Ring Enlargement and Sulfur-Transfer Processes in SiO_2-Catalyzed Reactions of Thiocarbonyl Compounds with Optically Active Oxiranes

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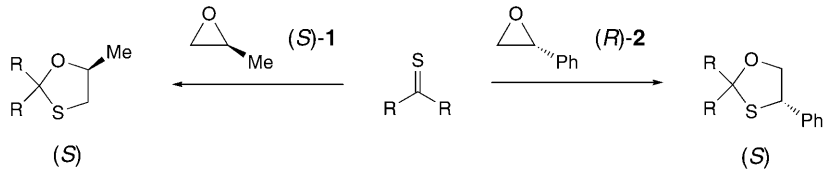
The reactions of 1,3-dioxolane-2-thione (**3**) with (*S*)-2-methyloxirane ((*S*)-**1**) and with (*R*)-2-phenyloxirane ((*R*)-**2**) in the presence of SiO_2 in anhydrous dichloroalkanes led to the optically active spirocyclic 1,3-oxathiolanes **8** with Me at C(7) and **9** with Ph at C(8), respectively (*Schemes 2* and *3*). The analogous reaction of 1,3-dimethylimidazolidine-2-thione (**4a**) with (*R*)-**2** yielded stereoselectively (*S*)-2-phenylthiirane ((*S*)-**10**) in 83% yield and 97% ee together with 1,3-dimethylimidazolidin-2-one (**11a**). In the cases of 3-phenyloxazolidine-2-thione (**4b**) and 3-phenylthiazolidine-2-thione (**4c**), the reaction with (*RS*)-**2** yielded the racemic thiirane (*RS*)-**10**, and the corresponding carbonyl compounds **11b** and **11c** (*Scheme 4* and *Table 1*). The analogous reaction of **4a** with 1,2-epoxycyclohexane (=7-oxabicyclo[4.1.0]heptane; **7**) afforded thiirane **12** and the corresponding carbonyl compound **11a** (*Scheme 5*). On the other hand, the BF_3-catalyzed reaction of imidazolidine-2-thione (**5**) with (*RS*)-**2** yielded the imidazolidine-2-thione derivative **13** almost quantitatively (*Scheme 6*). In a refluxing xylene solution, 1,3-diacetylimidazolidine-2-thione (**6**) and (*RS*)-**2** reacted to give two imidazolidine-2-thione derivatives, **13** and **14** (*Scheme 7*). The structures of **13** and **14** were established by X-ray crystallography (*Fig.*).

1. Introduction. – The regio- and stereoselective formation of 1,3-oxathiolanes in the *Lewis* acid-catalyzed reaction of thiocarbonyl compounds with oxiranes has been investigated thoroughly in recent years. So far, the reactions of oxiranes with 1,3-thiazole-5(4*H*)-thiones, cyclic trithiocarbonates, nonenolizable thioketones, enolizable thiocamphor, enolized dibenzyl thioketone, a rhodanine derivative, and thiolactones have been reported [1–13]. The results for this novel synthetic approach to 1,3-oxathiolanes show that the reactions proceed with high regio- and stereoselectivity *via* an S_N2-type mechanism (*Scheme 1*). In the case of 2-alkyl-substituted oxiranes (*e.g.*, (*S*)-**1**), the nucleophilic thiocarbonyl S-atom attacks preferentially at C(3) to give the 5-substituted 1,3-oxathiolanes with retention of the configuration at C(2) of the oxirane. On the other hand, 2-phenyl- and 2-vinyloxirane (*e.g.*, (*R*)-**2**) are attacked mainly at C(2) under inversion of the configuration to yield 4-phenyl- and 4-vinyl-substituted products.

Scheme 1



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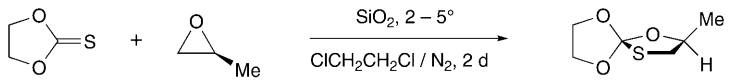
In addition to 1,3-oxathiolanes, the corresponding carbonyl compounds and 1,3-dithiolanes were sometimes isolated from the reactions of thicarbonyl compounds with oxiranes. The formation of the carbonyl compounds can be explained by the decomposition of 1,3-oxathiolanes in the presence of *Lewis* acids. However, the formation of 1,3-dithiolanes implies that the decomposition of 1,3-oxathiolanes should give thiiranes as the second product, which react again with thiocarbonyl compounds to produce the observed by-products. This proposal was supported by a control experiment, in which 4,4-dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione and 1,2-epithiocyclohexane (=7-thiabicyclo[4.1.0]heptane), in the presence of BF_3, afforded the corresponding spirocyclic 1,3-dithiolane in 85% yield with respect to the consumed thiazolethione derivative [3]. Analogous reactions have been reported where racemic oxiranes react with thiourea [14], with dimethylthioformamide [15], and with 3-methylbenzothiazole-2-thione [16], respectively, to give racemic thiiranes. If the conversion of oxiranes to thiiranes occurs stereoselectively, as shown in the reaction of stilbene oxides with 3-methylbenzothiazole-2-thione [16] (see also [17]), this methodology should be an attractive access to optically active thiiranes, because thiocarbonyl compounds, as well as optically active oxiranes, are conveniently accessible (for other approaches, see [17–20] and refs. cit. therein).

With the aim of further extending the scope of the formation of 1,3-oxathiolanes, reactions of 1,3-dioxolane-2-thione (**3**; *cf. Scheme 2*), 1,3-dimethylimidazolidine-2-thione (**4a**), 3-phenyloxazolidine-2-thione (**4b**), 3-phenylthiazolidine-2-thione (**4c**; *cf. Table 1*), imidazolidine-2-thione (**5**; *cf. Scheme 6*), and 1,3-diacetylimidazolidine-2-thione (**6**; *cf. Scheme 7*) with oxiranes were carried out. In the present paper, the results of the reactions with (*S*)-2-methyloxirane ((*S*)-**1**), (*R*)- and (*RS*)-2-phenyloxirane ((*R*)- and (*RS*)-**2**, resp.), and 1,2-epoxycyclohexane (=7-oxabicyclo[4.1.0]heptane, **7**; *cf. Scheme 5*) are described.

2. Results. – 2.1. *Reaction of 1,3-Dioxolane-2-thione* (**3**) *with (*S*)-2-Methyloxirane* ((*S*)-**1**). The reaction of (*S*)-**1** with **3** in a molar ratio of 1:2 was carried out in anhydrous 1,2-dichloroethane at 2–5° under an N_2 atmosphere in the presence of SiO_2. After stirring for 2 d, filtration and the usual workup by column chromatography (CC) gave the spirocyclic 1,3-oxathiolane **8** as the only product in 27% yield (*Scheme 2*).

Scheme 2

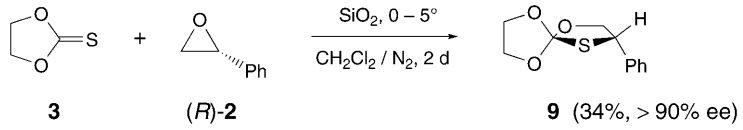


3 (*S*)-**1** **8** (27%)

The analogous reaction of **3** with (*R*)-2-phenyloxirane ((*R*)-**2**; molar ratio 1:1.5) in anhydrous CH_2Cl_2 at 0–5° for 2 d under an N_2 atmosphere in the presence of SiO_2 gave the spirocyclic 1,3-oxathiolane **9** in 34% yield (*Scheme 3*). The enantiomeric excess (ee) of the product (>90%) was determined by analytical HPLC (*S,S-Whelk-O-1*; hexane/i-PrOH/CH_2Cl_2 500:1:2).

The structures of **8** and **9** were assigned on the basis of their elemental analyses, MS, IR, ^{1}H- and ^{13}C-NMR (HSQC, HSQC-TOCSY, and HMBC in the case of **9**) data. The

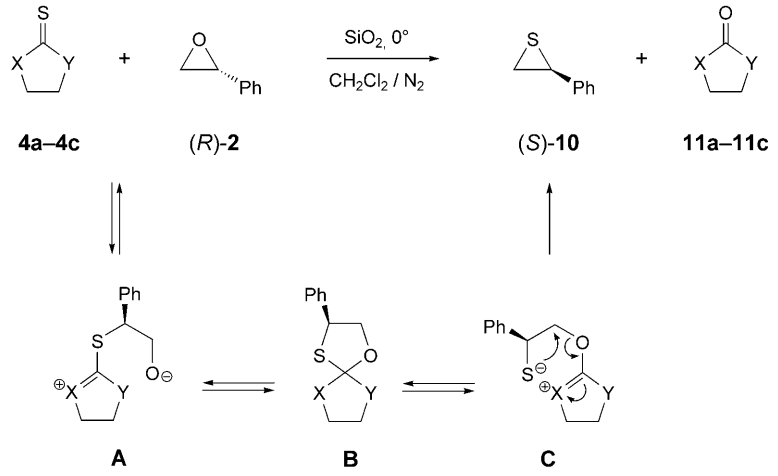
Scheme 3



formation of **8** proceeded by nucleophilic attack of the thiocarbonyl S-atom at C(3), and, for this reason, the configuration at C(2) of the oxirane (*S*)-**1** is retained. Therefore, the configuration at C(7) in **8** has to be (*S*). In the case of **9**, the nucleophilic S-atom attacked C(2) of (*R*)-**2** with inversion of the configuration, leading to the (*S*)-configuration at C(8) in **9**. These results are in accordance with those reported previously [7–11].

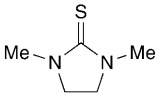
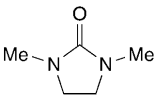
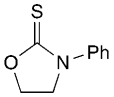
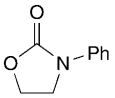
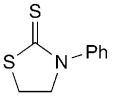
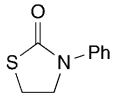
2.2. *Reaction of Heterocyclic Thiones* **4a**–**4c** *with* **2**. The reaction of **4a** with (*R*)-**2** (molar ratio 1:1.7) in anhydrous CH_2Cl_2 at 5° for 2 h under an N_2 atmosphere in the presence of SiO_2 afforded (*S*)-2-phenylthiirane ((*S*)-**10**) stereoselectively in 83% yield, together with the corresponding carbonyl compound **11a** (*Scheme 4* and *Table 1*). The ee value of **10** (97%) was determined by analytical HPLC (*S,S-Whelk-O-1*; hexane), and the configuration was assumed to be (*S*) by comparison of the observed optical rotation of the product (+) with that reported for (*R*)-**10** ($[\alpha]_D^{25} = -15.7$ ($c = 2.48$, heptane, 35.8% ee)) [17], see also [21])[2]). A repetition of the experiment with (*R*)-**2** (91.9% ee (HPLC); $[\alpha]_D^{25} = -21.8$ ($c = 1.35$, $CHCl_3$)) led to (*S*)-**10** with 93.5% ee (HPLC) and $[\alpha]_D^{25} = +29.2$ ($c = 1.17$, heptane).

Scheme 4



[2]) There is an inconsistency in the literature (see comment in [22]). For example, the partially stereoselective formation of (−)-(*R*)-**10** from (−)-(*S*)-styrene oxide, which had been prepared from (+)-(*S*)-mandelic acid, has been reported [17]. On the other hand, according to [20], the transformation of (+)-(*R*)-styrene oxide with NH_4SCN and $RuCl_3$ led to (−)-(*S*)-**10** in 78% optical purity. *Soai* and *Mukaiyama* described an enantioselective synthesis of (−)-(*R*)-**10** [19].

Table 1. *SiO_2-Catalyzed Reactions of* **4a**–**4c** *with* **2** *in CH_2Cl_2*

Substrates		Reaction time	Products and yields		
4a–**4c**	**2**		**10**	**11a**–**11c**	
 **4a**	(*R*)-**2**	2 h	(*S*)-**10** 83% (97% ee)	 **11a**	–
 **4b**	(*RS*)-**2**	10 h	(*RS*)-**10** 66%	 **11b**	79%
 **4c**	(*RS*)-**2**	10 h	(*RS*)-**10** 58%	 **11c**	92%

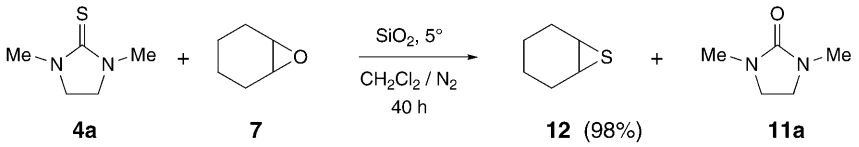
The analogous reactions of 3-phenyloxazolidine-2-thione (**4b**) and 3-phenylthiazolidine-2-thione (**4c**) with (*RS*)-**2** (molar ratio 1:2 in both cases) under the same conditions for 10 h afforded racemic thiirane (*RS*)-**10** in 66 and 58% yield, and the corresponding carbonyl compounds **11b** and **11c** in 79 and 92% yield, respectively (*Scheme 4* and *Table 1*).

A reaction mechanism for the stereoselective S transfer reaction is proposed in *Scheme 4*. In accordance with the previously described formation of 4-phenyl-1,3-oxthiolanes (*cf.* [7–11]), the ring opening of **2** by nucleophilic attack by the S-atom at C(2) occurs *via* inversion of the configuration, leading to intermediate **A**. Ring closure gives the 1,3-oxathiolane **B**, which, in the case of X = RN, rearranges to yield **C**. The latter then decomposes to give the isolated products **10** and **11**.

2.3. *Reaction of 1,3-Dimethylimidazolidine-2-thione* (**4a**) *with 1,2-Epoxycyclohexane* (**7**). The SiO_2-catalyzed reaction of **4a** with **7** (molar ratio of 1:3.75) in anhydrous CH_2Cl_2 at 5° under an N_2 atmosphere for 40 h gave thiabicyclo compound **12** in 98% yield based on the ^{1}H-NMR analysis of the reaction mixture and a weighed amount of 1,1,2,2-tetrachloroethane as a standard (*Scheme 5*).

2.4. *Reaction of Imidazolidine-2-thione* (**5**) *with* (RS)-**2**. To a suspension of 1 equiv. of **5** in anhydrous CH_2Cl_2 and Et_2O (9:1) under an N_2 atmosphere, 2.2 equiv. of $BF_3 \cdot Et_2O$ were added at −66°. After stirring the mixture for 15 min at −66°, 4 equiv. of

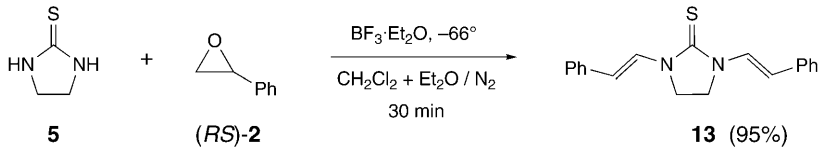
Scheme 5



4a **7** **12** (98%) **11a**

(*RS*)-**2** were added dropwise during 20 min. The reaction was quenched by addition of H_2O, and, after workup, a 95% yield of 1,3-bis[(*E*)-2-phenylethen-1-yl]imidazolidine-2-thione (**13**) was obtained as a yellow powder (*Scheme 6*).

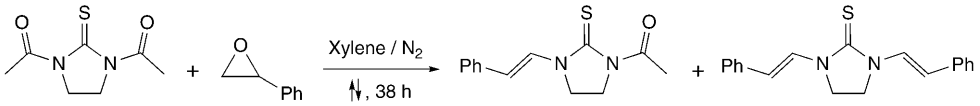
Scheme 6



5 (*RS*)-**2** **13** (95%)

The analogous BF_3-catalyzed reaction of 1,3-diacetylimidazolidine-2-thione (**6**) with (*RS*)-**2** in anhydrous CH_2Cl_2 at $-78°$ did not take place. Therefore, the reaction was carried out by heating a solution of **6** (1 equiv.) and (*RS*)-**2** (5 equiv.) in xylene under an N_2 atmosphere to reflux for 38 h. After workup, column chromatography of the residue gave two imidazolidine-2-thione derivatives **14** and **13** in 45 and 7% yield, respectively (*Scheme 7*).

Scheme 7



6 (*RS*)-**2** **14** (45%) **13** (7%)

The structures of **13** and **14** were assigned as usual (HSQC, HMBC, 1D-NOESY NMR spectra in the case of **13**). The 1D-NOESY spectrum of **13**, which has a molecular symmetry of C_{2v}, on irradiation of 2 H–C(1′) at 8.25 ppm, gave one NOE signal for four aromatic *ortho*-H-atoms at 7.41–7.39 ppm, indicating the (*E*)-configuration of the two olefinic bonds. On the other hand, irradiation of 2 H–C(2′) at 5.93 ppm led to another NOE signal at 4.02 ppm for four H-atoms of the ethylene group, indicating the s-*trans*-conformation of the two N–C(1′) bonds. Finally, the structures of **13** and **14** were established by X-ray crystallography (*Fig.*).

The five-membered ring of **13** is planar, and the whole molecule is essentially planar, with only small deviations of the Ph-ring planes from that of the five-membered ring. The maximum deviation from the mean plane of the molecule is 0.266(2) Å for N(3). As a result of the planarity, the molecular symmetry is close to C_{2v}.

The molecule of **14** is also almost planar with an r.m.s. deviation of all non-H-atoms from perfect C_s symmetry of 0.086 Å. The five-membered ring is very slightly puckered into a half-chair conformation twisted on C(4)–C(5).

3. Discussion and Conclusion. – The results presented show that 1,3-dioxolane-2-thione (**3**) reacts with optically active oxiranes (*S*)-**1** and (*R*)-**2** in the presence of SiO_2 to afford spirocyclic 1,3-oxathiolanes **8** and **9**, respectively, with high regio- and stereoselectivity. In contrast, the SiO_2-catalyzed reactions of the thiocarbonyl compounds **4a**–**4c** with phenyloxirane (**2**) do not give 1,3-oxathiolanes, but thiirane (*S*)-

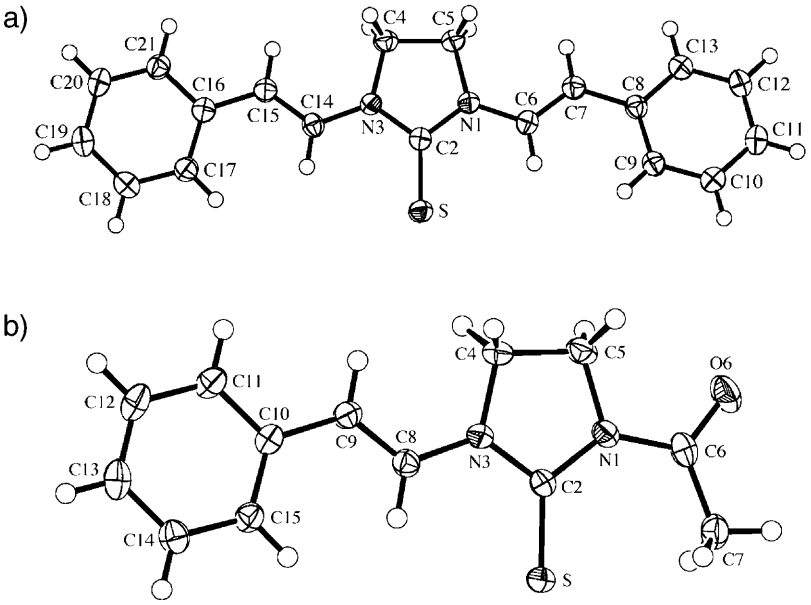


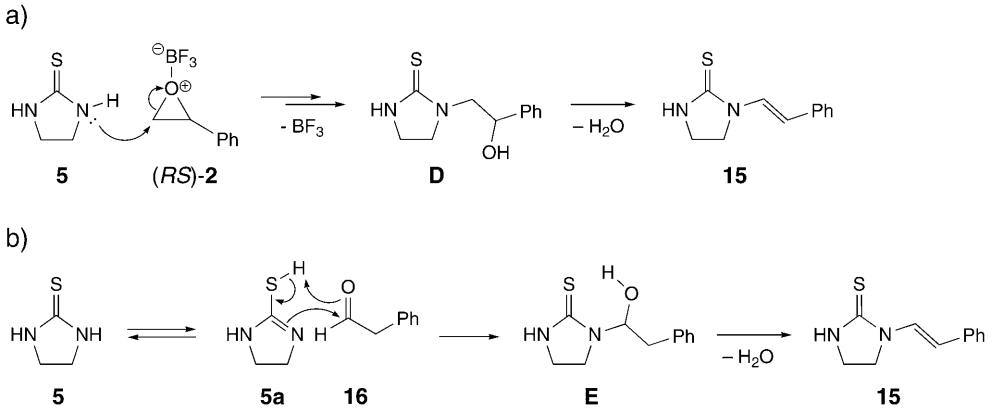
Figure. *ORTEP Plots* [23] *of the molecular structures of* a) **13** *and* b) **14** (arbitrary numbering of the atoms; displacement ellipsoids with 50% probability)

10 and the corresponding carbonyl compounds **11a**–**11c**. In the case of **4a** and (*R*)-**2**, the optically active thiirane (*S*)-**10** was formed in good yield and in high optical purity (*Scheme 4* and *Table 1*). The starting material **4a** can easily be regenerated by thionation of the byproduct **11a** with *Lawesson*'s reagent [24]. The analogous reaction of **4a** with oxirane **7** leads to thiirane **12** in 98% yield. This novel approach to thiiranes, including optically active ones, is very convenient and is worthy of further investigation in order to generalize this methodology[3]). It has to be pointed out that only thiocarbonyl compounds with an attached N-atom, *i.e.*, thiourea derivatives and analogues, undergo this S-transfer reaction efficiently, whereas thioketones, thiocarbonates, *etc.* yield mainly the ring-enlarged 1,3-oxathiolanes (*cf. Scheme 4*).

Imidazolidine-2-thione (**5**) and its 1,3-diacetyl derivative **6**, which is deactivated by two electron-withdrawing Ac groups, undergo very different reactions with (*RS*)-**2**, *i.e.*, the ring opening of the oxirane occurs *via* nucleophilic attack of the N-atom and subsequent extrusion of H_2O and AcOH, respectively, to give the *N*-styryl-substituted products, **13** and **14**, exclusively (*Scheme 7*). Neither 1,3-oxathiolanes nor thiirane **10** were observed. For the formation of **13**, two mechanisms are proposed in *Scheme 8*. *a*) The ring opening of the complexed oxirane *via* attack of the N-atom of **5** could lead to **D**, which undergoes elimination of H_2O to give **15**. An analogous reaction with the other NH group could afford **13**. There are two weak points in this mechanism: firstly, the N-atom has to be the more reactive nucleophile, and secondly, the ring opening of (*RS*)-**2** takes place by cleavage of the O–C(3) bond in a reaction, which is cata-

[3]) For previously described transformations of oxiranes into thiiranes, see [15–20] and refs. cit. therein.

Scheme 8



lyzed by the strong *Lewis* acid BF_3. This interpretation is contrary to the common observation for the ring opening of 2-phenyloxirane in the presence of *Lewis* acids. *b*) As a second mechanism, the enethiol form of **5**, *i.e.*, **5a**, could react with phenylacetaldehyde (**16**)[4]) in an ene-like reaction, leading to intermediate **E**. Dehydration of the latter yields again **15**. The second mechanism seems to be more reasonable, although there is no proof.

It is even more difficult to formulate a convincing mechanism for the transformation of **6** and (*RS*)-**2** to **13** and **14**. The simplest explanation would be a hydrolytic deacetylation followed by one of the sequences shown in *Scheme 8*.

We thank the analytical services of our institute for NMR and mass spectra and elemental analyses, Mr. *B. Bürgi* 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 [25]. Optical rotations: a *Perkin-Elmer-241* polarimeter ($c = 1$, in THF). IR Spectra: film or KBr, cm^{-1}. NMR Spectra: at 300 or 600 (^1H), and 75.5 or 150.9 MHz (^{13}C) in $CDCl_3$. Enantiomeric excesses (ee) were determined by anal. HPLC on a *(S,S)-Whelk-O-1* column.

2. *General Procedure for the Reactions of Thiocarbonyl Compounds* **3** *and* **4a**–**4c** *with Oxiranes* (*S*)-**1**, (*R*)-**2**, *and* **7**. To the soln. of **3** or **4a**–**4c** (*ca.* 1 mmol) and an oxirane (*ca.* 2 mmol) in anh. CH_2Cl_2 (10–15 ml) under an N_2 atmosphere, 4.5 g of silica gel were added at 0°. After stirring the suspension for 10 h–2 d at 0°, the mixture was filtered, and the residue was washed with Et_2O (4×). Then, the combined filtrate was evaporated *in vacuo*. The products were separated by column chromatography (CC; SiO_2; hexane/Et_2O).

3. *Reactions of 1,3-Dioxolane-2-thione* (**3**). 3.1. *With (*S*)-2-Methyloxirane* ((*S*)-**1**). Reaction of **3** (104 mg, 1 mmol) with (*S*)-**1** (116 mg, 2 mmol) in 15 ml of 1,2-dichloroethane and 4.5 g of SiO_2 at 2–5°, 2 d, and CC (SiO_2, hexane/Et_2O 1:1) yielded 44 mg (27%) of *(S)-7-methyl-1,4,6-trioxa-9-thiaspiro[4.4]nonane* (**8**). Colorless oil. $[\alpha]_D^{23} = +12.2$. ^1H-NMR (300 MHz, $CDCl_3$): 4.44 (*m*, H–C(7)); 4.21 (*m*, 2 H–C(2), 2 H–C(3)); 3.17 (*dd*,

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[4]) From some reactions of thiocarbonyl compounds with phenyloxirane, 2,4-diphenylbut-2-enal, *i.e.*, the product of the aldol condensation of phenylacetaldehyde (**16**), was isolated as a yellow oil. This indicates that the precursor **16** has been formed *in situ* by the BF_3-catalyzed ring opening (O–C(2) cleavage) of (*RS*)-**2** and a subsequent rearrangement *via* a 1,2-H shift.

J = 10.2, 4.6, 1 H–C(8)); 3.00 (*t*-like, $J \approx 10.0$, 1 H–C(8)); 1.44 (*d*, J = 6.1, Me). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 135.8 (*s*, C(5)); 77.9 (*d*, C(7)); 65.7, 64.8 (2*t*, C(2), C(3)); 40.1 (*t*, C(8)); 19.0 (*q*, Me). CI-MS (NH_3): 165 (5), 164 (7), 163 (100, $[M+H]^+$), 106 (25). Anal. calc. for $C_6H_{10}O_3S$ (162.21): C 44.43, H 6.21; found C 44.08, H 5.79.

3.2. *With (*R*)-2-Phenyloxirane* ((*R*)-**2**). Reaction of **3** (104 mg, 1 mmol) with (*R*)-**2** (240 mg, 2 mmol) in 15 ml of anh. CH_2Cl_2 and 4.5 g of SiO_2 at 0–5°, 2 d, and CC (SiO_2, hexane/Et_2O 3 : 1) yielded 76 mg (34%) of *(*S*)-8-phenyl-1,4,6-trioxa-9-thiaspiro[4.4]nonane* (**9**). Colorless oil. $[\alpha]_D^{23} = -10.3$. IR (film): 3061*w*, 3029*w*, 2975*m*, 2898*s*, 1602*w*, 1493*s*, 1453*s*, 1359*w*, 1346*w*, 1302*w*, 1276*m*, 1247*m*, 1210*s*, 1147v*s*, 1119v*s*, 1079*s*, 1063*s*, 1030v*s*, 1004v*s*, 950v*s*, 861*w*, 797*w*, 762*s*, 700v*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.48–7.46 (*m*, 2 arom. H); 7.35–7.32 (*m*, 2 arom. H); 7.29–7.26 (*m*, 1 arom. H); 4.86 (*dd*, J = 6.9, 5.9, H–C(8)); 4.41 (*dd*, J = 9.2, 5.7, 1 H–C(7)); 4.20–4.09 (*m*, 2 H–C(2), 2 H–C(3)); 4.08 (*dd*, J = 9.2, 7.0, 1 H–C(7)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 138.4 (*s*, 1 arom. C); 137.1 (*s*, C(5)); 128.8 (*d*, 2 arom. CH); 128.0 (*d*, 1 arom. CH); 127.9 (*d*, 2 arom. CH); 75.5 (*t*, C(7)); 65.6, 65.4 (2*t*, C(2), C(3)); 54.2 (*d*, C(8)). CI-MS (NH_3): 227 (6), 226 (13), 225 (100, $[M+H]^+$), 106 (12). Anal. calc. for $C_{11}H_{12}O_3S$ (224.28): C 58.91, H 5.39; found C 59.31, H 5.72.

4. *Reaction of 1,3-Dimethylimidazolidine-2-thione* (**4a**) *with* (*R*)-**2**. Reaction of **4a** (97 mg, 0.74 mmol) with (*R*)-**2** (150 mg, 1.25 mmol) in 10 ml of anh. CH_2Cl_2 and 3.6 g of SiO_2 at 0°, 2 h, and CC (SiO_2, hexane) yielded 84 mg (83%) of *(*S*)-2-phenylthiirane* ((*S*)-**10**) in 97% ee (HPLC) as a colorless oil and *1,3-dimethylimidazolidin-2-one* (**11a**; *Table 1*).

An analogous experiment was carried out with (–)-(*R*)-**2** (91.9% ee (HPLC)). The isolated (+)-(*S*)-**10** showed $[\alpha]_D^{23}$ +29.2 (c = 1.17, in heptane; 93.5% ee (HPLC)).

5. *Reaction of 3-Phenyloxazolidine-2-thione* (**4b**) *with* (*RS*)-**2**. Reaction of **4b** (94 mg, 0.5 mmol) with (*RS*)-**2** (120 mg, 1 mmol) in 10 ml of anh. CH_2Cl_2 and 3.0 g of SiO_2 at 0°, 10 h, and CC (SiO_2, hexane/AcOEt) yielded 45 mg (66%) of (*RS*)-**10** and 64 mg (79%) of *3-phenyloxazolidin-2-one* (**11b**; *Table 1*).

6. *Reaction of 3-Phenylthiazolidine-2-thione* (**4c**) *with* (*RS*)-**2**. Reaction of **4c** (49 mg, 0.25 mmol) with (*RS*)-**2** (60 mg, 0.5 mmol) in 10 ml of anh. CH_2Cl_2 and 1.5 g of SiO_2 at 0°, 10 h, yielded 19.6 mg (58%) of (*RS*)-**10** and 41 mg (92%) of *3-phenylthiazolidin-2-one* (**11c**) based on the ^{1}H-NMR analysis of the reaction mixture and a weighed amount of 1,1,2,2-tetrachloroethane as a standard (*Table 1*).

7. *Reaction of* **4a** *with 1,2-Epoxycyclohexane* (= 7-Oxabicyclo[4.1.0]heptane; **7**). Reaction of **4a** (104 mg, 0.8 mmol) with **7** (297 mg, 3 mmol) in 15 ml of anh. CH_2Cl_2 and 4.0 g of SiO_2 at 0°, 40 h, yielded 89 mg (98%) of *7-thiabicyclo[4.1.0]heptane* (**12**) based on the ^{1}H-NMR analysis of the reaction mixture and a weighed amount of 1,1,2,2-tetrachloroethane as a standard.

8. *Reaction of Imidazolidine-2-thione* (**5**) *with* (*RS*)-**2**. To the suspension of **5** (102 mg, 1 mmol) in anh. CH_2Cl_2 (18 ml) and Et_2O (2 ml) under an N_2 atmosphere, 2.2 equiv. of $BF_3 \cdot Et_2O$ were added at –66°, which led to an almost homogenous soln. After stirring the mixture for 15 min at –66°, 480 mg (4 mmol) of (*RS*)-**2** were added dropwise over 20 min. After stirring for an additional 10 min, the reaction was quenched by addition of H_2O, and the mixture was washed with sat. aq. NaCl soln. (3×). The combined org. layers were dried ($MgSO_4$) and evaporated *in vacuo*. The residue was washed with hexane (4×), filtered, and dried under high vacuum: 290 mg (95%) of *1,3-bis[(*E*)-2-phenylethen-1-yl]imidazolidine-2-thione* (**13**). Yellow powder. M.p. 248° (dec.). IR (KBr): 3054*m*, 3023*m*, 2953*w*, 2890*w*, 1641*s*, 1597*m*, 1574*w*, 1475*s*, 1450*s*, 1428*s*, 1386*s*, 1291*s*, 1261*s*, 1207*m*, 1182*m*, 1124*w*, 1084*m*, 1074*m*, 1031*w*, 978*w*, 952*s*, 939*s*, 904*w*, 869*m*, 841*w*, 830*w*, 821*m*, 760*m*, 748*s*, 691*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 8.25 (*d*, J = 14.7, 2 H–C(1′)); 7.41–7.39 (*m*, 4 arom. H); 7.32–7.30 (*m*, 4 arom. H); 7.21–7.18 (*m*, 2 arom. H); 5.93 (*d*, J = 14.7, 2 H–C(2′)); 4.02 (*s*, 2 H–C(4), 2 H–C(5)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 176.3 (*s*, C(2)); 136.4 (*s*, 2 arom. C); 129.0 (*d*, 4 arom. C); 126.97, 126.95 (2*d*, 2 arom. C, 2 C(1′)); 126.0 (*d*, 4 arom. C); 112.0 (*d*, 2 C(2′)); 44.4 (*t*, C(4), C(5)). CI-MS (NH_3): 309 (11), 308 (23), 307 (100, $[M+H]^+$), 277 (7).

Crystals of **13** suitable for the X-ray crystal-structure determination were grown from CH_2Cl_2/hexane.

9. *Reaction of 1,3-Diacetylimidazolidine-2-thione* (**6**) *with* (*RS*)-**2**. The soln. of **6** (186 mg, 1 mmol) and (*RS*)-**2** (600 mg, 5 mmol) in xylene was heated to reflux for 38 h. After evaporation of the solvent *in vacuo*, 10 ml of Et_2O/hexane (2 : 8) were added to the solid residue. The mixture was stirred vigorously for 5 min and then filtered. The filter cake was washed with hexane (3×). CC (SiO_2, hexane/ AcOEt 5 : 1) of the filter cake yielded 111 mg (45%) of *1-acetyl-3-[(*E*)-2-phenylethen-1-yl]imidazolidine-2-thione* (**14**) and 20 mg (7%) of **13**.

Data of **14**. Colorless crystals. M.p. 169.3–169.7°. IR (KBr): 3063*w*, 3046*w*, 3031*w*, 3002*w*, 2980*w*, 2949*w*, 2911*w*, 1682*s*, 1635*s*, 1597*m*, 1575*w*, 1487*s*, 1470*s*, 1448*m*, 1420*s*, 1388*s*, 1371*s*, 1324*m*, 1268*s* (br.), 1201*s*, 1100*m*, 1088*m*, 1071*m*, 1039*m*, 1021*m*, 963*m*, 942*s*, 902*w*, 861*w*, 836*w*, 825*m*, 752*s*, 718*w*, 690*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.20 (*d*, J = 14.8, H–C(1′)); 7.42–7.20 (*m*, 5 arom. H); 6.05 (*d*, J = 14.8, H–C(2′)); 4.16–4.10 (*m*, 2 H–C(5)); 3.88–3.83 (*m*, 2 H–C(4)); 2.88 (*s*, Me). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 175.9 (*s*, C=S); 171.7 (*s*, C=O); 135.5 (*s*, 1 arom. C); 128.7 (*d*, 2 arom. C); 127.2, 126.2 (2*d*, 1 arom. C, C(1′)); 125.9 (*d*, 2 arom. C);

114.8 (*d*, C(2′)); 43.7, 43.4 (2*t*, C(4), C(5)); 26.8 (*q*, Me). CI-MS (NH_3): 249 (6), 248 (16), 247 (100, $[M+H]^+$), 217 (9), 173 (23). Anal. calc. for $C_{13}H_{14}N_2OS$ (246.33): C 63.39, H 5.73, N 11.37, S 13.02; found C 63.25, H 5.72, N 11.41, S 12.81.

Crystals of **14** suitable for the X-ray crystal-structure determination were grown from CH_2Cl_2/hexane.

10. *X-Ray Crystal-Structure Determination of* **13** *and* **14** (*Table 2* and *Fig.*)[5]. All measurements were performed on a *Nonius KappaCCD* area-detector diffractometer [26] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream* 700 cooler. The data collection and refinement parameters are given in *Table 2*, and views of the molecules are shown in the *Figure*. Data reduction was performed with *HKL Denzo* and *Scalepack* [27]. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method [28] was applied. The structures were solved by direct methods using SIR92 [29], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and

Table 2. *Crystallographic Data of Compounds* **13** *and* **14**

		13	**14**
Crystallized from		CH_2Cl_2/hexane	CH_2Cl_2/hexane
Empirical formula		$C_{19}H_{18}N_2S$	$C_{13}H_{14}N_2OS$
Formula weight [g mol^{-1}]		306.42	246.33
Crystal color, habit		colorless, prism	colorless, prism
Crystal dimensions [mm]		0.12 × 0.17 × 0.30	0.15 × 0.22 × 0.25
Temp. [K]		160(1)	160(1)
Crystal system		monoclinic	monoclinic
Space group		$P2_1/c$	$P2_1/n$
Z		4	4
Reflections for cell determination		29762	19981
2θ Range for cell determination [°]		4–60	4–60
Unit cell parameters	a [Å]	15.7032(3)	9.6656(1)
	b [Å]	8.3479(2)	11.5899(2)
	c [Å]	12.3836(3)	10.8533(2)
	β [°]	104.668(1)	92.0332(7)
	V [Å^3]	1570.45(6)	1215.06(4)
D_X [gcm^{-3}]		1.296	1.346
μ(MoK_α) [mm^{-1}]		0.204	0.251
Scan type		ϕ and ω	ϕ and ω
2θ [°]		60	60
Transmission factors (min; max)		0.779; 0.980	0.897; 0.965
Total reflections measured		43637	32396
Symmetry independent reflections		4568	3548
Reflections with $I > 2\sigma(I)$		2973	2850
Reflections used in refinement		4568	3546
Parameters refined		200	155
Final $R(F)$ [$I > 2\sigma$ (I) reflections]		0.0512	0.0378
$wR(F^2)$ (all data)		0.1385	0.1060
Weighting parameters [a; b][a])		0.0709; 0.1534	0.0544; 0.3109
Goodness-of-fit		1.026	1.044
Secondary extinction coefficient		0.007(2)	–
Final Δ_{max}/σ		0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]		0.30; −0.32	0.37; −0.47

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

[5]) CCDC-286002–286003 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me group in **14**). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied in the case of **13**. In **14**, two reflections, whose intensities were considered to be extreme outliners, were omitted from the final refinement. Neutral atom scattering factors for non-H-atoms were taken from [30a], and the scattering factors for H-atoms were taken from [31]. Anomalous dispersion effects were included in F_c [32]; the values for f' and f'' were those of [30b]. The values of the mass attenuation coefficients are those of [30c]. All calculations were performed using the SHELXL97 [33] program.

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