Lewis Acid Catalyzed Reactions of Thioketones with 1,2-Epoxycyclohexane and 1,2-Epoxycyclopentane

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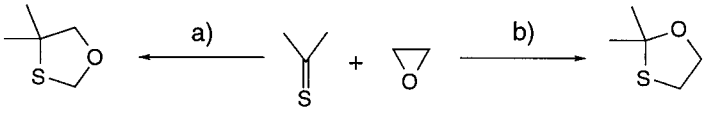
Non-enolizable thioketones and 1,2-epoxycycloalkanes undergo a *Lewis* acid catalyzed addition reaction to give 1,3-oxathiolanes. Appropriate reaction conditions are CH_2Cl_2 as the solvent, $BF_3 \cdot Et_2O$ as the *Lewis* acid, and a temperature between $-78°$ and r.t. Under the reaction conditions, the 1,3-oxathiolanes are only moderately stable. They decompose to yield the corresponding epithiocycloalkane and ketone. In general, 1,3-dithiolanes are isolated as minor products or, after prolonged reaction, as the main product. These secondary products are formed *via* the *Lewis* acid catalyzed reaction of the intermediate epithiocycloalkane and a second molecule of the thioketone. In the reaction of thiobenzophenone and 1,2-epoxycyclohexane, *trans*-8,8-diphenyl-7,9-dioxabicyclo[4.3.0]nonane is formed in small amounts as an additional side product (*Scheme 12*). In all cases, the newly formed heterocycle and the carbocycle are *trans*-fused. This result is consistent with a nucleophilic ring-opening of the complexed oxirane by the thioketone *via* inversion of the configuration and subsequent formation of the O(1)–C(2) bond of the 1,3-oxathiolane (*Scheme 13*). The surprising formation of the fused 1,4-oxathiepan derivative **23** (*Scheme 9*) is in accordance with an ionic reaction mechanism (*cf. Scheme 15*).

1. Introduction. – Various preparative methods for the synthesis of 1,3-oxathiolanes are known [2]. Among them are reactions between thiocarbonyl compounds and oxiranes. Depending on the reaction conditions, the oxirane serves as the precursor of a C–O–C fragment (*Path a*) or of a C–C–O fragment (*Path b*, *Scheme 1*). Whereas, in the first case, the reaction with C=S groups is believed to proceed *via* 1,3-dipolar cycloaddition of an intermediate carbonyl ylide (*cf.* [3][4])[2]), the reaction mechanism of the cycloaddition in the second case is a non-concerted one (*cf.* [1]).

Scheme 1



In reactions of type *b* with C=S groups, the ring opening of the oxirane *via* cleavage of a C–O bond requires an activation of the oxirane with an electrophile. For example, treatment of oxiranes **1** with isothiocyanates leads to 1,3-oxathiolan-2-imines **2** [6–10]

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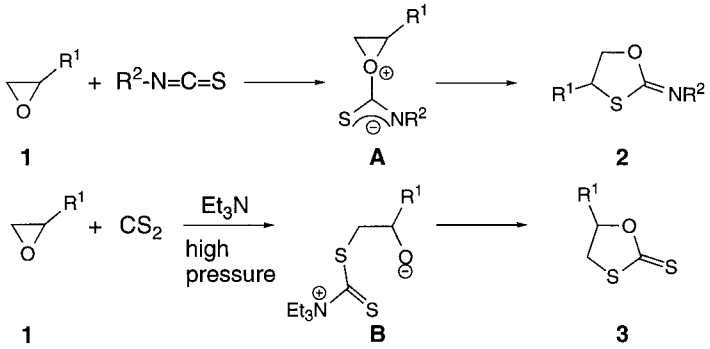
[1]) Part II of the planned Ph.D. thesis of *M.B.*, University of Zürich. For Part I, see [1].

[2]) Analogously, 1,3-oxathiolanes have been prepared by 1,3-dipolar cycloaddition of thiocarbonyl ylides with carbonyl compounds [5].

Scheme 2



(*cf.* [11]) (*Scheme 2*). It is most likely that zwitterions of type **A** are intermediates in these reactions[3])[4]).

Reactions of oxiranes with CS_2 have been described in several reports (*cf.* [13][14] and refs. cited therein). In general, product mixtures consisting of 1,3-oxathiolane-2-thiones **3**, 1,3-oxathiolan-2-ones, 1,3-dithiolane-2-thiones, and thiiranes were obtained in low yields. *Taniguchi et al.* showed that the reaction in the presence of Et_3N is markedly accelerated when it is performed under high pressure [13]. A reaction mechanism *via* intermediate **B** is proposed (*Scheme 2*); the latter is formed by the nucleophilic ring opening of the oxirane with the adduct of Et_3N and CS_2. Analogous reactions have been reported for epoxy-5α-cholestane derivatives, which produce steroidal 1,3-oxathiolane-2-thiones [15]. In these cases, the reaction at room temperature and normal pressure was catalyzed either by Et_3N or LiBr[5]).

On the other hand, formation of 1,3-oxathiolanes from oxiranes and non-cumulated C=S compounds is scarcely known [9b][21][22][6]). In these cases, the oxirane ring-opening by nucleophilic attack of the S-atom is accelerated by *Lewis* acids, *e.g.*, $BF_3 \cdot Et_2O$ [22]. Recently, we have reported the BF_3-catalyzed reaction of 1,3-thiazole-5(4*H*)-thiones **4** with oxiranes [1][24]. In the case of 1,2-epoxycyclohexane (**5a**), spirocyclic 1,3-oxathiolanes of type **6a** were formed as the main products (*Scheme 3*).

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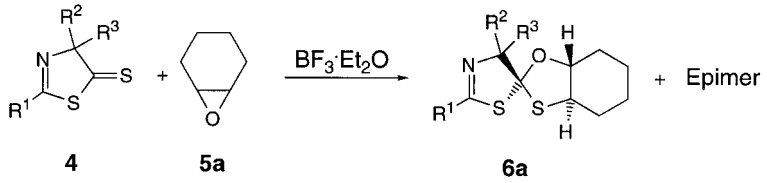
[3]) In some cases, the formation of mixtures of 1,3-oxathiolan-2-imines and 1,3-oxazolidine-2-thiones has been observed (*e.g.*, [6]). This result is easily explained by the presence of **A** as an intermediate.

[4]) The reaction of oxirane and HSCN gave 2-hydroxyethyl thiocyanate, which yielded 1,3-oxathiolan-2-imine on treatment with HCl [12].

[5]) Reactions of α-hydroxyoxiranes and CS_2 in the presence of NaH or KH yielded cyclic α-hydroxyxanthates (1,3-oxathiolane-2-thiones) [16–18]. This stereospecific transformation involves the initial formation of a xanthate anion, followed by an intramolecular nucleophilic opening of the oxirane. Analogously, α-hydroxyoxiranes were reacted with thiocarbonyl diimidazole to give a thioimidazolide, which, upon treatment with aniline, followed by hydrolysis of the intermediate iminocarbonate, yielded 3-(α-hydroxyalkyl)-1,3-oxathiolan-2-ones (cyclic thiocarbonates) in a stereospecific manner [19][20].

[6]) With the aim of converting 1,3-dithiolane-2-thiones to the corresponding 1,3-dithiolan-2-ones, reactions with oxiranes in the presence of $HBF_4 \cdot Et_2O$ have been performed [23]. The intermediate spirocyclic 1,3-oxathiolanes were detected but not isolated.

Scheme 3



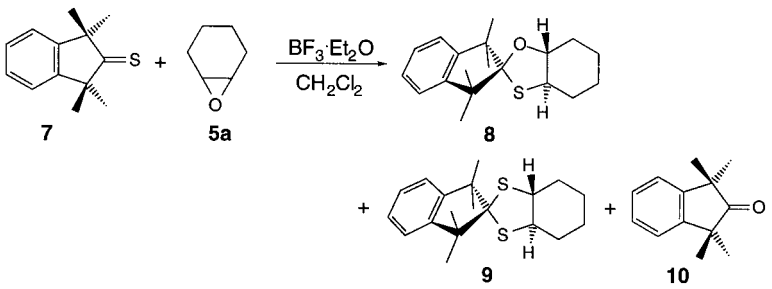
Analogously, cyclic thiocarbonates (*e.g.*, 1,3-dioxolane-2-thiones, 1,3-dithiolane-2-thiones) and oxiranes undergo a *Lewis* acid catalyzed addition reaction to give spirocyclic 1,3-oxathiolanes with an orthocarbonate structure [25].

To establish the scope and limitations, as well as the reaction mechanism, of this *Lewis* acid catalyzed 1,3-oxathiolane synthesis, we investigated reactions with other C=S compounds. In the present paper, the results of the reactions of 1,2-epoxycyclohexane oxide (**5a**) and 1,2-epoxy-cyclopentane oxide (**5b**) with various non-enolizable thioketones are described.

2. Results. – 2.1. *Reactions of 1,1,3,3-Tetramethylindane-2-thione* (**7**). The reaction of **7** with **5a** was carried out in dry CH_2Cl_2 under an N_2 atmosphere at room temperature (*Scheme 4*). The addition of $BF_3 \cdot Et_2O$ to the solution of **7** resulted in a slight reddening of the pink-orange color. After the addition of 3 equiv. of **5a**, the mixture was stirred overnight. As **7** was still not completely consumed (TLC), another 2.5 equiv. of **5a** were added, and the mixture was stirred until no **7** could be detected. After two days, the almost colorless solution was evaporated, and the products were separated by prep. TLC to give **8**, **9**, and **10** in 9, 20, and 51% yield, respectively (*Scheme 4, Table 1*). The structures of the spirocyclic 1,3-oxathiolane **8** and the 1,3-dithiolane **9** were established by X-ray crystal-structure determinations (*Fig. 1*). In both cases, the cyclohexane ring and the heterocycle are *trans*-fused.

As in previously described examples, the initially formed product is the 1:1 adduct **8** (*cf.* [1][23–25]). This has clearly been shown by performing the reaction under different conditions (*Table 1*). After 15 h at room temperature, when still 32% of **7** was recoverable, **8**, **9**, and **10** were obtained in 50, 16, and 41% yield, respectively, whereas after 1.5 h at 0°, the 1,3-oxathiolane **8** was nearly the sole product (69% isolated).

Scheme 4



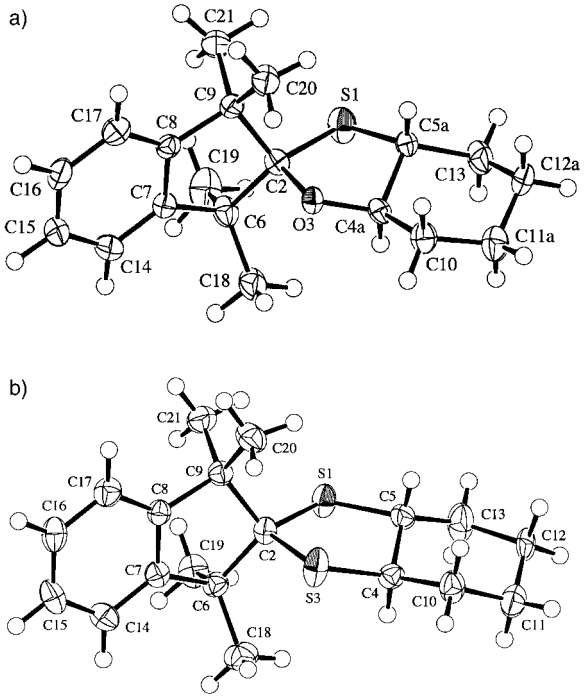


Fig. 1. *ORTEP Plots* [26] *of the molecular structures of* a) **8** *and* b) **9** (major conformations only; disorder not shown; only one of the three independent molecules of **9** shown; arbitrary numbering of the atoms; 50% probability ellipsoids)

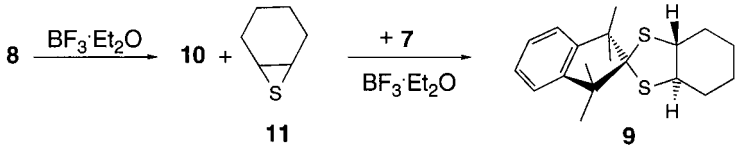
Table 1. *BF_3-Catalyzed Reaction of* **5a** *with* **7**

Ratio	Temp.	Reaction time	Yields of products [%][a])		
5a/7	[°]	[h]	**8**	**9**	**10**
5:1	r.t.	50	9	20	51
5:1	r.t.	15	50	16	21[b])
5:1	0°	1.5	69	2	–[c])

[a]) Calculated with respect to consumed **7**. [b]) Recovered **7**: 32%. [c]) Recovered **7**: 23%.

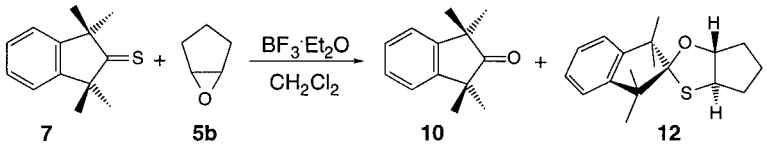
With the aim of corroborating the proposal that **9** and **10** are formed from **8** in a consecutive reaction (*Scheme 5*), several control experiments were carried out. *a*) To check the stability of **8** under the reaction conditions, a solution of **8** and 1.1 equiv. of $BF_3 \cdot Et_2O$ in CH_2Cl_2 was stirred at room temperature. After four days, no **8** could be detected, and 1,1,3,3-tetramethylindan-2-one (**10**) was isolated in 80% yield (*cf.* [23]). *b*) The BF_3-catalyzed reaction of **7** with 1,2-epithiocyclohexane (**11**), which is proposed to be the second product of the decomposition of **8**, gave, after 14 h at room temperature, dithiolane **9** as the only product (85% yield). *c*) On the other hand, all attempts to obtain **8** by treatment of a mixture of ketone **10** and epithio compound **11** with $BF_3 \cdot Et_2O$ were in vain; only starting material **10** was recovered.

Scheme 5



In an analogous manner, the reaction of **7** with an excess of 1,2-epoxycyclopentane (**5b**) was performed at room temperature overnight. Only **7** and the corresponding ketone **10** could be detected by TLC. After addition of another 2 equiv. of **5b** and stirring the mixture for an additional 14 h, 25% of **7** and 68% of **10** were isolated. Repeating the reaction at 0° overnight yielded **10** (77%)[7]) and the 1:1 adduct **12** (7%)[7]) (*Scheme 6*). When the reaction was carried out at −30° for 15 min, 64% of the starting material **7** was recovered, while **10** and **12** were isolated in 17 and 38% yield[8]), respectively[9]). The *trans*-fusion of cyclopentane and 1,3-oxathiolane was not proven but is assumed in analogy to other adducts (*vide infra*).

Scheme 6



2.2. *Reactions of 2,2,4,4-Tetramethyl-3-thioxocyclobutanone* (**13**). Because of the known high reactivity of **13**, the reaction with **5a** was performed at low temperature. To a solution of **13** in CH_2Cl_2 at −78°, 3 equiv. of **5a** were added, and the mixture was stirred for 2 h. Then, at −40°, another 3 equiv. of **5a** were added. Workup after 20 h yielded a unique product, which was identified as the 1:1 adduct **14** (*Scheme 7*). Repeating the reaction at room temperature led to a mixture of **14** and 1,3-dithiolane **15**, isolated in 23% and 14% yield, respectively[10]).

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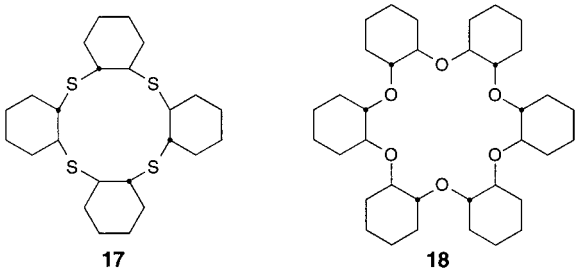
[7]) Yields calculated with respect to the amount of **7** consumed; 26% of **7** recovered.

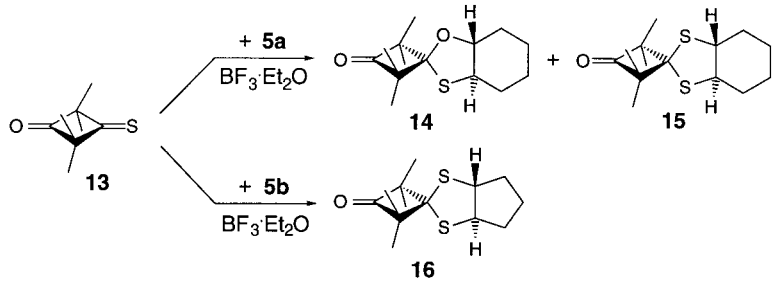
[8]) Calculated on the basis of the amount of **7** consumed.

[9]) Reducing the temperature to −78° was not appropriate, because the reaction was too slow.

[10]) Two additional products, which crystallized accidentally from fractions of the chromatographic separation, were obtained in very small amounts (< 1%). Their structures have been established by MS and X-ray crystallography as the cyclotetramer **17** of 1,2-epithiocyclohexane **11** and the cyclohexamer **18** of 1,2-epoxycyclohexene (**5a**). The crystal structures will be published elsewhere.



Scheme 7



The analogous reaction of **13** with **5b** was carried out at room temperature. After stirring the mixture overnight, **13** was completely consumed (TLC), and 1,3-dithiolane **16** was isolated as the only product in 26% yield. When the reaction was performed at $-78°$ for 14 h, 25% of **13** were recovered, and **16** was obtained in 25% yield. The expected 1,3-oxathiolane, which must have been formed as the initial product, could not be detected.

Crystals of **16** suitable for an X-ray crystal-structure determination were grown from CH_2Cl_2/i-PrOH. The molecular structure is shown in *Fig. 2*; the cyclopentane and 1,3-dithiolane rings are *trans*-fused.

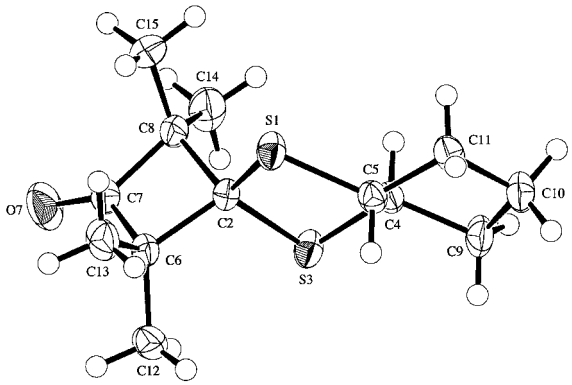


Fig. 2. *ORTEP Plot* [26] *of the molecular structure of* **16** (arbitrary numbering of the atoms; 50% probability ellipsoids)

2.3. *Reactions with 2,2,4,4-Tetramethylcyclobutane-1,3-dithione* (**19**). To a solution of dithione **19** in CH_2Cl_2, 2.2 equiv. of $BF_3 \cdot Et_2O$ and 5 equiv. of **5a** were added, and the mixture was stirred at room temperature. Another 2 equiv. of **5a** were added after 2.5 h and again after 14 h. After 26.5 h, the mixture was almost colorless, and no **17** could be detected by TLC. The usual workup of the complex mixture, and separation by prep. TLC and HPLC gave the mono-adducts **20**, **21**, and **14** in 4, 2, and 31% yield, respectively, as well as the bis-adducts *trans*-**22** and *cis*-**22** in 21 and 16% yield, respectively (*Scheme 8*). Crystallization of the minor fraction of the bis-adducts from i-PrOH/CH_2Cl_2 gave single crystals suitable for an X-ray analysis. The molecular structure of *cis*-**22a** is shown in *Fig. 3*. The molecule is almost σ-symmetric with two

Scheme 8

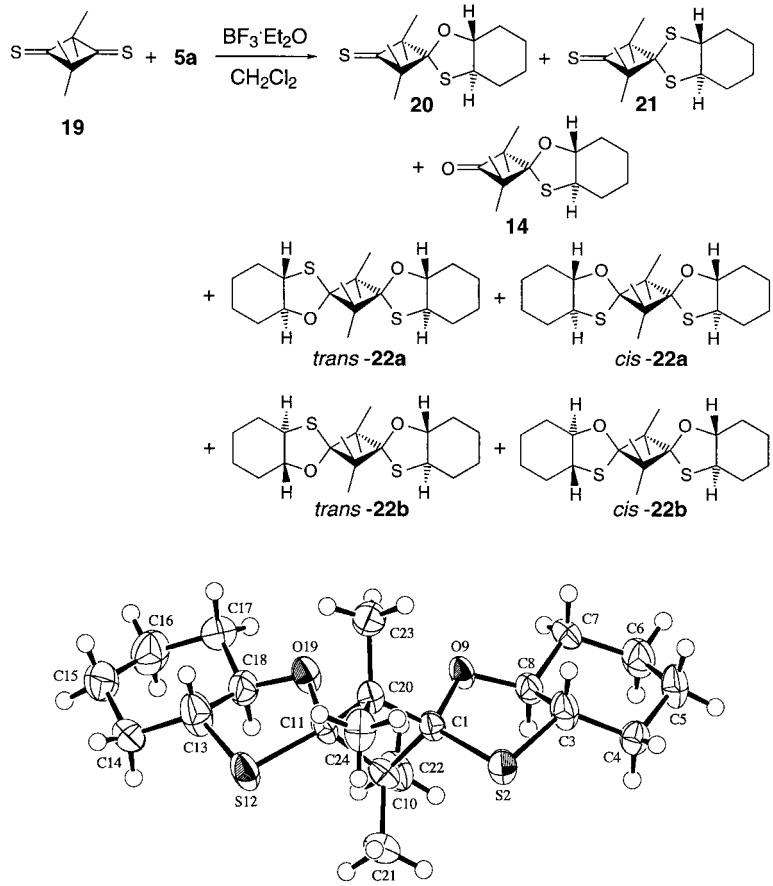


Fig. 3. *ORTEP Plot* [26] *of the molecular structure of one of the two symmetry-independent molecules of* cis-**22a** (arbitrary numbering of the atoms; 50% probability ellipsoids)

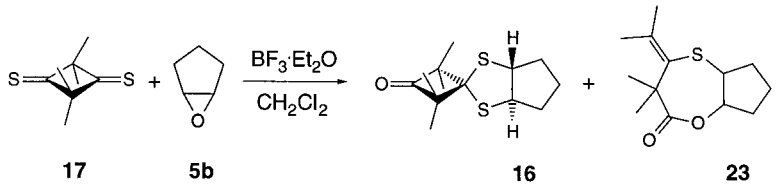
trans-fused 7-oxa-9-thiabicyclo[4.3.0]nonane ring systems and both cyclohexane rings in the chair conformation.

The ^{1}H- and ^{13}C-NMR spectra of *cis*-**22**, which was isolated after chromatography, showed 6 *s* and 6 *q*, respectively, for Me groups. In addition, two *s* for C(1) and C(6) of the fused-ring systems, as well as for Me_2C, appear in the ^{13}C-NMR spectrum. These data are in agreement with the presence of a mixture of *cis*-**22a** and *cis*-**22b** that differ in the relative configurations of the fused rings, *i.e.*, the four Me groups of the σ-symmetric *cis*-**22a** are all different, whereas *cis*-**22b**, with C_2 symmetry, contains only two types of Me groups. Similarly, the NMR data of the other fraction of the bis-adducts are consistent with the presence of a mixture of *trans*-**22a** and *trans*-**22b**.

Repeating the reaction of **19** with only 2 equiv. of **5a** and workup after 30 min gave mixtures of the mono-adducts **20** and **21** in 10% yield, and of bis-adducts **22** in 15% yield. In addition, 27% of **19** were recovered.

The reaction of **19** with **5b** led to a quite different result. Apparently, many side reactions produced many products in low yields. The only products which were isolated and characterized were **16** and the fused 1,4-oxathiepane derivative **23** (9 and 17% yield, resp.; *Scheme 9*). The structure of the unexpected ring-enlargement product **23** has been established by X-ray crystal-structure analysis; the molecular structure is shown in *Fig. 4*.

Scheme 9



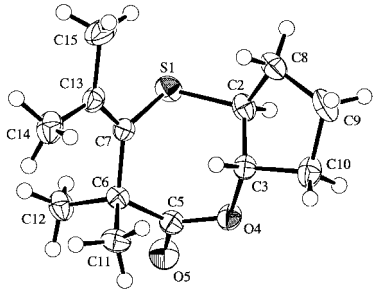


Fig. 4. *ORTEP Plot* [26] *of the molecular structure of* **23** (arbitrary numbering of the atoms; 50% probability ellipsoids)

2.4. *Reactions with 9*H-*Xanthene-9-thione* (**24**). After the addition of $BF_3 \cdot Et_2O$ to a solution of **24** in CH_2Cl_2, the color changed to red-brown. Then, 5 equiv. of **5a** were added, and the mixture was stirred overnight. The usual workup gave, in addition to 9% recovered **24**, the 1,3-dithiolane **26** and xanthone (**27**) in 6 and 90% yield[11]), respectively (*Scheme 10*).

With the aim of obtaining the expected initial product **25**, the reaction was performed at $-78°$. After 10 min, 50% of **24** was recovered. The main product (44%) was again xanthone (**27**), but the 1,3-oxathiolane **25** was also isolated (5%).

The spirocyclic products **25** and **26** were crystallized from i-PrOH/CH_2Cl_2 and $CHCl_3$/CH_2Cl_2, respectively, and their structures were established by X-ray crystallography (*Fig. 5*).

All attempts to obtain addition products of **24** and **5b**, *i.e.*, a spirocyclic 1,3-oxathiolane or 1,3-dithiolane corresponding to **25** and **26**, respectively, failed. The only product which could be detected was **27**, even when the reaction was performed at $-78°$ for only 1 to 3 min[12]).

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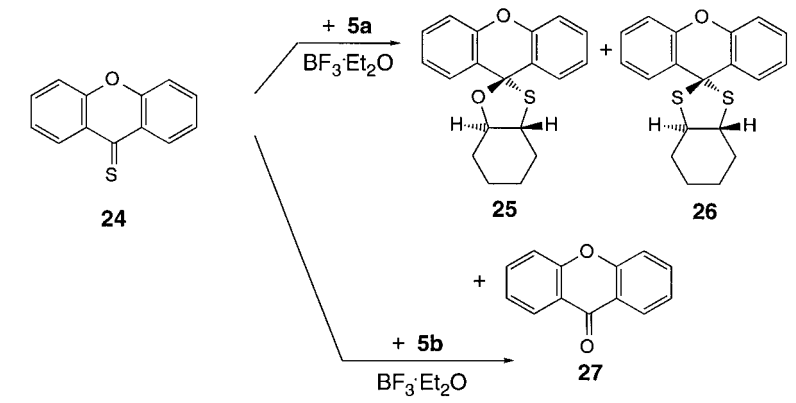
[11]) Yields with respect to the amount of **24** consumed.

[12]) After 1 min at $-78°$, 66% of **24** was recovered, and 29% of **27** was isolated as the only product.

Scheme 10



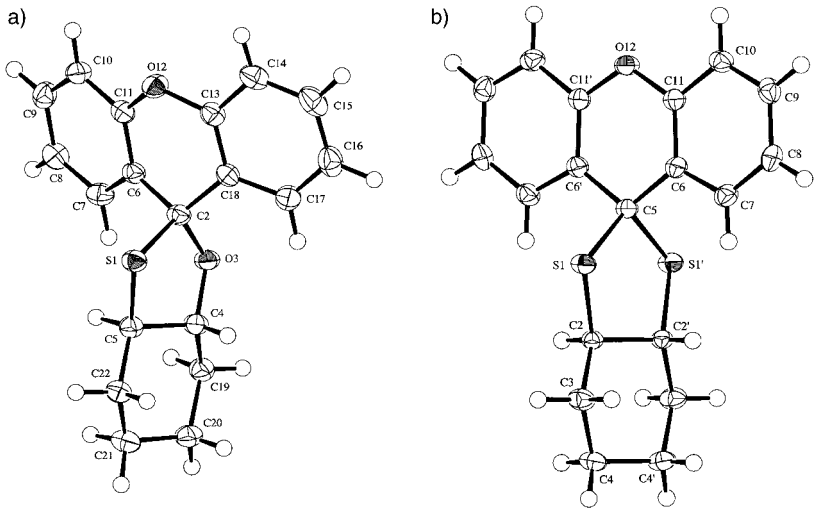


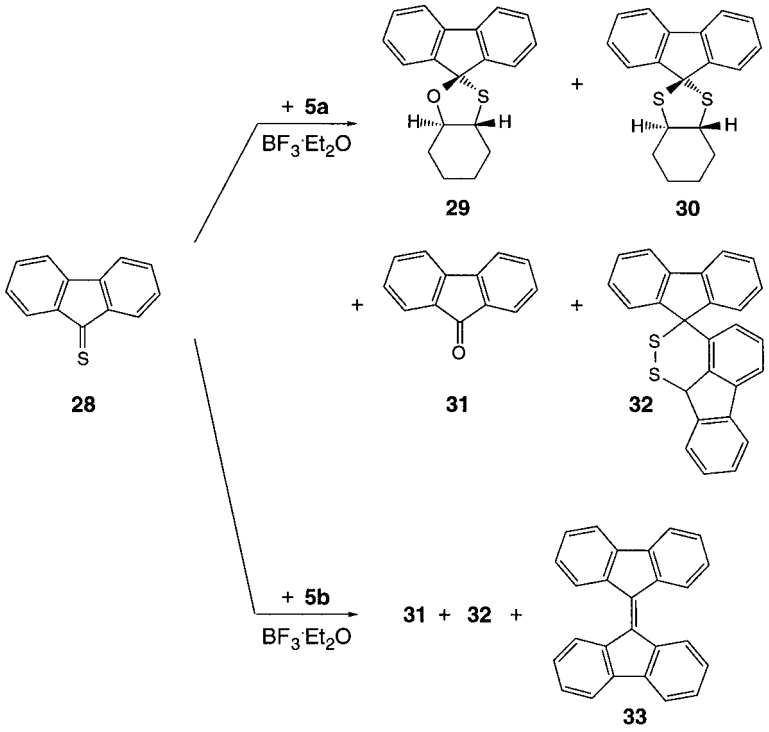
Fig. 5. *ORTEP Plots* [26] *of the molecular structures of* a) **25** *and* b) **26** (major conformation of **26** only shown; disorder not shown; arbitrary numbering of the atoms; 50% probability ellipsoids)

2.5. *Reactions with 9*H*-Fluorene-9-thione* (**28**). As expected, **28** proved to be a very reactive thioketone. Performing the reaction with **5a** at room temperature (15 min) or at −78° (30 min) gave similar results: *ca.* 3% of the 1,3-oxathiolane **29**, 7–10% of the 1,3-dithiolane **30**, and 78–80% of 9*H*-fluoren-9-one (**31**) were isolated (*Scheme 11*). In addition, *ca.* 5% of 1,2-dithiane **32**, the known dimer of **28** [27], which is formed *via* a *Diels-Alder* reaction, was obtained.

Repeating the reaction at −78° with workup after only 2 min yielded **29** (11%), **31** (70%), and **32** (15%), but none of the 1,3-dithiolane **30** was detected.

The analogous reaction of **28** with **5b** was also performed under different conditions, but no adduct could be isolated. The only indication for the expected addition reaction was the formation of 9*H*-fluoren-9-one (**31**), the product of the

Scheme 11



decomposition of the initially formed 1,3-oxathiolane (*cf. Sect. 2.1*). For example, workup of the reaction mixture after 1 min at −78° yielded **31**, **32**, and bis-fluorenylidene (**33** [28], *Scheme 11*) (37, 16, and 2%, resp.).

2.6. *Reactions with Thiobenzophenone* (**34a**) *and 4,4′-Dimethoxythiobenzophenone* (**34b**). To a mixture of **34a** and $BF_3 \cdot Et_2O$ in CH_2Cl_2 at −30°, 7 equiv. of **5a** were added all at once, leading to a color change from deep blue to red-orange. The reaction was complete after 10 min; the sole product was benzophenone (**38a**), isolated in 85% yield. The analogous reaction at −50° gave the 1,3-dithiolane **36a** and the 1,3-dioxolane **37a**[13]) (4 and 5% yield), in addition to 67% of **38a** (*Scheme 12*).

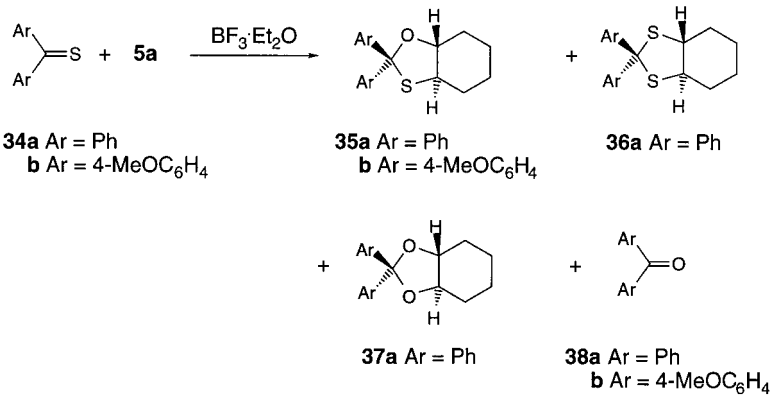
After crystallization from i-PrOH/CH_2Cl_2, the structure of **37a** has been established by X-ray crystallography (*Fig. 6*).

The reaction of the more stable **34b** with **5a** was performed at −78°. After a reaction time of 30 s, the 1,3-oxathiolane **35b** and 4,4′-dimethoxybenzophenone (**38b**) were isolated in 20 and 78% yield, respectively.

3. Discussion. – The intention of the present study was to establish the reaction of thioketones with oxiranes as a method for the preparation of 1,3-oxathiolanes. For convenience, we have chosen compounds with non-tautomerizable thiocarbonyl

[13]) In a control experiment, a mixture of benzophenone (**38a**) and **5a** was treated with $BF_3 \cdot Et_2O$ at 0°. After 120 min, **37a** was isolated in low yield (6%).

Scheme 12



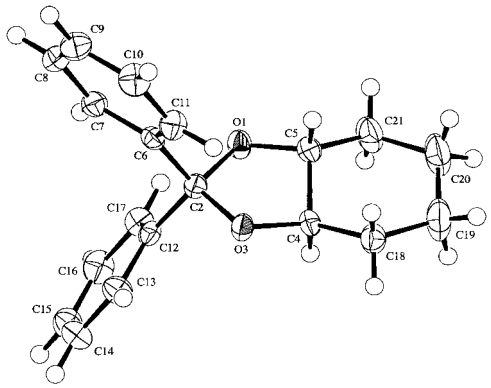


Fig. 6. *ORTEP Plot* [26] *of the molecular structure of* **37a** (major conformation only shown; disorder not shown; arbitrary numbering of the atoms; 50% probability ellipsoids)

groups. Because of the pronounced tendency of enolizable thioketones to exist predominantly in the enethiol form [29], they show a different reactivity, *e.g.*, they undergo other reactions with oxiranes (*cf.* [30][31]).

Based on the described results, we propose that the reaction of thioketones and oxiranes **5** proceeds by activation of the oxirane *via* complexation with the *Lewis* acid[14]) and nucleophilic ring opening to give a zwitterion of type **C** (*Scheme 13*). The latter then cyclizes to give the 1,3-oxathiolane. In all investigated cases, the *cis*-fused oxiranes **5a** and **5b** were transformed into *trans*-fused 1,3-oxathiolanes, *i.e.*, the nucleophilic ring opening occurs with inversion of the configuration at one stereogenic center. This is in accordance with the proposed mechanism, which is analogous to that of the formation of 1,3-dioxolanes from ketones and oxiranes. The mechanism of this latter reaction has been studied thoroughly [32][33].

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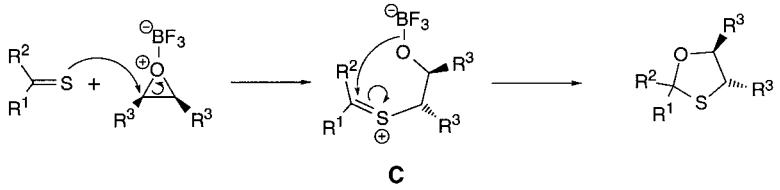
[14]) The presence of a *Lewis* acid is necessary as in its absence no reaction occurs.

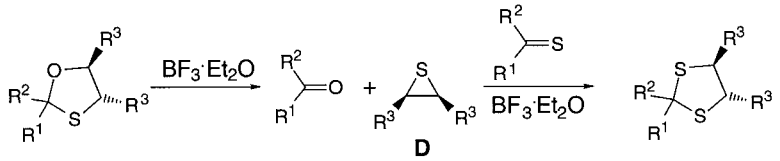
Scheme 13



C

In addition to 1,3-oxathiolanes, the corresponding 1,3-dithiolanes, as well as the carbonyl analogue of the starting thioketone, are formed under the reaction conditions. Under more drastic conditions, these compounds are obtained as the main or sole products. Their formation can be rationalized by assuming a decomposition of the primarily formed 1,3-oxathiolane to give a thiirane **D**, and a second molecule of the thioketone undergoes an acid-catalyzed reaction to give the 1,3-dithiolane (*Scheme 14*). This mechanistic proposal is supported by results of several control experiments (*cf. Sect. 2.1*).

Scheme 14

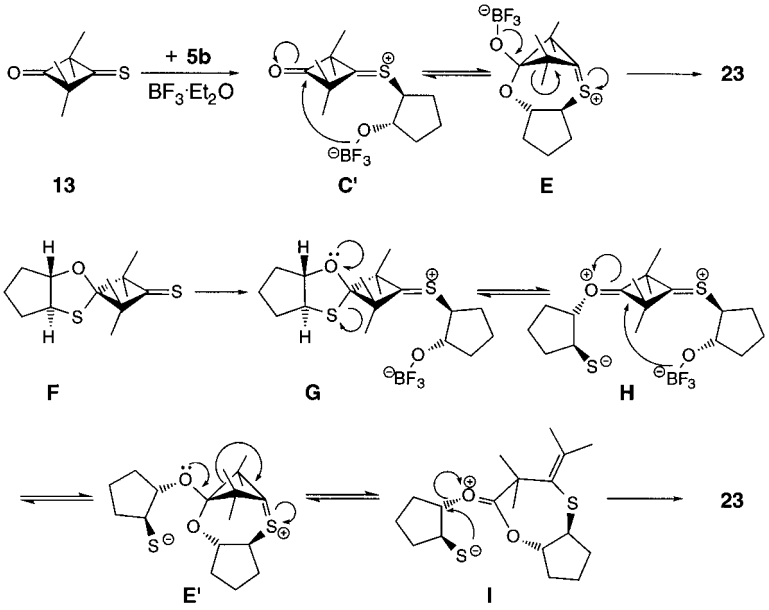


D

On the other hand, 1,2-epithiocyclohexane (**11**) and 1,1,3,3-tetramethylindan-2-one (**10**) in the presence of $BF_3 \cdot Et_2O$ do not react to give a 1,3-oxathiolane, but the analogous reaction of 1,2-epoxycyclohexane (**5a**) and benzophenone (**38a**) at 0° gave the corresponding 1,3-oxathiolane **37a** in low yield.

Apparently, the 1,3-oxathiolanes formed from 1,2-epoxycyclopentane (**5b**) are less stable than the homologues from **5a**. In general, the amount of secondary products was larger, and, in some cases, the initially formed products could not be detected. For instance, the reaction of the dithione **17** with **5b** yielded only the 1,3-dithiolane **16** and the unexpected product **23**. Formally, the formation of the latter can be explained *via* the intermediate zwitterion **C′** (*Scheme 15*). Nucleophilic attack of the alkoxide O-atom at the C=O group of the cyclobutanone leads to the bridged acetal **E** which, *via* ring opening, yields the final product **23**. On the other hand, no **23** was formed in the reaction of **5b** with **13**, and, therefore, the alternative intermediate **G**, instead of **C′** seems to be more likely. A conceivable mechanism for formation of the zwitterion **G** is the addition of a second molecule of **5b** to the 1:1 adduct **F**. A transacetalization of **G** can lead to the bridged acetal **E′**, followed by the opening of the four-membered ring to give **I**. The latter then decomposes to yield 1,2-epithiocyclopentane and **23**. Although 1,2-epithiocyclopentane could not be isolated nor detected, its intermediate formation is strongly indicated by the presence of the 1,3-dithiolane **16** (*Scheme 9*, *cf.* also *Scheme 5*).

Scheme 15



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, Dr. *J. Romanski* and Dr. *M. Kägi* for samples of the thioketones, and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for financial support.

Experimental Part

1. *General.* See [34].

2. *Reaction of 1,2-Epoxycycloalkanes with Thioketones. General Procedure.* To a soln. of a thioketone (*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. Then, the mixture was stirred for *ca.* 30 min. Several equiv. of *1,2-epoxycyclohexane* (**5a**) or *1,2-epoxycyclopentane* (**5b**) were added dropwise at different temp. (from $-78°$ up to r.t.), depending on the reactivity of the starting materials. The reaction time varied from 0.5 min to more than 2 d, taking into account the reactivity of the starting materials as well as the stability of the products. When the reaction was terminated (TLC), the mixture was extracted 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. *With 1,1,3,3-Tetramethylindane-2-thione* (**7**). *a*) Reaction of **5a** (272 mg, 2.8 mmol) with **7** (112 mg, 0.55 mmol), 50 h, r.t.; CC and PLC (hexane/AcOEt 20:1) yielded 15 mg (9.0%) of *1,1,3,3-tetramethylspiro-[indane-2,8′-(7′-oxa-9′-thiabicyclo[4.3.0]nonane)]* (**8**), 35 mg (20.0%) of *1,1,3,3-tetramethylspiro[indane-2,8′-(7′,9′-dithiabicyclo[4.3.0]nonane)]* (**9**), and 53 mg (51.4%) of *1,1,3,3-tetramethylindan-2-one* (**10**).

Data of **8**: Colorless crystals. M.p. 170–171°. IR (KBr): 2940*s*, 2860*m*, 1480*m*, 1450*m*, 1375*m*, 1360*w*, 1290*w*, 1070*s*, 1028*m*, 990*m*, 952*m*, 913*w*, 900*w*, 770*s*. ^{1}H-NMR: 7.77–7.13 (*m*, 4 arom. H); 3.51–3.43 (*m*, H–C(6′)); 2.85 (*ddd*, $^3J = 11.4$, 9.8, 3.5, H–C(1′)); 2.22–2.17, 2.10–2.01 (2*m*, 2 CH_2); 1.84–1.68 (*m*, 2 CH_2); 1.40, 1.39, 1.28, 1.27 (4*s*, 4 Me). ^{13}C-NMR: 148.9, 148.2 (2*s*, 2 arom. C); 126.9, 126.8, 122.5, 122.3 (4*d*, 4 arom. C); 110.9 (*s*, spiro-C); 87.7 (*d*, C(6′)); 52.8 (*d*, C(1′)); 51.9, 51.4 (2*s*, 2 Me_2C); 32.4 (*q*, Me); 30.2 (*t*, CH_2); 29.9 (*q*, Me); 29.1, 25.4 (2*t*, 2 CH_2); 23.9 (*q*, Me); 23.9 (*t*, CH_2); 22.0 (*q*, Me). CI-MS: 320 (100, $[M+NH_4]^+$), 303 (19, $[M+1]^+$), 206 (13), 115 (10). Anal. calc. for $C_{19}H_{26}OS$ (302.48): C 75.45, H 8.66; found: C 75.25, H 8.66.

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

Data of **9**: Colorless crystals. M.p. 108–109°. IR (KBr): 2990*w*, 2925*s*, 2855*m*, 1480*m*, 1445*s*, 1375*m*, 1310*w*, 1270*w*, 1187*w*, 1027*w*, 908*m*, 766*m*. ^{1}H-NMR: 7.20–7.11 (*m*, 4 arom. H); 3.07–3.03 (*m*, H–C(1′), H–C(6′)); 2.11–2.03 (*m*, 2 CH_2); 1.86–1.83 (*m*, 2 CH_2); 1.60, 1.44 (2*s*, 4 Me). ^{13}C-NMR: 149.2 (*s*, 2 arom. C); 126.9, 122.3 (2*d*, 4 arom. C); 87.6 (*s*, spiro-C); 59.1 (*d*, C(1′), C(6′)); 51.7 (*s*, 2 Me_2C); 30.1 (*q*, 2 Me); 30.0 (*t*, 2 CH_2); 29.3 (*q*, 2 Me); 25.3 (*t*, 2 CH_2). CI-MS: 319 (100, $[M+1]^+$), 205 (10).

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

An analogous experiment with **5a** (245 mg, 2.5 mmol) and **7** (102 mg, 0.5 mmol), 15 h, r.t. gave 52 mg (34.4%) of **8**, 17 mg (10.7%) of **9**, and 21 mg (22.3%) of **10**; 33 mg (32.4%) of **7** were recovered.

The reaction of **5a** (406 mg, 4.2 mmol) and **7** (169 mg, 0.83 mmol) at 0°, 1.5 h, yielded 124 mg (49.4%) of **8** and 3 mg (11.1%) of **9**; 46 mg (27.2%) of **7** were recovered.

b) Reaction of **5b** (554 mg, 6.5 mmol) with **7** (168 mg, 0.82 mmol), 15 h, 0°, CC and PLC (hexane/AcOEt 20:1) yielded 13 mg (5.5%) of *1,1,3,3-tetramethylspiro[indane-2,3′-(2′-oxa-4′-thiabicyclo[3.3.0]octane)]* (**12**) and 88 mg (57.5%) of **10**; 43 mg (25.6%) of **7** were recovered.

Data of **12**: Colorless oil. IR ($CHCl_3$): 2965*m*, 2876*w*, 1479*m*, 1458*m*, 1378*w*, 1312*w*, 1262*s*, 1102*s*, 1023*s*, 907*w*. ^{1}H-NMR: 7.24–7.13 (*m*, 4 arom. H); 4.09 (*ddd*, ^3J = 11.3, 10.2, 6.5, H–C(1′)); 3.30 (*ddd*, ^3J = 12.1, 10.2, 6.4, H–C(5′)); 2.26–2.12, 1.97–1.75, 1.60–1.40 (3*m*, 3 CH_2); 1.50, 1.44, 1.39, 1.34 (4*s*, 4 Me). ^{13}C-NMR: 148.8, 148.1 (2*s*, 2 arom. C); 127.1, 127.0 (2*d*, 2 arom. C); 123.9 (*s*, spiro-C); 122.6, 122.3 (2*d*, 2 arom. C); 95.1 (*d*, C(1′)); 55.5 (*d*, C(5′)); 52.4, 51.8 (2*s*, 2 Me_2C); 32.1, 29.5 (2*q*, 2 Me); 26.4 (*t*, CH_2); 24.2 (*q*, Me); 24.1, 23.2 (2*t*, CH_2); 22.1 (*q*, Me). CI-MS: 289 (100, $[M+1]^+$), 233 (7), 206 (11), 188 (18), 171 (7), 160 (6), 145 (6).

An analogous experiment with **5b** (344 mg, 4.1 mmol) and **7** (108 mg, 0.53 mmol), 0.25 h, −30° gave 21 mg (13.7%) of **12** and 6 mg (6.0%) of **10**; 69 mg (63.9%) of **7** were recovered.

2.2. *With 2,2,4,4-Tetramethyl-3-thioxocyclobutanone* (**13**). *a*) Reaction of **5a** (316 mg, 3.2 mmol) with **13** (84 mg, 0.54 mmol), 20 h, −78° to r.t.; CC (hexane/AcOEt 50:1) yielded 67 mg (48.8%) of *2,2,4,4-tetramethylspiro[cyclobutane-1,8′-(7′-oxa-9′-thiabicyclo[4.3.0]nonane)]-3-one* (**14**). Colorless oil. IR ($CHCl_3$): 2962*m*, 2944*m*, 2865*w*, 1769*s*, 1463*w*, 1454*w*, 1381*w*, 1262*s*, 1220*m*, 1084*s*, 1024*m*. ^{1}H-NMR: 3.18 (*ddd*, ^3J = 10.7, 9.6, 3.7, H–C(6′)); 2.74 (*ddd*, ^3J = 11.4, 9.6, 3.5, H–C(1′)); 2.21–2.09, 1.90–1.74 (2*m*, 2 CH_2); 1.50–1.20 (*m*, 2 CH_2); 1.26, 1.23, 1.16, 1.11 (4*s*, 4 Me). ^{13}C-NMR: 221.5 (*s*, C=O); 98.4 (*s*, spiro-C); 88.1 (*d*, C(6′)); 66.0, 65.1 (2*s*, 2 Me_2C); 52.8 (*d*, C(1′)); 30.4, 29.2, 25.4 (3*t*, 3 CH_2); 24.4 (*q*, Me); 23.9 (*t*, CH_2); 23.7, 18.4, 17.0 (3*q*, 3 Me). CI-MS: 255 (100, $[M+1]^+$), 184 (72).

An analogous experiment with **5a** (315 mg, 3.2 mmol) and **13** (148 mg, 0.95 mmol), 14 h, r.t.; CC and PLC (hexane/AcOEt 50:1) gave 56 mg (23.2%) of **14** and 37 mg (14.4%) of *2,2,4,4-tetramethylspiro[cyclobutane-1,8′-(7′,9′-dithiabicyclo[4.3.0]nonan)]-3-one* (**15**)[10]. Colorless crystals. M.p. 62–63.5°. IR (KBr): 2965*m*, 2928*s*, 2857*m*, 1778v*s*, 1452*w*, 1441*m*, 1375*w*, 1362*m*, 1263*w*, 1248*w*, 1169*w*, 1130*w*, 1027*m*, 930*m*, 834*w*. ^{1}H-NMR: 2.94–2.88 (*m*, H–C(1′), H–C(6′)); 2.20–2.10, 1.90–1.80 (2*m*, 2 CH_2); 1.60–1.25 (*m*, 2 CH_2); 1.36, 1.27 (2*s*, 4 Me). ^{13}C-NMR: 220.8 (*s*, C=O); 73.1 (*s*, spiro-C); 66.2 (*s*, 2 Me_2C); 59.3 (*d*, C(1′), C(6′)); 29.9, 25.3 (2*t*, 4 CH_2); 23.8, 23.6 (2*q*, 4 Me). CI-MS: 271 (100, $[M+1]^+$), 200 (29).

The reaction of **5a** (739 mg, 7.5 mmol) and **13** (184 mg, 1.07 mmol) at r.t., 25 h, yielded 84 mg (30.8%) of **14**.

b) Reaction of **5b** (410 mg, 4.9 mmol) with **13** (171 mg, 1.1 mmol), 14 h, r.t., and CC (hexane/AcOEt 50:1) yielded 74 mg (26%) of *2,2,4,4-tetramethylspiro[cyclobutane-1,3′-(2′,4′-dithiabicyclo[3.3.0]octan)]-3-one* (**16**). Colorless crystals. M.p. 70–72°. IR (KBr): 2963*m*, 2827*w*, 1775v*s*, 1745*w*, 1453*m*, 1380*w*, 1365*w*, 1027*w*, 933*w*. ^{1}H-NMR: 3.23–3.11 (*m*, H–C(1′), H–C(5′)); 2.29–2.17, 2.04–1.93, 1.65–1.47 (3*m*, 3 CH_2); 1.36, 1.27 (2*s*, 4 Me). ^{13}C-NMR: 220.6 (*s*, C=O); 87.7 (*s*, spiro-C); 67.0 (*s*, 2 Me_2C); 64.9 (*d*, C(1′), C(5′)); 28.5, 26.6 (2*t*, 3 CH_2); 23.5, 23.3 (2*q*, 4 Me). CI-MS: 257 (100, $[M+1]^+$), 186 (21). Anal. calc. for $C_{13}H_{20}OS_2$ (256.43): C 60.89, H 7.86; found: C 60.69, H 7.68.

Crystals of **16** suitable for X-ray crystal-structure determination were grown from CH_2Cl_2/i-PrOH.

An analogous experiment with **5b** (442 mg, 5.3 mmol) and **13** (172 mg, 1.1 mmol), 14 h, −78°, gave 53 mg (18.8%) of **16**; 47 mg (27.3%) of **13** were recovered.

2.3. *With 2,2,4,4-Tetramethylcyclobutane-1,3-dithione* (**19**). *a*) Reaction of **5a** (739 mg, 7.5 mmol) with **19** (184 mg, 1.07 mmol), 25 h, r.t.; CC (hexane/AcOEt 20:1) and PLC (hexane/AcOEt 50:1) yielded 11 mg (3.8%) of *2,2,4,4-tetramethylspiro[cyclobutane-1,8′-(7′-oxa-9′-thiabicyclo[4.3.0]nonane)]-3-thione* (**20**)[15], 6 mg (2.0%) of *2,2,4,4-tetramethylspiro[cyclobutane-1,8′-(7′,9′-dithiabicyclo[4.3.0]nonane)]-3-thione* (**21**)[15], 29 mg

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[15]) The mixture **20**/**21** obtained after CC and PLC was separated by HPLC (*Bischoff Nucleosil 100* (7 μm), hexane/AcOEt 100:1).

(10.7%) of **14**, 85 mg (21.6%) of trans-*1′,1′,3′,3′-tetramethyldispiro[7-oxa-9-thiabicyclo[4.3.0]nonane-8,1′-cyclobutan-3′,8″-(7″-oxa-9″-thiabicyclo[4.3.0]nonane)]* (*trans*-**22a**/*trans*-**22b**), and 66 mg (16.7%) of cis-*1′,1′,3′,3′-tetramethyldispiro[7-oxa-9-thiabicyclo[4.3.0]nonane-8,1′-cyclobutan-3′,8″-(7″-oxa-9″-thiabicyclo[4.3.0]nonane)]* (*cis*-**22a**/*cis*-**22b**).

Data of **20**: Red oil. IR ($CHCl_3$): 2970*m*, 2944*s*, 2863*m*, 1464*s*, 1450*m*, 1374*w*, 1360*m*, 1303*m*, 1261*w*, 1092*w*, 1070*s*, 1001m, 946*w*, 898*w*, 843*w*. ^{1}H-NMR: 3.30–3.21 (*m*, H–C(6′)); 2.84–2.75 (*m*, H–C(1′)); 2.25–2.10, 1.94–1.75 (2*m*, 2 CH_2); 1.54–1.25 (*m*, 2 CH_2); 1.36, 1.31, 1.27, 1.22 (4*s*, 4 Me). ^{13}C-NMR: 235.8 (*s*, C=S); 102.2 (*s*, spiro-C); 88.0 (*d*, C(6′)); 69.7, 68.7 (2*s*, 2 Me_2C); 52.8 (*d*, C(1′)); 30.2, 29.2 (2*t*, 2 CH_2); 28.2, 27.7 (2*q*, 2 Me); 25.4, 23.9 (2*t*, 2 CH_2); 22.4, 21.0 (2*q*, 2 Me). CI-MS: 271 (100, $[M+1]^+$).

Data of **21**: Red oil. IR ($CHCl_3$): 2930*s*, 2860*m*, 1734*w*, 1464*m*, 1448*m*, 1375*w*, 1360*w*, 1302*m*, 1262*m*, 1223*w*, 1142*m*, 1094*m*, 1010*w*, 918*w*, 809*w*. ^{1}H-NMR: 2.98–2.93 (*m*, H–C(1′), H–C(6′)); 2.30–2.06, 1.93–1.80 (2*m*, 2 CH_2); 1.60–1.25 (*m*, 2 CH_2); 1.45, 1.36 (2*s*, 4 Me). ^{13}C-NMR: 69.5 (*s*, 2 Me_2C); 59.4 (*d*, C(1′), C(6′)); 30.0 (*t*, 2 CH_2); 27.6, 27.3 (2*q*, 4 Me); 25.3 (*t*, 2 CH_2); the signals for C=S and spiro-C could not be detected. CI-MS: 287 (100, $[M+1]^+$).

Data of trans-**22a**/trans-**22b**: Colorless crystals. M.p. 153–155°. IR (KBr): 2936*s*, 2858*w*, 1466*m*, 1448*m*, 1376*w*, 1350*w*, 1260*w*, 1204*w*, 1093*m*, 1070*s*, 1030*m*, 1004*m*, 968*w*, 916*w*, 895*w*, 834*w*. ^{1}H-NMR: 3.14–3.04 (*m*, H–C(6), H–C(6″)); 2.65–2.55 (*m*, H–C(1), H–C(1″)); 2.19–2.05 (*m*, 2 CH_2); 1.87–1.70 (*m*, 2 CH_2); 1.46–1.30 (*m*, 4 CH_2); 1.19, 1.17, 1.16, 1.13 (4*s*, 4 Me). ^{13}C-NMR: 101.6 (*s*, 2 spiro-C); 87.4, 87.3 (2*d*, C(6), C(6″)); 55.4, 54.4 (2*s*, 2 Me_2C); 52.4, 52.3 (2*d*, C(1), C(1″)); 30.3, 29.2, 25.5 (3*t*, 6 CH_2); 24.2, 24.1 (2*q*, 2 Me); 24.0 (*t*, 2 CH_2); 23.0, 22.8 (2*q*, 2 Me). CI-MS: 369 (40, $[M+1]^+$), 255 (100), 184 (32).

Data of cis-**22a**/cis-**22b**: Colorless crystals. M.p. 127–129°. IR (KBr): 2934*s*, 2856*m*, 1467*m*, 1450*m*, 1374*m*, 1350*m*, 1260*w*, 1205*m*, 1094*m*, 1071*s*, 1052*m*, 984*m*, 959*m*, 899*w*, 865*w*, 833*w*. ^{1}H-NMR: 3.22–3.10 (*m*, H–C(6), H-C(6″)); 2.64–2.54 (*m*, H–C(1), H–C(1″)); 2.25–2.17 (*m*, CH_2); 2.13–2.03 (*m*, CH_2); 1.88–1.71 (*m*, CH_2); 1.49–1.13 (*m*, CH_2); 1.32, 1.28, 1.23, 1.05, 0.97, 0.91 (6*s*, 4 Me). ^{13}C-NMR: 102.8 (*s*, 2 spiro-C); 88.0, 87.8 (2*d*, C(6), C(6″)); 56.2, 54.4 (2*s*, 2 Me_2C); 52.0, 51.9 (2*d*, C(1), C(1″)); 30.5, 30.4 (2*t*, CH_2); 29.9 (*q*, Me); 29.2, 29.1 (2*t*, CH_2); 28.6, 27.2 (2*q*, Me); 25.5, 24.0 (2*t*, CH_2); 18.4, 17.1, 15.6 (3*q*, Me). CI-MS: 369 (52, $[M+1]^+$), 255 (100), 184 (20).

Crystals of *cis*-**22a** suitable for X-ray crystal-structure determination were grown from CH_2Cl_2/i-PrOH.

An analogous experiment of **5a** (160 mg, 1.6 mmol) with **19** (141 mg, 0.82 mmol), 0.5 h, r.t.; CC (hexane/AcOEt 20:1) and PLC (hexane/AcOEt 50:1) gave 19 mg (6.3%) of *trans*-**22a**/*trans*-**22b** and 13 mg (4.3%) of *cis*-**22a**/*cis*-**22b**[16]); 38 mg (27.0%) of **19** were recovered.

b) Reaction of **5b** (800 mg, 9.5 mmol) with **19** (234 mg, 1.36 mmol), 3 h, r.t.; CC (hexane/AcOEt 20:1) and PLC (hexane/AcOEt 50:1) yielded 29 mg (8.3%) of **16** and 55 mg (16.9%) of *4,4-dimethyl-5-(1-methylethylidene)-6-thia-2-oxabicyclo[5.3.0]decan-3-one* (**23**). Colorless crystals. M.p. 91–93°. IR (KBr): 2980*m*, 2937*m*, 2870*m*, 1725*vs*, 1468*w*, 1450*w*, 1392*m*, 1365*m*, 1291*w*, 1238*s*, 1220*m*, 1191*w*, 1121*vs*, 1103*s*, 1090*s*, 1060*m*, 750*w*. ^{1}H-NMR: 4.57–4.48 (*m*, H–C(1)); 3.02 (*ddd*, ^3J = 12.2, 10.2, 6.9, H–C(7)); 2.11–1.97, 1.83–1.71, 1.57–1.42 (3*m*, 3 CH_2); 2.04, 1.94, 1.65, 1.60 (4*s*, 4 Me). ^{13}C-NMR: 175.1 (*s*, C=O); 142.4, 124.8 (2*s*, Me_2C=*C*); 79.9 (*d*, C(1)); 55.5 (*s*, Me_2C); 50.5 (*d*, C(7)); 28.8 (*t*, 1 CH_2); 27.1 (*q*, 1 Me); 26.8 (*t*, 1 CH_2); 25.8, 25.7, 22.4 (3*q*, 3 Me); 19.4 (*t*, 1 CH_2). CI-MS: 258 (39, $[M+NH_4]^+$), 241 (100, $[M+1]^+$). Anal. calc. for $C_{13}H_{20}O_2S$ (239.57): C 65.18, H 8.41; found: C 65.08, H 8.27.

Crystals of **23** suitable for X-ray crystal-structure determination were grown from CH_2Cl_2/hexane.

2.4. *With 9H-Xanthene-9-thione* (**24**). *a*) Reaction of **5a** (490 mg, 5 mmol) with **24** (210 mg, 0.99 mmol) 14 h, r.t.; CC (hexane/AcOEt 20:1) and PLC (hexane/CH_2Cl_2 4:1) yielded 19 mg (9.0%) of **24**, 160 mg (83.4%) of *9H-xanthen-9-one* (**27**), and 17 mg (5.3%) of *spiro[7,9-dithiabicyclo[4.3.0]nonane-8,9′-[9H]xanthene]* (**26**). Colorless crystals. M.p. 191–193°. IR (KBr): 2933*s*, 2851*m*, 1658*m*, 1621*w*, 1608*m*, 1480*m*, 1461*m*, 1442*s*, 1330*m*, 1268*w*, 1186*w*, 1018*m*, 987*w*, 874*w*, 841*w*, 758*m*. ^{1}H-NMR: 8.10–8.05 (*m*, 2 arom. H); 7.30–7.22 (*m*, 2 arom. H); 7.20–7.13 (*m*, 2 arom. H); 7.07–7.03 (*m*, 2 arom. H); 3.78–3.66 (*m*, H–C(1), H–C(6)); 2.30–1.25 (*m*, 4 CH_2). ^{13}C-NMR: 150.0 (*s*, 2 arom. C); 130.1, 128.7 (2*d*, 4 arom. C); 127.1 (*s*, 2 arom. C); 123.4, 116.2 (2*d*, 4 arom. C); 62.5 (*d*, C(1), C(6)); 60.4 (*s*, spiro-C); 29.5, 15.2 (2*t*, 4 CH_2). CI-MS: 327 (96, $[M+1]^+$), 261 (100), 213 (29).

Crystals of **26** suitable for X-ray crystal-structure determination were grown from CH_2Cl_2/$CHCl_3$.

An analogous experiment with **5a** (495 mg, 5 mmol) and **24** (212 mg, 1 mmol), 10 min, –78°, and CC (hexane/CH_2Cl_2 3:1) yielded 107 mg (50.5%) of **24**, 85 mg (43.8%) of **27**, and 16 mg (5.2%) of *spiro[7-oxa-9-thiabicyclo[4.3.0]nonane-8,9′-[9H]xanthene]* (**25**). Colorless crystals. M.p. 164–166°. IR ($CHCl_3$): 2943*m*,

[16]) The mixture **20**/**21** was not further purified.

2862*m*, 1601*m*, 1575*w*, 1475*m*, 1454*s*, 1313*m*, 1293*w*, 1261*m*, 1249*w*, 1216*m*, 1100*m*, 1067*m*, 1014*w*, 918*w*, 882*w*. ^{1}H-NMR: 7.95–7.90 (*m*, 1 arom. H); 7.80–7.73 (*m*, 1 arom. H); 7.38–7.30 (*m*, 2 arom. H); 7.24–7.15 (*m*, 4 arom. H); 4.10 (*ddd*, ^3J = 11.0, 9.7, 3.8, H–C(6)); 3.24 (*ddd*, ^3J = 11.7, 9.7, 3.6, H–C(1)); 2.40–2.15, 2.05–1.85 (2*m*, 2 CH_2); 1.75–1.40 (*m*, 2 CH_2). ^{13}C-NMR: 150.9, 150.3 (2*s*, 2 arom. C); 129.2, 129.1, 127.7 (3*d*, 3 arom. C); 127.1 (*s*, 1 arom. C); 126.7 (*d*, 1 arom. C); 126.0 (*s*, 1 arom. C); 116.6, 116.4 (2*d*, 4 arom. C); 89.2 (*d*, C(6)); 86.2 (*s*, spiro-C); 55.2 (*d*, C(1)); 30.8, 28.7, 25.5, 24.0 (4*t*, 4 CH_2). CI-MS: 311 (100, $[M+1]^+$), 197 (24).

Crystals of **25** suitable for X-ray crystal-structure determination were grown from CH_2Cl_2/i-PrOH.

b) Reaction of **5b** (420 mg, 5 mmol) with **24** (212 mg, 1 mmol), 3 min, −78°, and CC (hexane/CH_2Cl_2 3:1) yielded 98 mg (50.0%) of **27** as the only product; 93 mg (43.9%) of **24** were recovered.

2.5. *With 9*H*-Fluorene-9-thione* (**28**). *a*) Reaction of **5a** (690 mg, 7 mmol) with **28** (200 mg, 1.02 mmol), 0.5 h, −78°, CC (hexane/AcOEt 20:1) and PLC (hexane/CH_2Cl_2 2:1) yielded 8 mg (2.7%) of *spiro[9*H*-fluorene-9,8′-(7′-oxa-9′-thiabicyclo[4.3.0]nonane)]* (**29**) and 33 mg (10.8%) of *spiro[7,9-dithiabicyclo[4.3.0]nonane-8,9′-[9*H*]fluorene]* (**30**), 141 mg (76.8%) of *9*H*-fluorene-9-one* (**31**), and 19 mg (9.5%) of *10b′*H*-spiro[fluorene-9,3′-fluoreno[9,1-*cd*][1,2]dithiane]* (**32**) [27].

Data of **29**: Colorless crystals. M.p. 110–111°. IR (KBr): 2934*m*, 2860*m*, 1446*m*, 1347*w*, 1292*w*, 1260*w*, 1203*m*, 1088*m*, 1066*m*, 1008*m*, 963*w*, 937*w*, 887*w*, 862*w*, 768*m*, 747*m*, 730*m*, 683*w*. ^{1}H-NMR: 7.71–7.67 (*m*, 1 arom. H); 7.60–7.54 (*m*, 3 arom. H); 7.39–7.28 (*m*, 4 arom. H); 4.05 (*ddd*, ^3J = 10.7, 9.5, 3.7, H–C(6′)); 3.42 (*ddd*, ^3J = 11.7, 9.5, 3.5, H–C(1′)); 2.39–2.24, 2.04–1.90 (2*m*, 2 CH_2); 1.74–1.40 (*m*, 2 CH_2). ^{13}C-NMR: 148.3, 148.1, 139.3, 138.5 (4*s*, 4 arom. C); 129.5, 129.4, 128.5, 128.1, 125.6, 124.5, 119.8, 119.7 (8*d*, 8 arom. C); 94.5 (*s*, spiro-C); 88.5 (*d*, C(6′)); 55.1 (*d*, C(1′)); 31.0, 29.5, 25.6, 24.4 (4*t*, 4 CH_2). EI-MS: 294 (17, $M^{+\cdot}$), 180 (100), 149 (17), 81 (20), 57 (23).

Data of **30**: Colorless crystals. M.p. 173–175°. IR (KBr): 2931*m*, 2857*w*, 1474*w*, 1440*m*, 1330*w*, 1262*m*, 1213*w*, 1186*w*, 1091*w*, 1007*w*, 915*w*, 821*w*, 787*w*, 737*s*. ^{1}H-NMR: 7.77–7.72 (*m*, 2 arom. H); 7.63–7.58 (*m*, 2 arom. H); 7.38–7.30 (*m*, 4 arom. H); 3.76–3.70 (*m*, H–C(1), H–C(6)); 2.31–2.25, 2.04–1.95 (2*m*, 2 CH_2); 1.72–1.41 (*m*, 2 CH_2). ^{13}C-NMR: 151.2, 138.4 (2*s*, 4 arom. C); 128.4, 128.2, 125.4, 119.7 (4*d*, 8 arom. C); 65.2 (*s*, spiro-C); 61.7 (*d*, C(1), C(6)); 30.1, 25.3 (2*t*, 4 CH_2). CI-MS: 311 (100, $[M+1]^+$), 197 (8).

An analogous experiment with **5a** (680 mg, 6.9 mmol) and **28** (196 mg, 1.0 mmol) at r.t. (0.25 h) gave 10 mg (3.4%) of **29**, 21 mg (6.8%) of **30**, 145 mg (80.6 %) of **31**, and 21 mg (10.7%) of **32**.

b) The reaction of **5b** with **28** was performed at different temperatures, but no spirocyclic 1,3-oxathiolane or 1,3-dithiolane was observed. For instance, from the reaction of **5b** (434 mg, 5.2 mmol) and **28** (188 mg, 0.96 mmol) at −78° (1 min), only **31** (63 mg, 36.4 %), **32** (60 mg, 31.9%), and *9,9′-bifluorenylidene* (**33**) [28] (6 mg, 3.8%) were obtained.

2.6. *With Thiobenzophenone* (**34a**). *a*) Reaction of **5a** (665 mg, 6.7 mmol) with **34a** (198 mg, 1 mmol), 10 min, −50°; CC (hexane/AcOEt 30:1) yielded 12 mg (3.8%) of *8,8-diphenyl-7,9-dithiabicyclo[4.3.0]nonane* (**36a**), 15 mg (5.4%) of *8,8-diphenyl-7,9-dioxabicyclo[4.3.0]nonane* (**37a**), and 122 mg (67.0%) of *benzophenone* (**38a**).

Data of **36a**: Colorless crystals. M.p. 143–145.5°. IR (KBr): 2935*m*, 2921*m*, 2854*m*, 1590*w*, 1486*m*, 1441*s*, 1325*w*, 1316*w*, 1279*m*, 1150*w*, 1078*m*, 1032*w*, 862*w*, 756*m*, 742*s*, 696*s*. ^{1}H-NMR: 7.65–7.58 (*m*, 4 arom. H); 7.35–7.20 (*m*, 6 arom. H); 3.45–3.33 (*m*, H–C(1), H–C(6)); 2.30–2.15, 2.00–1.83 (2*m*, 2 CH_2); 1.70–1.20 (*m*, 2 CH_2). ^{13}C-NMR: 146.9 (*s*, 2 arom. C); 128.0, 127.9, 126.9 (3*d*, 10 arom. C); 72.8 (*s*, C(8)); 61.1 (*d*, C(1), C(6)); 29.8, 25.3 (2*t*, 4 CH_2). CI-MS: 313 (100, $[M+1]^+$), 213 (13), 199 (58), 183 (20), 102 (55).

Data of **37a**: Colorless crystals. M.p. 138–139°. IR (KBr): 2938*m*, 2860*m*, 1490*w*, 1447*m*, 1358*w*, 1318*w*, 1240*m*, 1226*m*, 1112*s*, 1082*s*, 1070*s*, 1030*w*, 965*m*, 944*m*, 910*m*, 782*s*, 760*m*, 700*s*. ^{1}H-NMR: 7.60–7.54 (*m*, 4 arom. H); 7.38–7.26 (*m*, 6 arom. H); 3.49–3.40 (*m*, H–C(1), H–C(6)); 2.29–2.22, 1.86–1.82, 1.62–1.54, 1.38–1.21 (4*m*, 4 CH_2). ^{13}C-NMR: 143.8 (*s*, 2 arom. C); 127.9, 127.7, 126.0 (3*d*, 10 arom. C); 108.7 (*s*, C(8)); 80.9 (*d*, C(1), C(6)); 28.8, 23.6 (2*t*, 4 CH_2). CI-MS: 281 (100, $[M+1]^+$), 203 (14), 183 (6). Anal. calc. for $C_{19}H_{20}O_2$ (280.37): C 81.40, H 7.19; found: C 81.16, H 6.99.

Crystals of **37a** suitable for X-ray crystal-structure determination were grown from CH_2Cl_2/i-PrOH.

An analogous experiment with **5a** (770 mg, 7.9 mmol) and **34a** (268 mg, 1.35 mmol), 1 min, −78°; CC and PLC (hexane/AcOEt 30:1) yielded 36 mg (9.0%) of *8,8-diphenyl-7-oxa-9-thiabicyclo[4.3.0]nonane* (**35a**) in addition to **36a**, **37a**, and **38a**.

Data of **35a**: Colorless crystals. M.p. 90–92°. IR (KBr): 2940*m*, 2860*m*, 1487*m*, 1447*m*, 1352*w*, 1260*w*, 1230*w*, 1207*w*, 1182*w*, 1060*m*, 1022*m*, 962*w*, 858*w*, 762*m*, 748*m*, 704*m*. ^{1}H-NMR: 7.60–7.55 (*m*, 2 arom. H); 7.46–7.41 (*m*, 2 arom. H); 7.38–7.20 (*m*, 6 arom. H); 3.58 (*ddd*, ^3J = 11.2, 9.7, 3.7, H–C(6)); 3.23 (*ddd*, ^3J = 11.5, 9.7, 3.5, H–C(1)); 2.36–2.14, 1.95–1.75 (2*m*, 2 CH_2); 1.75–1.22 (*m*, 2 CH_2). ^{13}C-NMR: 146.5, 146.0 (2*s*, 2 arom. C); 128.0, 127.9, 127.4, 127.3, 126.8, 126.5 (6*d*, 10 arom. C); 97.5 (*s*, C(8)); 87.2 (*d*, C(6)); 55.3 (*d*, C(1)); 30.5, 29.2,

25.5, 23.9 (4*t*, 4 CH_2). CI-MS: 297 (12, $[M+1]^+$), 200 (60), 183 (100). Anal. calc. for $C_{19}H_{20}OS$ (296.43): C 76.98, H 6.80; found: C 76.81, H 6.85.

2.7. *With 4,4′-Dimethoxythiobenzophenone* (**34b**). Reaction of **5a** (528 mg, 5.4 mmol) with **34b** (200 mg, 0.77 mmol), 30 s, −78°; CC and PLC (hexane/AcOEt 10:1) yielded 145 mg (77.5%) of *4,4′-dimethoxybenzophenone* (**38b**) and 55 mg (20.1%) of *8,8-bis(4-methoxyphenyl)-7-oxa-9-thiabicyclo[4.3.0]nonane* (**35b**). Colorless crystals. M.p. 140–142°. IR (KBr): 2932*s*, 2857*m*, 1636*s*, 1604*s*, 1505*m*, 1448*w*, 1416*w*, 1306*m*, 1294*m*, 1255*s*, 1172*m*, 1150*m*, 1097*w*, 1027*s*, 967*w*, 930*m*, 852*s*, 838*s*, 765*s*. ^{1}H-NMR: 7.52–7.46 (*m*, 2 arom. H); 7.36–7.30 (*m*, 2 arom. H); 6.91–6.85 (*m*, 2 arom. H); 6.83–6.77 (*m*, 2 arom. H); 3.82, 3.78 (2*s*, 2 MeO); 3.57 (*ddd*, ^3J = 11.2, 9.7, 3.7, H–C(6)); 3.24 (*ddd*, ^3J = 11.5, 9.7, 3.4, H–C(1)); 2.33–2.16, 1.95–1.78, 1.74–1.58, 1.50–1.25 (4*m*, 4 CH_2). ^{13}C-NMR: 158.8, 158.7, 139.0, 138.2 (4*s*, 4 arom. C); 128.2, 127.9, 113.2, 113.1 (4*d*, 8 arom. C); 97.2 (*s*, C(8)); 87.0 (*d*, C(6)); 55.4 (*d*, C(1)); 55.2 (*q*, 2 MeO); 30.6, 29.3, 25.5, 21.0 (4*t*, 4 CH_2). CI-MS: 357 (100, $[M+1]^+$), 243 (50), 135 (9).

3. *Control Experiments.* 3.1. *Reaction of* **7** *with 1,2-Epithiocyclohexane* (**11**). According to the *General Procedure* in *Sect. 2*, the reaction of **7** (105 mg, 0.52 mmol) with **11** (212 mg, 1.9 mmol) at r.t. (14 h) yielded 142 mg (85.9%) of **9**.

3.2. *Decomposition of* **8**. A soln. of **8** (31 mg, 0.10 mmol) and 1.1 equiv. of $BF_3 \cdot Et_2O$ in 7 ml of CH_2Cl_2 was stirred at r.t. After 4 d, no **8** could be detected (TLC). After workup and CC (hexane/AcOEt 20:1), 17 mg (87.7%) of **10** were isolated.

3.3. *Attempted Reaction of* **10** *with* **11**. According to the *General Procedure* in *Sect. 2*, a soln. of 380 mg (2.0 mmol) of **10**, 1.1 equiv. of $BF_3 \cdot Et_2O$, and 950 mg (8.3 mmol) of **11** was stirred at r.t. Even after 2 d, no **8** could be detected by TLC. After usual workup, only **10** could be isolated (367 mg (96.6%)).

3.4. *Reaction of* **5a** *with* **38a**. According to the *General Procedure* in *Sect. 2*, **5a** (686 mg, 7 mmol) was added to a CH_2Cl_2 soln. of **38a** (364 mg, 2 mmol) and 1.1 equiv. of $BF_3 \cdot Et_2O$. The mixture was stirred at r.t. for 2 h. The usual workup gave 33 mg (5.9%) of **37a**.

4. *X-Ray Crystal-Structure Determination of* **8**, **9**, **16**, *cis*-**22a**, **23**, **25**, **26**, *and* **37a** (see *Table 2* and *Figs. 1–6*)[17]). 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. An empirical absorption correction was applied in the case of **26** [35]. Data collection and refinement parameters are given in *Table 2*, views of the molecules are shown in *Figs. 1–6*. The structures were solved by direct methods with SHELXS86 [36]. 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* using 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 case of **8**, **9**, **16**, **23**, and **25**. Neutral-atom scattering factors for non-H-atoms were taken from [37a] and the scattering factors for H-atoms from [38]. Anomalous dispersion effects were included in F_c [39]. The values for f' and f'' were those of [37b]. The values of the mass-attenuation coefficients were those of [37c]. The calculations were performed with the TEXSAN crystallographic software package [40].

In the case of **8**, the cyclohexane ring is disordered over two orientations, which result from alternative chair conformations of the cyclohexane ring and a twist of the adjacent five-membered ring. The cyclohexane C-atoms bonded to the S- and O-atoms are disordered, as well as the two C-atoms opposite to these: two positions were refined for C(4), C(5), C(11), and C(12), while C(10) and C(13)[18]) occupy common positions in each conformation. The site-occupation factors of the disordered atoms were initially refined and then held fixed. The major conformation has 60% occupancy. All of the H-atoms, except those bonded to the disordered cyclohexane ring, were placed in the positions indicated by a difference electron-density map, and their positions were allowed to refine together with individual isotropic displacement parameters. The cyclohexane H-atoms were fixed in geometrically calculated positions with d(C–H) = 0.95 Å and they were assigned fixed isotropic displacement parameters with a value equal to 1.2 U_{eq} of the parent C-atom.

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[17]) 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-133972–133979 for **8**, **9**, **16**, *cis*-**22a**, **23**, **25**, **26**, and **37a**, respectively. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 EZ, UK (fax: +44-(0)12 23-33 60 33 or e-mail: deposit@ccdc.cam.ac.uk).

[18]) Arbitrary numbering of the crystal-structure determination.

Table 2. *Crystallographic Data of Compounds* **8**, **9**, **16**, cis-**22a**, **23**, **25**, **26**, *and* **37a**

	8	**9**	**16**	*cis*-**22a**	**23**	**25**	**26**	**37a**
Crystallized from	i-PrOH/CH_2Cl_2	i-PrOH/CH_2Cl_2	i-PrOH/CH_2Cl_2	i-PrOH/CH_2Cl_2	CH_2Cl_2/hexane	i-PrOH/CH_2Cl_2	$CHCl_3$/CH_2Cl_2	i-PrOH/CH_2Cl_2
Empirical formula	$C_{19}H_{26}OS$	$C_{19}H_{26}S_2$	$C_{13}H_{20}OS_2$	$C_{20}H_{32}O_2S_2$	$C_{13}H_{20}O_2S$	$C_{19}H_{18}O_2S$	$C_{19}H_{18}OS_2$	$C_{19}H_{20}O_2$
Formula weight [g·mol^{-1}]	302.47	318.53	256.42	368.59	240.36	310.41	326.47	280.36
Crystal color, habit	colorless, prism	colorless, prism	colorless, prism	colorless, prism	colorless, prism	colorless, prism	colorless, prism	colorless, prism
Crystal dimensions [mm]	0.27 × 0.30 × 0.45	0.15 × 0.20 × 0.40	0.30 × 0.38 × 0.48	0.33 × 0.35 × 0.45	0.28 × 0.32 × 0.45	0.30 × 0.38 × 0.38	0.38 × 0.48 × 0.50	0.25 × 0.33 × 0.45
Temp. [K]	173(1)	173(1)	173(1)	173(1)	173(1)	173(1)	173(1)	173(1)
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*Pbca*	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/n$
Z	8	6	4	8	4	4	4	4
Reflections for cell determination	25	25	25	25	25	25	25	25
2θ Range for cell determination [°]	32 – 37	32 – 38	38 – 40	35 – 39	38 – 40	38 – 40	39 – 40	37 – 40
Unit cell parameters								
a [Å]	8.117(6)	12.006(2)	6.294(1)	10.590(3)	12.158(2)	11.131(3)	12.392(4)	11.854(1)
b [Å]	17.359(5)	21.368(3)	15.816(2)	16.027(2)	9.159(3)	10.252(3)	11.545(2)	8.892(1)
c [Å]	23.902(4)	10.481(1)	13.840(1)	23.901(1)	11.713(2)	14.331(3)	10.706(3)	14.3447(8)
α [°]	90	97.58(1)	90	90	90	90	90	90
β [°]	90	97.69(1)	92.11(1)	91.595(9)	92.25(1)	111.66(2)	95.48(2)	96.069(5)
γ [°]	90	89.43(1)	90	90	90	90	90	90
V [Å^3]	3368(3)	2641.4(6)	1376.6(3)	4055(1)	1303.2(4)	1519.9(6)	1524.5(7)	1503.5(2)
D_x [g cm^{-3}]	1.193	1.201	1.237	1.207	1.225	1.356	1.422	1.238
μ(MoK_α) [mm^{-1}]	0.190	0.295	0.366	0.272	0.233	0.217	0.348	0.0786
$2\theta_{(max)}$ [°]	55	50	60	55	55	55	60	60
Total reflections measured	5194	9791	4485	10146	3340	3878	2412	4843
Symmetry-independent reflections	3874	9307	4005	9299	3002	3497	2201	4378
Reflections used [$I > 2\sigma(I)$]	2748	6643	3306	6415	2433	2860	1966	2988
Parameters refined	291	677	165	433	226	272	119	208
Final R	0.0586	0.0442	0.0378	0.0780	0.0386	0.0436	0.0467	0.0559
wR ($w = [\sigma^2(F_o) + (0.005\,F_o)^2]^{-1}$)	0.0534	0.0412	0.0378	0.0701	0.0384	0.0459	0.0563	0.0541
Goodness of fit	2.417	1.600	1.957	3.393	1.979	2.289	3.861	2.252
Secondary extinction coefficient	$1.9(4)\cdot10^{-7}$	$2.0(2)\cdot10^{-7}$	$8.3(9)\cdot10^{-7}$	–	$5(1)\cdot10^{-7}$	$7(2)\cdot10^{-7}$	–	–
Final Δ_{max}/σ	0.001	0.03	0.0008	0.0002	0.0002	0.0003	0.0001	0.001
$\Delta\rho$(max;min) [e·Å^{-3}]	0.30; −0.28	0.31; −0.29	0.32; −0.24	0.80; −0.83	0.31; −0.18	0.44; −0.36	0.60; −0.68	0.32; −0.39

In the case of **9**, there are three independent molecules in the asymmetric unit, but no additional crystallographic symmetry could be found. In each molecule, the cyclohexane ring is disordered over two orientations. The disorder is similar to that found in **8** and was treated in an analogous fashion. The major conformation in each molecule has *ca*. 58% occupancy.

In the case of **26**, the cyclohexane ring is again similarly disordered. Two positions were defined for C(2) and C(4), while C(3)[18]) occupies a common position in each conformation; the remaining atoms in this ring are generated by the crystallographic C_2 symmetry. The major conformation has *ca*. 80% occupancy.

The same sort of disorder is also displayed by the cyclohexane ring of **37a**. Two positions were defined for C(4) and C(5)[18]). While C(18) and C(21) occupy common positions in each conformation, the atoms C(19) and C(20) are also disordered, but it was not possible to successfully refine any disordered positions for these atoms. Instead, they have been treated as ordered atoms in the model, although the elongation of the displacement ellipsoids clearly shows the presence of the disorder. The major conformation has *ca*. 79% occupancy.

For **16**, C(4) and C(5) at the junction of the fused five-membered rings are disordered over two orientations, which result from alternative half-chair twists of these rings. The disorder was treated analogously to that in the structures described above. The major conformation has *ca*. 53% occupancy.

For *cis*-**22a**, there are two independent molecules in the asymmetric unit. There is some indication of potential conformational disorder of the five- and six-membered rings in this structure as well. The elevated *R* factors, small peaks of residual electron density, the slight elongation of some atomic displacement ellipsoids and the unduly short lengths of some C–C bonds are indicators of this. However, attempts to model any disorder were unsuccessful.

For **9**, **16**, *cis*-**22**, **26**, and **37a**, all of the H-atoms were fixed in geometrically calculated positions with $d(\mathrm{C-H}) = 0.95$ Å, and they were assigned fixed isotropic displacement parameters with a value equal to 1.2 U_{eq} of the parent atom. For **23** and **25**, 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.

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