdot Et_2O$, the CH_2Cl_2 solution was cooled to $-78°$ and 3 equiv. of **2a** were added. As the oxirane was consumed faster than the thiazole-thione **1a** (TLC), another equiv. of **2a** was added in order to completely consume the thiocarbonyl compound. The mixture was allowed to warm to room temperature overnight, and the solution turned almost colorless. Two products were detected (TLC), isolated by column chromatography, and identified as the diastereoisomeric 1:1 adducts **3a** and **4a** (*Scheme 2* and *Table 1*).

Scheme 2

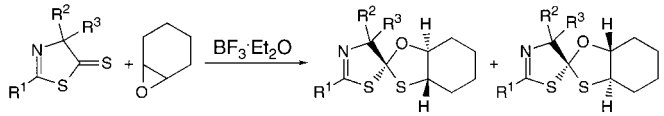


Table 1. *Formation of Spirocyclic 1,3-Oxathiolanes* **3** and **4** *from the BF_3-Catalyzed Reaction of 1,3-Thiazole-5(4*H*)-thiones* **1** *and 1,2-Epoxycyclohexane* (**2a**)

1		Reaction time [h]	Ratio **3**/**4**	Yield [%]
a	$R^1 = Ph$, $R^2 = R^3 = Me$	18[a])	1.7:1	84
b	$R^1 = Ph$, $R^2 - R^3 = -(CH_2)_4-$	5[a])	2.7:1	74
c	$R^1 = PhCH_2$, $R^2 = R^3 = Me$	19[b])	3.5:1	79

[a]) At $-78°$. [b]) At room temperature.

The two diastereoisomers showed pronounced differences in the ^{1}H-NMR spectra in the region of the CH groups of the fused ring system. For instance, in **3a** the signal of CHO appears at 3.67 ppm as *ddd* with $J = 10.9$, 9.9, and 3.7 Hz, and CHS absorbs at 2.89 ppm as *ddd* with $J = 11.7$, 9.9, and 3.5 Hz ($\Delta\delta = 0.78$ ppm). The corresponding signals of **4a** are at 3.51 ppm (*ddd*, $J = 10.9$, 9.9, and 3.7 Hz) and 3.10 ppm (*ddd*, $J =$ 11.4, 9.9, and 3.5 Hz; $\Delta\delta = 0.41$ ppm). This characteristic pattern remained similar in the adducts with thiazole-thiones **1b** and **1c** and was used for distinguishing between the diastereoisomers.

In the case of the reaction of 2-phenyl-3-thia-1-azaspiro[4.4]non-1-ene-4-thione (**1b**) with **2a**, the visual observation as well as TLC control indicated that this compound was more reactive than **1a**. It was completely consumed within 5 h. Apart from **3b**/**4b**, the corresponding 1,3-thiazol-5(4*H*)-one **5b** (*cf. Scheme 4*) was isolated in 20% yield. 2-Benzyl-4,4-dimethyl-1,3-thiazole-5(4*H*)-thione (**1c**) was found to be considerably less reactive than **1a** and **1b**. Its consumption at $-78°$ in the presence of 5 equiv. of **2a** was slow and, therefore, the reaction was carried out at room tem-

perature after 2 additional equiv. of **2a** had been added. By analogy to the experiments with **1a** and **1b**, the two 1:1 adducts **3c** and **4c** were separated chromatographically.

In all three cases, the spirocyclic 1:1 adducts were isolated in good yields (*Table 1*), but the ratio of the diastereoisomers varied from case to case.

The diastereoisomers **3b** and **4b** were recrystallized from CH_2Cl_2/i-PrOH, and their structures were established by X-ray crystal-structure analysis (*Fig. 1*). In both molecules, the 1,3-oxathiolane and cyclohexane rings are *trans*-fused, in accordance with $^3J(2,3)$[3]) values of 9.8 and 10.0 Hz, respectively. Since the space groups of **3b** and **4b** are centrosymmetric, the crystals are racemic. The molecule **3b** has the (2*R**,3*R**,5*S**)- and the molecule **4b** the (2*R**,3*R**,5*R**)-configuration. In both structures, each five-membered ring has the envelope conformation with C(3), C(5), and C(9), and C(2), C(5), and C(9), respectively, forming the envelope flaps in the oxathiolane, thiazole, and cyclopentane rings. The cyclohexane ring of **3b** and **4b** has the chair conformation with S(1) and O(4) in equatorial positions.

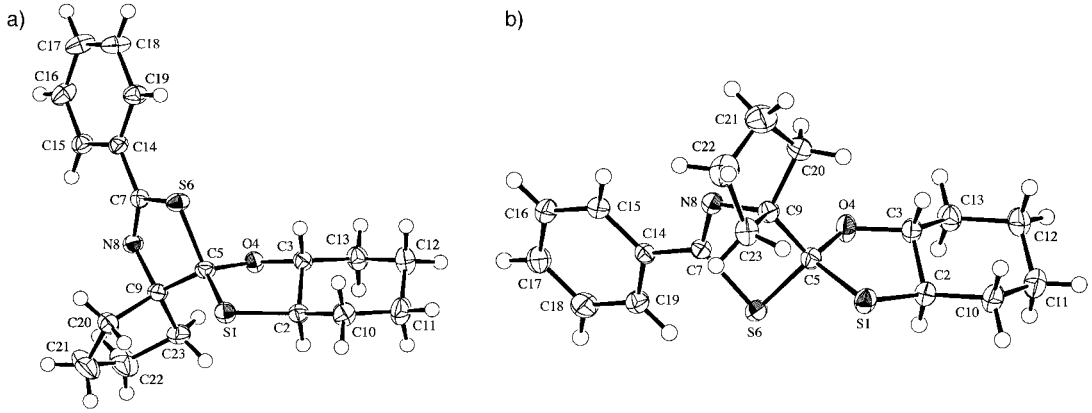
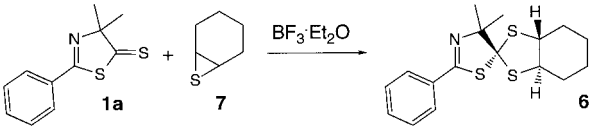


Fig. 1. *ORTEP Plots* [7] *of the molecular structures of* a) **3b** *and* b) **4b** (arbitrary numbering of the atoms; 50% probability ellipsoids)

In addition to the experiments at −78°, the reaction of **1a** and **2a** was also carried out at room temperature. Besides **3a** and **4a**, isolated in 79% yield, the unexpected spirocyclic dithiolane **6** (*Scheme 3*) with three S-atoms was obtained in *ca.* 1% yield.

Scheme 3



By analogy to previous results [5][8], we proposed that **6** was formed *via* the reaction of **1a** with 1,2-epithiocyclohexane (7-thiabicyclo[4.1.0]heptane; **7**), which could be generated *in situ* by the decomposition of **3** or **4** (*cf.* [6]). The second product

[3]) The arbitrary atom numbering in *Fig. 1* is used.

of this decomposition should be 1,3-thiazol-5(4*H*)-one **5a** (*cf. Scheme 4*). To confirm this proposal, a control experiment with **1a** and commercially available **7** was carried out at 0°. Unfortunately, it was not possible to achieve complete conversion of **1a**, probably due to the very high reactivity of **7**, which polymerized partially under the reaction conditions. Therefore, 60% of **1a** was recovered. The only product, which could be isolated in 85% yield (with respect to consumed **1a**), was the dithiolane **6**.

Crystals suitable for an X-ray crystal-structure analysis were grown, and the structure of **6** was established (*Fig. 2*). The five-membered ring containing S(1) and S(3) has the half-chair conformation twisted on the C(4)–C(5)bond, while the thiazole ring has the envelope conformation with the spiro atom, C(2), as the envelope flap[4]). The cyclohexane ring shows again the chair conformation with S(1) and S(3) occupying the equatorial positions.

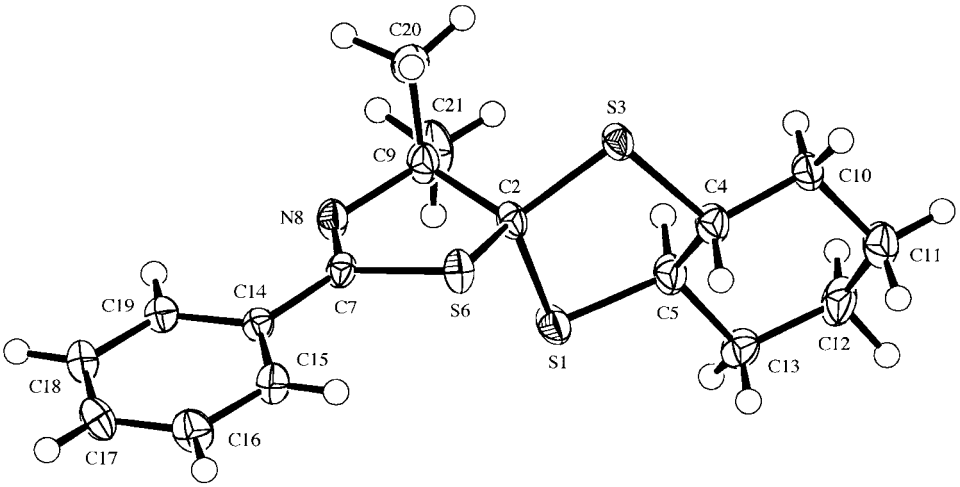


Fig. 2. *ORTEP Plot* [7] *of the molecular structure of* **6** (arbitrary numbering of the atoms; 50% probability ellipsoids)

2.2. *Reactions with 1,2-Epoxycyclopentane* (*6-Oxabicyclo[3.1.0]hexane*; **2b**). In general, under the same conditions for the reactions of **2a** with 1,3-thiazole-5(4*H*)-thiones **1**, **2b** showed the greater reactivity, which was reflected in shorter reaction times. In the case of **1a**, 5 equiv. of **2b** were added in portions at −78° to the CH_2Cl_2 solution containing $BF_3 \cdot Et_2O$, and the color changed from orange to lemon yellow. The usual workup of the mixture, followed by separation by column chromatography, resulted in the two diastereoisomeric 1 : 1 adducts, **8a** and **9a**, in 76% yield (ratio **8a**/**9a** 8.5 : 1; *Scheme 4* and *Table 2*). These products show a similar pattern in the ^{1}H-NMR spectra, with $\Delta\delta$(CHO, CHS) = 0.93 and 0.56 ppm, respectively. The ^3J(CHO,CHS) values of 10.2 and 10.3 Hz, respectively, indicate the *trans*-fusion of the cyclopentane ring. In addition to **8a** and **9a**, a small amount of the corresponding thiazolone **5a** has been isolated.

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4) The arbitrary atom numbering in *Fig. 2* is used.

Scheme 4

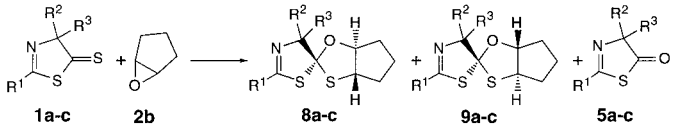


Table 2. *Products of the BF_3-Catalyzed Reaction of 1,3-Thiazole-5(4*H*)-thiones* **1** *and 1,2-Epoxycyclopentane* (**2b**)

1		Ratio **8**/**9**	Yield [%]	**5** [%]
a	R^1 = Ph, R^2 = R^3 = Me	8.5 : 1	76	7
b	R^1 = Ph, R^2–R^3 = –$(CH_2)_4$–	20 : 1	65	13
c	R^1 = $PhCH_2$, R^2 = R^3 = Me	7.7 : 1	75	6

Crystals of **8a** and **9a** suitable for X-ray crystal-structure analysis were grown from CH_2Cl_2/i-PrOH, and the structures were established (*Fig. 3*). In both cases, the space group is centrosymmetric and, therefore, the crystals are racemic. Two independent molecules are in the asymmetric unit of **8a**, but there are no significant geometrical differences between them. The asymmetric unit also contains a H_2O molecule, which forms H-bonds with each of the independent molecules. Each of the five-membered rings containing heteroatoms has the envelope conformation with C(3) and C(5) being the envelope flap in the oxathiolane and thiazole ring, respectively[5]). The *trans*-fused cyclopentane ring is a half-chair twisted at the C(2)–C(3) bond. In the asymmetric unit of **9a**, there are also two independent molecules, and, again, there are no significant differences in their conformations. The five-membered ring with S(6) and N(8) has the envelope conformation with C(2) as the envelope flap. The *trans*-fused oxathiolane ring and the cyclopentane ring are half-chairs with each being twisted at the C(4)–C(5) bond.

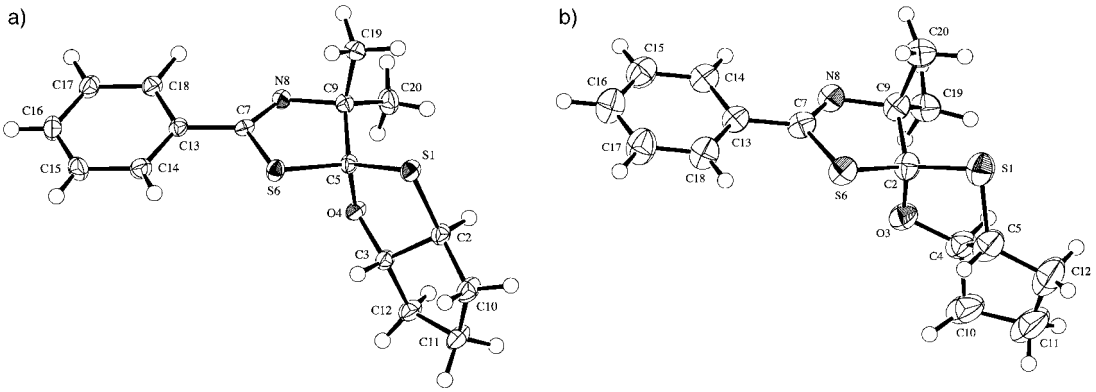


Fig. 3. *ORTEP Plots* [7] *of the molecular structures of* a) **8a** *and* b) **9a** (only one of the two independent molecules in the asymmetric unit is shown in each case; arbitrary numbering of the atoms; 50% probability ellipsoids)

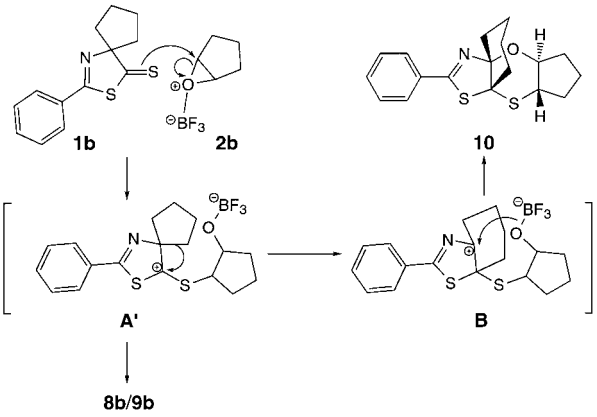
5) The arbitrary atom numbering in *Fig. 3* is used.

The reaction of **1b** with **2b** was performed under similar conditions, and the two 1:1 adducts **8b** and **9b** were isolated in a ratio of 20:1 and a total yield of 73%. The ^{1}H-NMR pattern of the CH protons of the cyclopentane ring is analogous to those of **8a** and **9a**, the structures of which have been established by X-ray crystal-structure analysis. Again, the corresponding thiazolone **5b** was formed as a minor product.

Because of the pronounced lower reactivity of **1c** in the reaction with **2a**, **1c** was allowed to react with 3 equiv. of **2b** at room temperature, and the mixture was stirred overnight. The separation of the products by column chromatography gave the 1:1 adducts **8c** and **9c**, and minor amounts of **5c** (*Table 2*).

In the case of the reaction of **1b** and **2b**, a small amount (2%) of a fourth compound was isolated. Based on the spectral data, it is apparent that this 1:1 adduct has a rearranged structure. An X-ray crystal-structure determination revealed the propellane structure **10** (*Scheme 5* and *Fig. 4*). The five-membered ring with S(7) and N(9) has the envelope conformation with C(2) as the envelope flap whereas the cyclopentane ring is a half-chair twisted at the C(5)–C(6) bond. Both six-membered rings have the chair conformation[6]). A reaction mechanism for the formation of **10** is proposed in *Scheme 5*: the key step is a *Wagner-Meerwein* rearrangement of the zwitterion **A**′ to give the ring-enlarged zwitterion **B** which then collapsed to yield **10**.

Scheme 5



3. Discussion. – The chemistry of oxiranes is almost totally concerned with the cleavage of the strained three-membered ring by reaction with electrophiles or *via* nucleophilic attack (*cf.* [9]). For example, the mechanism of the *Lewis*-acid-catalyzed reaction between oxiranes and carbonyl compounds, resulting in the formation of 1,3-dioxolanes, has been carefully studied [10]. On the other hand, thiocarbonyl compounds participate in a wide range of ring-forming reactions, showing superior reactivity in comparison with the corresponding carbonyl analogues. In many of these 'cycloaddition' reactions, discrete ionic or biradical intermediates are involved. Such an

6) The arbitrary atom numbering in *Fig. 4* is used.

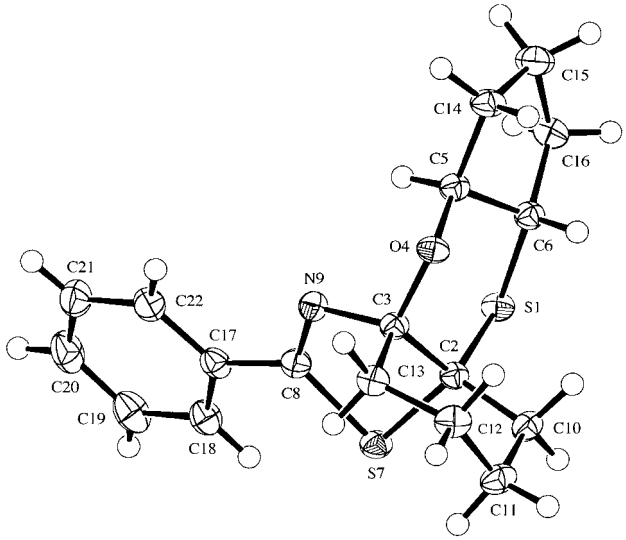


Fig. 4. *ORTEP Plot* [7] *of the molecular structure of* **10** (arbitrary numbering of the atoms; 50% probability ellipsoids).

ionic mechanism has also been proposed for the formation of 1,3-oxathiolans in the *Lewis*-acid-catalyzed reaction of thiocarbonyl compounds with oxiranes [4] [5].

The results reported in the present paper confirm the previously proposed mechanism, shown in *Scheme 1*. In particular, the isolation of **10**, the product of a *Wagner-Meerwein*-type rearrangement in the ionic intermediate, clearly confirms our hypotheses.

The reaction of the bicyclic oxiranes provides additional information concerning the mechanism displayed in *Scheme 1*. The results obtained with **2a** and **2b** are similar. These oxiranes possess a relatively rigid structure, with *cis*-fused rings. In all cases, products with *trans*-fused ring systems were obtained. This was confirmed by X-ray crystal-structure analyses, as well as by the ^3J values in the ^{1}H-NMR spectra, which are in the range of 10 Hz, corresponding to an axial-axial interaction of the CH protons. Thus, the stereochemistry observed for the products indicates that an inversion at one of the oxirane C-atoms has occurred during the ring formation. This is in accorance with an S_N2 attack of the thiocarbonyl S-atom at the complexed oxirane, leading to a zwitterionic intermediate of type **A** (*Scheme 1*).

Apparently, some of the spirocyclic 1,3-oxathiolanes are not very stable. The isolation of the 1,3-thiazol-5(4*H*)-ones **9a**–**c** indicates that, once the 1,3-oxathiolane ring is formed, it may, in some cases, decompose easily, giving the carbonyl and an epithio compound (*cf.* [6]). The formation of **6**, most likely from 1,2-epithiocyclohexane (**7**), generated *in situ* under the reaction conditions, and **1a** supports this supposition.

In summary, we have further generalized the *Lewis*-acid-catalyzed reaction of thiocarbonyl compounds and oxiranes as a convenient access to 1,3-oxathiolanes.

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 [11].

2. *Reactions of 1,2-Epoxycycloalkanes with 1,3-Thiazole-5(4*H*)-thiones. General Procedure*. To a soln. of a thiazole-thione **1** (*ca*. 1 mmol) in dry CH_2Cl_2 (10–15 ml) under N_2, $BF_3 \cdot Et_2O$ (1.1 equiv.) was added at r.t. In general, this leads to a more or less pronounced change in the color of the soln. towards deep orange-red. Then, the mixture was stirred for *ca*. 30 min. Several equiv. of the 1,2-epoxycycloalkane **2** were added dropwise at $-78°$ or at r.t., depending upon the reactivity of the starting materials.[7]) After complete consumption of **1** (TLC), the reaction mixture was extracted with NaCl-sat. H_2O. The combined org. layers were dried ($MgSO_4$) and evaporated *i.v.* The products were separated by chromatography (SiO_2; CC or prep. TLC).

*(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]* (**3a** and **4a**, resp.). Reaction of *4,4-dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione* (**1a**; 221 mg, 1 mmol) with *1,2-epoxycyclohexane* (= *7-oxabicyclo[4.1.0]heptane*; **2a**; 394 mg, 4 mmol) (18 h) and CC (hexane/AcOEt 20 : 1) yielded 168 mg (53%) of **3a** and 100 mg (31%) of **4a**.

Data of **3a**: colorless oil. IR ($CHCl_3$): 2945*s*, 2863*s*, 1592*s*, 1575*s*, 1490*m*, 1448*s*, 1380*m*, 1360*m*, 1351*w*, 1330*w*, 1313*m*, 1298*w*, 1262*s*, 1221*w*, 1176*m*, 1142*w*, 1117*w*, 1094*m*, 1065*s*, 1040*s*, 1002*w*, 962*s*, 920*m*, 896*s*, 873*s*, 834*m*, 794*s*, 783*s*, 766*m*, 757*m*, 748*m*, 728*m*, 691*s*. ^{1}H-NMR: 7.81–7.77 (*m*, 2 arom. H); 7.47–7.35 (*m*, 3 arom. H); 3.67 (*ddd*, ^3J = 10.9, 9.9, 3.7, H–C(6)); 2.89 (*ddd*, ^3J = 11.7, 9.9, 3.5, H–C(1)); 2.24–2.12, 1.94–1.79 (2*m*, 2 CH_2); 1.57, 1.46 (2*s*, 2 Me); 1.55–1.25 (*m*, 2 CH_2). ^{13}C-NMR: 165.2 (*s*, C=N); 133.7 (*s*, 1 arom. C); 130.9, 128.3, 127.9 (3*d*, 5 arom. C); 116.1 (*s*, spiro-C); 87.2 (*d*, C(6)); 81.6 (*s*, Me_2C); 52.5 (*d*, C(1)); 29.7, 29.1, 25.3 (3*t*, 3 CH_2); 25.2 (*q*, Me); 23.7 (*t*, CH_2); 20.9 (*q*, Me). CI-MS: 320 (100, $[M+1]^+$), 206 (6). Anal. calc. for $C_{17}H_{21}NOS_2$ (319.49): C 63.91, H 6.63, N 4.38; found: C 64.12, H 6.96, N 4.52.

Data of **4a**: colorless oil. IR ($CHCl_3$): 2945*s*, 2864*m*, 1592*s*, 1576*s*, 1490*m*, 1448*s*, 1378*m*, 1360*m*, 1332*w*, 1313*w*, 1297*w*, 1261*s*, 1203*w*, 1177*w*, 1139*w*, 1118*w*, 1090*w*, 1060*s*, 1016*s*, 998*m*, 957*s*, 916*w*, 898*m*, 875*m*, 809*w*, 787*s*, 772*m*, 763*s*, 748*s*, 728*s*, 691*s*. ^{1}H-NMR: 7.81–7.76 (*m*, 2 arom. H); 7.46–7.35 (*m*, 3 arom. H); 3.51 (*ddd*, ^3J = 10.9, 9.9, 3.7, H–C(6)); 3.10 (*ddd*, ^3J = 11.4, 9.9, 3.5, H–C(1)); 2.27–2.15, 1.92–1.81 (2*m*, 2 CH_2); 1.64, 1.40 (2*s*, 2 Me); 1.57–1.22 (*m*, 2 CH_2). ^{13}C-NMR: 163.9 (*s*, C=N); 133.7 (*s*, 1 arom. C); 131.0, 128.3, 128.2 (3*d*, 5 arom. C); 117.6 (*s*, spiro-C); 90.3 (*d*, C(6)); 83.6 (*s*, Me_2C); 53.8 (*d*, C(1)); 30.8, 28.3, 25.2 (3*t*, 3 CH_2); 24.2 (*q*, Me); 23.8 (*t*, CH_2); 20.3 (*q*, Me). CI-MS: 320 (100, $[M+1]^+$), 206 (9). Anal. calc. for $C_{17}H_{21}NOS_2$ (319.49): C 63.91, H 6.63, N 4.38; found: C 63.99, H 6.78, N 4.08.

In an analogous experiment carried out at r.t., 67% **3a**, 12% **4a**, and 5 mg (1%) of *(1*RS*,6*RS*)-4′,5′-dihydro-4′,4′-dimethyl-2′-phenylspiro[7,9-dithiabicyclo[4.3.0]nonane-8,5′-[1,3]thiazole]* **6** were isolated. White powder. M.p. 116.5–117.5°. IR (KBr): 2968*w*, 2933*s*, 2853*m*, 1590*m*, 1573*s*, 1488*m*, 1447*s*, 1374*m*, 1352*w*, 1335*w*, 1314*w*, 1277*w*, 1259*s*, 1205*m*, 1166*m*, 1076*w*, 1001*w*, 989*w*, 952*s*, 870*s*. ^{1}H-NMR: 7.76–7.72 (*m*, 2 arom. H); 7.45–7.33 (*m*, 3 arom. H); 3.32–3.23 (*m*, H–C(6) or H–C(1)); 3.15 (*ddd*, ^3J = 11.4, 10.4, 3.5, H–C(1) or H–C(6)); 2.24–2.08, 1.90–1.85 (2*m*, 2 CH_2); 1.64, 1.61 (2*s*, 2 Me); 1.57–1.30 (*m*, 2 CH_2). ^{13}C-NMR: 166.2 (*s*, C=N); 133.4 (*s*, 1 arom. C); 131.2, 128.4, 127.9 (3*d*, 5 arom. C); 92.5 (*s*, spiro-C); 81.7 (*s*, Me_2C); 60.6, 59.8 (2*d*, C(1), C(6)); 30.2, 29.1, 25.2, 25.1 (4*t*, 4 CH_2); 24.0, 23.5 (2*q*, 2 Me). CI-MS: 336 (100, $[M+1]^+$), 206 (6), 199 (8). Anal. calc. for $C_{17}H_{21}NS_3$ (335.56): C 60.85, H 6.31, N 4.17; found: C 60.84, H 6.24, N 4.06.

Crystals of **6** suitable for X-ray crystal-structure determination were grown from CH_2Cl_2/i-PrOH.

*(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)]* (**3b** and **4b**, resp.). Reaction of *2-phenyl-3-thia-1-azaspiro[4.4]non-1-ene-4-thione* (**1b**; 257 mg, 1.05 mmol) with **2a** (612 mg, 6.2 mmol) (5 h) and CC (hexane/AcOEt 33 : 1) yielded 195 mg (54%) of **3b** and 71 mg (20%) of **4b**.

Data of **3b**: colorless crystals. M.p. 110.5–112°. IR (KBr): 2935*s*, 2850*m*, 1590*m*, 1570*m*, 1485*w*, 1445*m*, 1345*w*, 1330*w*, 1258*m*, 1210*w*, 1088*w*, 1063*s*, 995*s*, 965*m*, 951*s*, 890*m*, 785*m*, 768*s*, 690*s*. ^{1}H-NMR: 7.84–7.80 (*m*, 2 arom. H); 7.46–7.35 (*m*, 3 arom. H); 3.70 (*ddd*, ^3J = 10.9, 9.8, 3.6, H–C(6″)); 2.90 (*ddd*, ^3J = 11.7, 9.8, 3.5, H–C(1″)); 2.42–1.20 (*m*, 8 CH_2). ^{13}C-NMR: 164.4 (*s*, C=N); 134.0 (*s*, 1 arom. C); 130.9, 128.3, 128.0 (3*d*, 5 arom. C); 115.8 (*s*, spiro-C(8″)); 92.2 (*s*, spiro-C(1)); 87.0 (*d*, C(6″)); 52.8 (*d*, C(1″)); 39.2, 32.4, 29.9, 29.2, 25.6, 25.4, 25.2, 23.8 (8*t*, 8 CH_2). CI-MS: 346 (100, $[M+1]^+$), 171 (39). Anal. calc. for $C_{13}H_{20}NOS_2$ (345.53): C 66.12, H 6.71, N 4.05; found: C 66.12, H 6.47, N 4.08.

Crystals of **3b** suitable for X-ray crystal-structure determination were grown from CH_2Cl_2/i-PrOH.

Data of **4b**: colorless crystals. M.p. 140–141°. IR (KBr): 2925*s*, 2860*m*, 1593*s*, 1575*m*, 1490*m*, 1450*s*, 1352*w*, 1313*w*, 1255*m*, 1288*m*, 1130*w*, 1065*s*, 980*s*, 950*s*, 915*w*, 900*m*, 768*s*, 690*s*. ^{1}H-NMR: 7.83–7.78 (*m*, 2 arom. H);

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[7]) In general, 1,2-epoxycyclopentane (**2b**) was more reactive than 1,2-epoxycyclohexane (**2a**) (shorter reaction times).

7.47–7.35 (*m*, 3 arom. H); 3.62–3.52 (*m*, H–C(6″)); 3.15 (*ddd*, ^3J = 11.5, 10.0, 3.5, H–C(1″)); 2.30–1.12 (*m*, 8 CH_2). ^{13}C-NMR: 163.0 (*s*, C=N); 134.0 (*s*, arom. C); 130.8, 128.3, 128.2 (3*d*, 5 arom. C); 117.2 (*s*, spiro-C(8″)); 94.3 (*s*, spiro-C(1)); 90.6 (*d*, C(6″)); 53.9 (*d*, C(1″)); 38.6, 32.0, 31.0, 28.3, 25.2, 25.1, 23.8 (7*t*, 8 CH_2). CI-MS: 346 (100, $[M+1]^+$). Anal. calc. for $C_{13}H_{20}NOS_2$ (345.53): C 66.05, H 6.71, N 4.05; found: C 66.19, H 6.50, N 4.14.

Crystals of **4b** suitable for X-ray crystal-structure determination were grown from CH_2Cl_2/i-PrOH.

In addition to **3b** and **4b**, 49 mg (20%) of *2-phenyl-3-thia-1-azaspiro[4.4]non-1-en-4-one* (**5b**) were isolated (*cf.* [12]). Yellow crystals. M.p. 53–54.5°. IR (KBr): 2936*m*, 1701*s*, 1665*m*, 1594*w*, 1578*w*, 1510*w*, 1486*m*, 1448*m*, 1367*w*, 1300*w*, 1247*m*, 1210*w*, 1026*w*, 1006*w*, 952*m*, 884*w*, 806*w*, 767*m*, 692*m*. ^{1}H-NMR: 7.86–7.83 (*m*, 2 arom. H); 7.55–7.44 (*m*, 3 arom. H); 2.20–1.92 (*m*, 4 CH_2). ^{13}C-NMR: 212.1 (*s*, C=O); 160.5 (*s*, C=N); 133.7 (*s*, 1 arom. C); 131.6, 128.7, 128.0 (3*d*, 5 arom. C); 93.6 (*s*, spiro-C); 39.0, 26.2 (2*t*, 4 CH_2). CI-MS: 232 (100, $[M+1]^+$), 203 (11), 170 (64).

*(1*RS*,6*RS*,8*SR*)- and (1*RS*,6*RS*,8*RS*)-2′-Benzyl-4′,5′-dihydro-4′,4′-dimethylspiro[7-oxa-9-thiabicyclo[4.3.0]-nonane-8,5′-[1,3]thiazole]* (**3c** and **4c**, resp.). Reaction of *2-benzyl-4,4-dimethyl-1,3-thiazole-5(4*H*)-thione* (**1c**; 324 mg, 1.38 mmol) with **2a** (944 mg, 9.6 mmol) (19 h) and CC (hexane/AcOEt 9 : 1) yielded 282 mg (61%) of **3c** and 81 mg (18%) of **4c**.

Data of **3c**: colorless crystals. M.p. 71.5–73°. IR ($CHCl_3$): 2946*s*, 1865*m*, 1612*s*, 1601*s*, 1496*m*, 1454*s*, 1380*m*, 1362*m*, 1351*w*, 1263*m*, 1235*m*, 1223*m*, 1201*w*, 1096*m*, 1066*s*, 1039*s*, 962*m*, 879*m*, 870*m*, 790*s*, 742*m*, 701*s*. ^{1}H-NMR: 7.38–7.25 (*m*, 5 arom. H); 3.90, 3.77 (*AB*, J_{AB} = 14.9, PhCH_2); 3.56 (*ddd*, ^3J = 11.0, 9.9, 3.7, H–C(6)); 2.85 (*ddd*, ^3J = 11.4, 9.9, 3.4, H–C(1)); 2.25–2.08, 1.96–1.77 (2*m*, 2 CH_2); 1.62–1.20 (*m*, 2 CH_2); 1.52, 1.39 (2*s*, 2 Me). ^{13}C-NMR: 168.0 (*s*, C=N); 135.7 (*s*, 1 arom. C); 129.0, 128.5, 127.0 (3*d*, 5 arom. C); 116.5 (*s*, spiro-C); 87.1 (*d*, C(6)); 80.7 (*s*, Me_2C); 52.4 (*d*, C(1)); 41.8 (*t*, PhCH_2); 29.7, 29.1, 25.3 (3*t*, 3 CH_2); 25.2 (*q*, Me); 23.7 (*t*, CH_2); 20.7 (*q*, Me). CI-MS: 334 (100, $[M+1]^+$), 159 (7). Anal. calc. for $C_{18}H_{23}NOS_2$ (333.52): C 64.82, H 6.95, N 4.20; found: C 64.98, H 6.85, N 4.15.

Data of **4c**: colorless oil. IR ($CHCl_3$): 2943*s*, 2863*m*, 1721*m*, 1760*w*, 1613*m*, 1600*m*, 1496*m*, 1455*m*, 1380*w*, 1360*w*, 1280*m*, 1262*m*, 1100*w*, 1061*m*, 1016*s*, 871*w*. ^{1}H-NMR: 7.37–7.24 (*m*, 5 arom. H); 3.94, 3.81 (*AB*, J_{AB} = 14.8, PhCH_2); 3.54–3.42 (*m*, H–C(6)); 2.99 (*ddd*, ^3J = 11.4, 9.9, 3.6, H–C(1)); 2.27–2.13, 1.95–1.77 (2*m*, 2 CH_2); 1.55–1.22 (*m*, 2 CH_2); 1.58, 1.33 (2*s*, 2 Me). ^{13}C-NMR: 166.7 (*s*, C=N); 135.7 (*s*, 1 arom. C); 129.0, 128.6, 127.1 (3*d*, 5 arom. C); 117.9 (*s*, spiro-C); 90.1 (*d*, C(6)); 82.7 (*s*, Me_2C); 53.6 (*d*, C(1)); 41.8 (*t*, PhCH_2); 30.7, 28.2, 25.1 (3*t*, 3 CH_2); 24.0 (*q*, Me); 23.7 (*t*, CH_2); 20.0 (*q*, Me). CI-MS: 334 (100, $[M+1]^+$). Anal. calc. for $C_{18}H_{23}NOS_2$ (333.52): C 64.82, H 6.95, N 4.20; found: C 64.77, H 7.05, N 4.25.

*(1*RS*,3*SR*,5*RS*)- and (1*RS*,3*RS*,5*RS*)-4′,5′-Dihydro-4′,4′-dimethyl-2′-phenylspiro[2-oxa-4-thiabicyclo[3.3.0]-octane-3,5′-[1,3]thiazole]* (**8a** and **9a**, resp.). Reaction of **1a** (327 mg (1.48 mmol)) with *1,2-epoxycyclopentane* (*= 6-oxabicyclo[3.1.0]hexane*; **2b**; 527 mg, 6.3 mmol) (10 h) and CC (hexane/AcOEt 40 : 1) yielded 307 mg (68%) **8a**, 36 mg (8%) **9a**.

Data of **8a**: colorless crystals. M.p. 92–94°. IR (KBr): 3500*w*, 2970*m*, 2930*m*, 2875*w*, 1588*m*, 1573*m*, 1490*w*, 1446*m*, 1376*w*, 1359*w*, 1333*w*, 1315*w*, 1294*w*, 1263*m*, 1246*m*, 1211*m*, 1093*s*, 1031*s*, 952*s*, 904*w*, 796*s*, 770*s*, 692*m*. ^{1}H-NMR: 7.81–7.78 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 4.15 (*ddd*, ^3J = 11.3, 10.2, 6.6, H–C(1)); 3.22 (*ddd*, ^3J = 12.2, 10.2, 6.4, H–C(5)); 2.28–2.17, 2.01–1.90, 1.77–1.49 (3*m*, 3 CH_2); 1.61, 1.45 (2*s*, 2 Me). ^{13}C-NMR: 165.5 (*s*, C=N); 133.6 (*s*, 1 arom. C); 131.2, 128.4, 128.0 (3*d*, 5 arom. C); 125.9 (*s*, spiro-C); 94.3 (*d*, C(1)); 82.2 (*s*, Me_2C); 54.9 (*d*, C(5)); 25.8 (*t*, CH_2); 24.8 (*q*, Me); 23.5, 23.4 (2*t*, 2 CH_2); 21.3 (*q*, Me). CI-MS: 306 (100, $[M+1]^+$), 145 (7). Anal. calc. for $C_{16}H_{19}NOS_2$ (305.47): C 62.91, H 6.27, N 4.59; found: C 62.58, H 6.18, N 4.52.

Crystals of **8a** suitable for X-ray crystal-structure determination were grown from CH_2Cl_2/i-PrOH.

Data of **9a**: colorless crystals. M.p. 71–73°. IR (KBr): 2970*m*, 2930*m*, 2870*w*, 1595*s*, 1575*m*, 1488*w*, 1445*s*, 1375*w*, 1355*m*, 1312*w*, 1260*s*, 1240*m*, 1210*m*, 1095*s*, 1073*s*, 1007*m*, 994*m*, 950*s*, 900*w*, 862*m*, 811*m*, 768*m*, 690*s*. ^{1}H-NMR: 7.81–7.76 (*m*, 2 arom. H); 7.46–7.35 (*m*, 3 arom. H); 4.03 (*ddd*, ^3J = 11.2, 10.3, 6.5, H–C(1)); 3.47 (*ddd*, ^3J = 12.2, 10.3, 6.5, H–C(5)); 2.34–2.10, 2.05–1.87, 1.72–1.44 (3*m*, 3 CH_2); 1.69, 1.40 (2*s*, 2 Me). ^{13}C-NMR: 163.7 (*s*, C=N); 133.5 (*s*, 1 arom. C); 131.1, 128.4, 128.1 (3*d*, 5 arom. C); 125.2 (*s*, spiro-C); 97.3 (*d*, C(1)); 84.2 (*s*, Me_2C); 56.4 (*d*, C(5)); 26.0, 24.8 (2*t*, 2 CH_2); 23.6 (*q*, Me); 22.5 (*t*, CH_2); 20.3 (*q*, Me). CI-MS: 306 (100, $[M+1]^+$), 145 (14). Anal. calc. for $C_{16}H_{19}NOS_2$ (305.47): C 62.91, H 6.27, N 4.59; found: C 62.95, H 6.21, N 4.58.

Crystals of **9a** suitable for X-ray crystal-structure determination were grown from CH_2Cl_2/i-PrOH.

In addition to **8a** and **9a**, 22 mg (7%) of *4,4-dimethyl-2-phenyl-1,3-thiazol-5(4*H*)-one* (**5a**) were isolated (*cf.* [13]). Yellow oil. IR ($CHCl_3$): 3212*m*, 3010*m*, 1707*s*, 1634*m*, 1533*s*, 1475*w*, 1451*m*, 1365*m*, 1248*m*, 1190*w*, 1178*m*, 1012*w*, 887*w*. ^{1}H-NMR: 7.85–7.82 (*m*, 2 arom. H); 7.54–7.48 (*m*, 3 arom. H); 1.55 (*s*, 2 Me). ^{13}C-NMR: 211.5

(*s*, C=O); 161.0 (*s*, C=N); 133.6 (*s*, 1 arom. C); 131.9, 128.8, 128.1 (3*d*, 5 arom. C); 84.1 (*s*, Me_2C); 24.7 (*q*, 2 Me). CI-MS: 206 (100, $[M+1]^+$).

*(1″*RS,*3″*SR,*5″*RS*)- and (1″*RS,*3″*RS,*5″*RS*)-4′,5′-Dihydro-2′-phenyldispiro[cyclopentane-1,4′-[1,3]thiazole-5′,3″-(2″-oxa-4″-thiabicyclo[3.3.0]octane)]* (**8b** and **9b**, resp.). Reaction of **1b** (242 mg, 0.98 mmol) with **2b** (502 mg, 6 mmol) (5 h) and CC (hexane/AcOEt 33:1) yielded 201 mg (62%) **8b** and 10 mg (3%) **9b**.

Data of **8b**: colorless oil. IR ($CHCl_3$): 2964*s*, 2874*m*, 1716*m*, 1592*m*, 1574*m*, 1490*w*, 1460*m*, 1448*s*, 1325*w*, 1294*w*, 1260*s*, 1240*m*, 1092*s*, 970*s*. ^{1}H-NMR: 7.84–7.79 (*m*, 2 arom. H); 7.43–7.36 (*m*, 3 arom. H); 4.17 (*ddd*, ^3J = 11.3, 10.2, 6.5, H–C(1″)); 3.22 (*ddd*, ^3J = 12.1, 10.2, 6.4, H–C(5″)); 2.50–1.50 (*m*, 7 CH_2). ^{13}C-NMR: 164.3 (*s*, C=N); 133.8 (*s*, 1 arom. C); 130.8, 128.2, 127.9 (3*d*, 5 arom. C); 125.5 (*s*, spiro-C(5′)); 94.0 (*d*, C(1″)); 93.1 (*s*, spiro-C(1)); 55.0 (*d*, C(5″)); 38.3, 32.7, 25.7, 25.4, 25.0, 23.5, 23.4 (7*t*, 7 CH_2). CI-MS: 332 (100, $[M+1]^+$).

Data of **9b**: colorless oil. IR ($CHCl_3$): 2964*m*, 1720*m*, 1602*w*, 1576*w*, 1486*w*, 1449*w*, 1261*s*, 1208*w*, 1097*s*, 1015*s*. ^{1}H-NMR: 7.81–7.78 (*m*, 2 arom. H); 7.43–7.36 (*m*, 3 arom. H); 4.15–4.05 (*m*, H–C(1″)); 3.52 (*ddd*, ^3J = 12.1, 10.3, 6.5, H–C(5″)); 2.40–1.40 (*m*, 7 CH_2). ^{13}C-NMR: 133.8 (*s*, 1 arom. C); 130.9, 128.3, 128.1 (3*d*, 5 arom. C); 97.5 (*d*, C(1″)); 94.9 (*s*, spiro-C(1)); 56.4 (*d*, C(5″)); 37.8, 32.0, 25.9, 25.1, 24.9, 22.3 (6*t*, 7 CH_2). The signals for C=N and spiro-C(5′) were not found. CI-MS: 332 (100, $[M+1]^+$), 171 (6).

In addition to **8b** and **9b**, 30 mg (13%) **5b**, and 5 mg (2%) of *15-phenyl-2-oxa-8,16-dithia-14-azatetracyclo[7.4.3.0^{1,9}.0^{3,7}]hexadec-14-ene* (**10**) were isolated. Colorless crystals. M.p. 149–151°. IR ($CHCl_3$): 2963*m*, 2870*w*, 1726*m*, 1603*w*, 1577*w*, 1448*m*, 1262*s*, 1174*w*, 1098*s*, 1015*s*, 966*w*, 864*w*, 809*m*. ^{1}H-NMR: 7.86–7.84 (*m*, 2 arom. H); 7.49–7.40 (*m*, 3 arom. H); 4.20–4.15 (*m*, H–C(3)); 2.72 (*ddd*, ^3J = 12.0, 9.7, 7.2, H–C(7)); 2.49–2.32, 2.14–1.98 (2*m*, 2 CH_2); 1.87–1.36 (*m*, 5 CH_2). ^{13}C-NMR: 164.5 (*s*, C=N); 133.5 (*s*, 1 arom. C); 131.7, 128.6, 127.9 (3*d*, 5 arom. C); 106.2 (*s*, C(1)); 79.9 (*d*, C(3)); 65.8 (*s*, C(9)); 41.0 (*d*, C(7)); 35.1, 33.4, 28.5, 26.1, 23.6, 20.6, 18.4 (7*t*, 7 CH_2). CI-MS: 332 (100, $[M+1]^+$), 228 (15).

Crystals of **10** suitable for X-ray crystal-structure determination were grown from the oil.

*(1*RS,*3*SR,*5*RS*)- and (1*RS,*3*RS,*5*RS*)-2′-Benzyl-4′,5′-dihydro-4′,4′-dimethylspiro[2-oxa-4-thiabicyclo[3.3.0]octane-3,5′-[1,3]thiazole]* (**8c** and **9c**, resp.). Reaction of **1c** (206 mg, 0.88 mmol) with **2b** (237 mg, 2.8 mmol) (15 h) and CC (hexane/AcOEt 13:1) yielded 186 mg (66%) **8c** and 24 mg (9%) **9c**.

Data of **8c**: colorless oil. IR ($CHCl_3$): 3020*w*, 2965*m*, 1718*m*, 1675*m*, 1601*w*, 1496*m*, 1455*m*, 1383*w*, 1262*s*, 1210*w*, 908*w*. ^{1}H-NMR: 7.39–7.27 (*m*, 5 arom. H); 4.05 (*ddd*, ^3J = 11.3, 10.2, 6.5, H–C(1)); 3.92, 3.79 (*AB*, J_{AB} = 14.9 PhCH_2); 3.20 (*ddd*, ^3J = 12.1, 10.2, 6.4, H–C(5)); 2.28–2.17, 2.01–1.89, 1.79–1.44 (3*m*, 3 CH_2); 1.57, 1.40 (2*s*, 2 Me). ^{13}C-NMR: 167.8 (*s*, C=N); 135.5 (*s*, 1 arom. C); 128.9, 128.5, 127.0 (3*d*, 5 arom. CH); 126.2 (*s*, spiro-C); 94.1 (*d*, C(1)); 81.4 (*s*, Me_2C); 54.7 (*d*, C(5)); 41.7 (*t*, PhCH_2); 25.7 (*t*, CH_2); 24.7 (*q*, Me); 23.4, 23.2 (2*t*, 2 CH_2); 21.0 (*q*, Me). CI-MS: 320 (100, $[M+1]^+$), 238 (19), 220 (9), 159 (6).

Data of **9c**: colorless oil. IR ($CHCl_3$): 2964*s*, 2870*m*, 1730*m*, 1614*m*, 1600*m*, 1496*w*, 1456*m*, 1379*w*, 1360*w*, 1262*m*, 1239*m*, 1223*m*, 1097*s*, 1078*s*, 1010*s*, 994*m*, 868*w*. ^{1}H-NMR: 7.36–7.25 (*m*, 5 arom. H); 3.98 (*ddd*, ^3J = 11.2, 10.3, 6.5, H–C(1)); 3.93, 3.80 (*AB*, J_{AB} = 14.8, PhCH_2); 3.36 (*ddd*, ^3J = 12.2, 10.3, 6.6, H–C(5)); 2.25–2.13, 2.01–1.88, 1.70–1.45 (3*m*, 3 CH_2); 1.62, 1.32 (2*s*, 2 Me). ^{13}C-NMR: 166.4 (*s*, C=N); 135.6 (*s*, 1 arom. C); 129.0, 128.6, 127.3 (3*d*, 5 arom. CH); 97.1 (*d*, C(1)); 83.3 (*s*, Me_2C); 56.2 (*d*, C(5)); 41.7 (*t*, PhCH_2); 26.0, 24.7 (2*t*, 2 CH_2); 23.6 (*q*, Me); 22.4 (*t*, CH_2); 20.1 (*q*, Me). The signal for spiro-C(5′) was not found. CI-MS: 320 (100, $[M+1]^+$), 238 (7), 159 (14).

In addition to **8c** and **9c**, 12 mg (6%) of *2-benzyl-4,4-dimethyl-1,3-thiazol-5(4*H*)-one* (**5c**) were isolated. Yellow oil. IR ($CHCl_3$): 3032*w*, 2964*m*, 2935*w*, 1720*s*, 1704*w*, 1623*m*, 1496*m*, 1455*m*, 1378*w*, 1360*w*, 1262*s*, 1209*m*, 939*w*. ^{1}H-NMR: 7.37–7.27 (*m*, 5 arom. H); 3.97 (*s*, PhCH_2); 1.44 (*s*, 2 Me). ^{13}C-NMR: 211.5 (*s*, C=O); 163.9 (*s*, C=N); 134.5 (*s*, 1 arom. C); 129.1, 128.9, 127.6 (3*d*, 5 arom. C); 83.3 (*s*, Me_2C); 43.5 (*t*, PhCH_2); 24.4 (*q*, 2 Me). CI-MS: 220 (100, $[M+1]^+$), 191 (8).

3. *Reaction of 1,2-Epithiocyclohexane* (*7-Thiabicyclo[4.1.0]heptane,* **7**) *with* **1a**. Reaction of **1a** (220 mg, 1 mmol) with **7** (757 mg, 85% techn., 5.6 mmol) according to the *General Procedure* in *Sect. 2* (50 h), and CC (hexane/AcOEt 30:1) yielded 115 mg (85% with respect to consumed **1a**) of **6** (131 mg (60%) of **1a** recovered).

4. *X-Ray Crystal-Structure Determination of* **3b**, **4b**, **6**, **8a, 9a**, *and* **10** (see *Table 3* and *Figs. 1–4*)[8]). All measurements were made on a *Rigaku-AFC5R* diffractometer with graphite-monochromated MoK_α radiation

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[8]) 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-126149–126154 for **3b**, **4b**, **6**, **8a**, **9a**, and **10**, 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).

Table 3. *Crystallographic Data of Compounds* **3b**, **4b**, **6**, **8a**, **9a**, *and* **10**

	3b	**4b**	**6**	**8a**	**9a**	**10**
Crystallized from	CH_2Cl_2/i-PrOH	CH_2Cl_2/i-PrOH	CH_2Cl_2/i-PrOH	CH_2Cl_2/i-PrOH	hexane	oil
Empirical formula	$C_{19}H_{23}NOS_2$	$C_{19}H_{23}NOS_2$	$C_{17}H_{21}NS_3$	$C_{16}H_{19}NOS_2 \cdot 1/2\,H_2O$	$C_{16}H_{19}NOS_2$	$C_{18}H_{21}NOS_2$
Formula weight [g·mol^{-1}]	345.52	345.52	335.54	314.46	305.45	331.49
Crystal color, habit	colorless, prism	colorless, irreg. prism	colorless, prism	colorless, prism	colorless, prism	colorless, plate
Crystal dimensions [mm]	$0.28 \times 0.40 \times 0.45$	$0.35 \times 0.40 \times 0.42$	$0.35 \times 0.40 \times 0.43$	$0.28 \times 0.30 \times 0.40$	$0.28 \times 0.38 \times 0.45$	$0.17 \times 0.32 \times 0.35$
Temp. [K]	173(1)	173(1)	173(1)	173(1)	173(1)	173(1)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Z	4	4	4	4	4	4
Reflections for cell determination	25	25	25	25	25	25
2θ Range for cell determination [°]	38–40	38–40	39–40	39–40	38–40	39–40
Unit cell parameters a [Å]	9.418(2)	9.858(2)	10.181(2)	11.630(3)	11.438(2)	11.063(4)
b [Å]	11.369(2)	10.966(2)	10.748(2)	12.703(2)	16.514(3)	7.434(3)
c [Å]	16.497(2)	16.364(4)	15.751(2)	11.425(4)	8.677(2)	19.781(3)
α [°]	90	90	90	90.50(2)	100.34(2)	90
β [°]	93.07(1)	96.92(2)	95.83(1)	101.44(2)	92.47(2)	98.65(2)
γ [°]	90	90	90	110.18(2)	102.20(2)	90
V [Å^3]	1763.8(5)	1756.1(6)	1714.7(3)	1547.3(7)	1570.4(5)	1608.2(9)
D_x [g cm^{-3}]	1.301	1.307	1.300	1.350	1.292	1.369
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]	0.306	0.307	0.425	0.343	0.334	0.332
$2\theta_{(\max)}$ [°]	60	60	55	55	55	55
Total reflections measured	5675	5650	4370	7435	7562	4184
Symmetry-independent reflections	5138	5116	3930	7085	7202	3694
Reflections used [$I > 2\sigma(I)$]	4093	4031	3293	5712	5294	2995
Parameters refined	301	300	274	523	514	284
Final R	0.0402	0.0410	0.0457	0.0418	0.0738	0.0353
wR ($w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$)	0.0391	0.0403	0.0442	0.0416	0.0751	0.0348
Goodness of fit	1.964	1.861	2.763	2.264	3.632	1.648
Secondary extinction coefficient	$7.9(7) \cdot 10^{-7}$	–	–	$6.5(8) \cdot 10^{-7}$	$2.2(2) \cdot 10^{-6}$	$2.8(6) \cdot 10^{-7}$
Final $\Delta_{\max}/\sigma$	0.002	0.0009	0.0002	0.003	0.0002	0.0008
$\Delta\rho$ (max; min) [e·Å^{-3}]	0.44; −0.43	0.42; −0.27	0.90; −0.51	0.85; −0.33	0.56; −0.85	0.31; −0.25

($\lambda = 0.71069$ 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. Empirical absorption corrections were applied in the cases of **6** and **9a**. Data collection and refinement parameters are given in *Table 3*, views of the molecules are shown in *Figs. 1–4*. The structures were solved by direct methods with SHELXS86 [14] for **3b**, **4b**, **8a**, and **9a**, and SIR92 [15] for **6** and **10**. In the case of **8a**, the asymmetric unit contains two independent molecules of the compound and one H_2O molecule, while for **9a**, there are two independent molecules in the asymmetric unit. The atomic coordinates for these two compounds were tested carefully for a relationship from a higher symmetry space group with the MISSYM routine [16] of the program PLATON [17], but none could be found. For each structure, all non-H-atoms were refined anisotropically. All H-atoms were placed in the positions indicated by a difference electron-density map and, except for those of the H_2O molecule in **8a**, their positions were allowed to be refined together with individual isotropic displacement parameters. The positions of the H_2O H-atoms were not refined, and they were assigned fixed isotropic displacement parameters with a value equal to 1.2 U_{eq} of the O-atom. Refinement of each structure was carried out on F with full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o| - |F_c|)^2$. A correction for secondary extinction was applied in the cases of **3b**, **8a**, **9a**, and **10**. Neutral-atom-scattering factors for non-H-atoms were taken from [18a] and the scattering factors for H-atoms from [19]. Anomalous dispersion effects were included in F_{calc} [20]. The values for f' and f'' were those of [18b]. The values of the mass-attenuation coefficients are those of [18c]. The calculations were performed using the TEXSAN crystallographic software package [21] for **3b**, **4b**, **8a**, and **9a**, and the teXsan crystallographic software package [22] for **6** and **10**.

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Received June 11, 1999