Synthesis of Stable Cyclic Sulfinamides with a Hydroperoxy Function by Oxidation of Isothiazolium Salts

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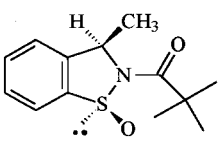
The oxidation of isothiazolium salts **4** to stable 2-aryl-2,3,4,5,6,7-hexahydro-3-hydroperoxy-1,2-benzisothiazole 1-oxides *rac-cis*-**6** (sultims) as a new class of cyclic sulfinamides is described. The formations of the oxidation products *rac-cis*-**6** as well as 3-hydroperoxy and 3-hydroxy sultams, **8** and **9**, respectively, and isothiazol-3(2*H*)-one 1,1-dioxides **10** are presented.

Introduction. – The synthetic usefulness of the sulfinyl group for the control of numerous asymmetric reactions is well-documented in the literature [1]. The preparation of the chiral cyclic sulfinamide **1** was described in a series of recent publications. This novel source of chiral sulfoxides has been applied for the control of aldol condensations [2][3] and the asymmetric synthesis of amines [4].

α-Sulfinyl-substituted radicals, prepared from the corresponding 5-phenylseleno compound **2**, undergo addition reactions with (alk-2-enyl)tributyltin derivatives to give 5-(alk-2-enyl)-2-(1-phenylethyl)isothiazolidin-3-one 1-oxides with excellent diastereoselectivity [5][6]. Altering the stereochemical course of allylation reactions of cyclic α-sulfinyl radicals with diarylureas has been also investigated [7].



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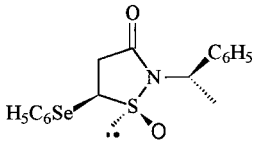

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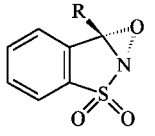

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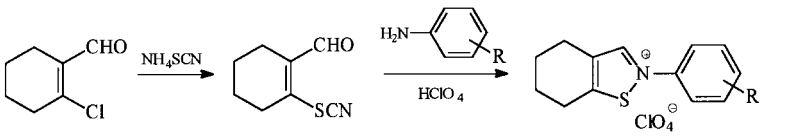
Here, we report the synthesis of stable 2-aryl-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1-oxides **6** (sultims) with a hydroperoxy function (*cf. Scheme 2*), a new class of cyclic sulfinamides which combines chirality and oxidizing functionality. So far, only the application of oxaziridines **3** [8][9] as oxidants, derived from saccharine and 3-hydroperoxytoluene-2,α-sultams **8** has been described. Sultams **8** have been synthesized by oxidation of bicyclic isothiazolium salts **4** [10].

In the course of our study on the oxidation of isothiazolium salts **4**, we have investigated the influence of the substituents of the 2-aryl ring and the stereochemical aspects of the formation of sultims **6** [11].

Results and Discussion. – The starting materials, bicyclic isothiazolium salts **4a–l**, were prepared according to our reported synthesis by cyclocondensation of thiocyanates with anilines (*Scheme 1*) [12][13].

Scheme 1



4 (for R, see *Scheme 2*)

The oxidation of **4a**, and **4d–g**, containing electron-withdrawing substituents in the *ortho*-position of the 2-aryl ring (R = 2-halogen, 2-CF_3) with 30% H_2O_2 in AcOH at room temperature gave sultims *rac-cis*-**6a**, and **6d–g**, respectively, in moderate-to-good yield (42–70%; *Scheme 2* and *Table 1*). These stable compounds were identified by ^{1}H- and ^{13}C-NMR spectra, and the *cis*-configuration was confirmed by X-ray crystal-structure analysis of **6a** (*cf. Fig.*). This result is contrary to our previous finding [10] that isothiazolium salts **4** with electron-donating substituents gave only sultams **8** in moderate-to-good yield, *e.g.*, 2-Me.

We suggested that the basicity of the aniline used for the preparation of salts **4** influenced the formation of the products. Sultims *rac-cis*-**6** were only obtained from salts **4** when the aniline had a low pK_a [14]. Consequently, we have chosen *meta*- and *para*-substituted anilines with low and high basicity (*Table 1*).

As expected, the oxidation of *para*- and *meta*-substituted salts **4b,c,h** (low pK_a) led to the formation of *rac-cis*-**6b,c,h** as the major products, respectively (*Table 1*). In these cases, *rac-cis*-**6** was obtained together with small amounts of **8**.

Scheme 2

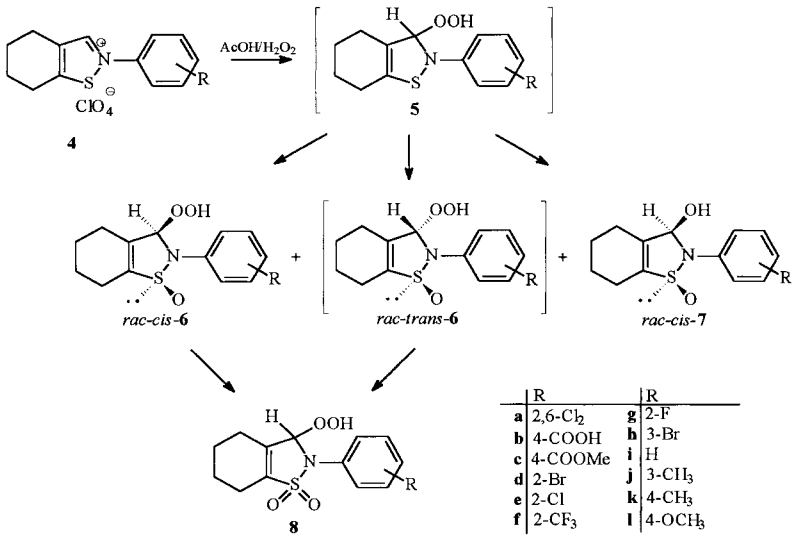


Table 1. *Product Distribution of* rac-cis-**6** *and* **8** *by the Oxidation of the Salts* **4a**–**l** *with* H_2O_2

Entry	Substrate	R[a])	pK_a of aniline	Reaction time [h]	Overall yield[b]) [%]	*rac-cis*-**6** [%]	**8** [%]
1	**4a**	2,6-Cl_2	0.00	3	42	42	
2	**4b**	4-COOH	2.42	3	42	38	4
3	**4c**	4-COOMe	2.47	3	57	54	3
4	**4d**	2-Br	2.53	3	80	70	10
5	**4e**	2-Cl	2.65	3	70	70	–
6	**4f**	2-CF_3	2.85	3	50	50	–
7	**4g**	2-F	3.20	3	43	43	–
8	**4h**	3-Br	3.58	3	62	58	4
9	**4i**	H	4.63	24	54	–	54
10	**4j**	3-CH_3	4.73	8 days[c])	45	–	45
11	**4k**	4-CH_3	5.08	24	63	–	63
12	**4l**	4-OCH_3	5.34	24	49	–	49

[a]) Arranged by increasing pK_a. [b]) Based on the used salts **4**. [c]) At 5° (ice-bath).

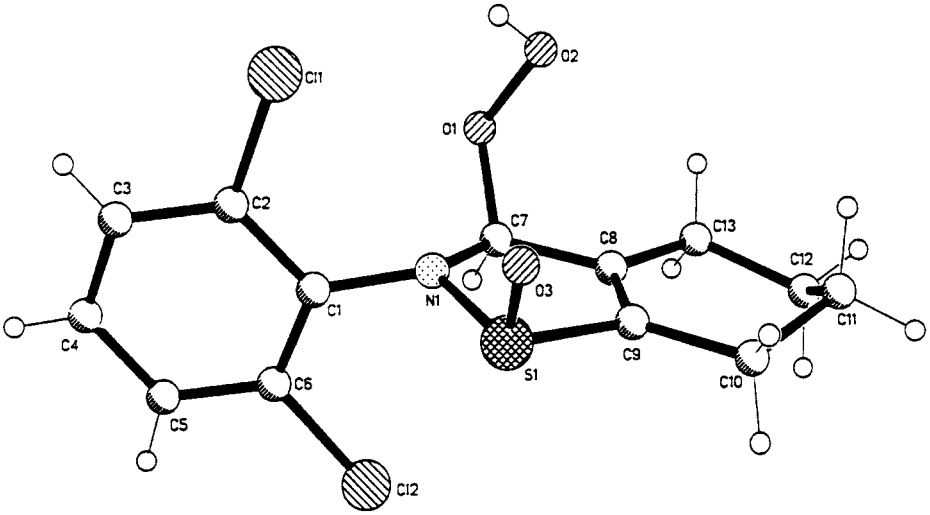


Figure. *Structure of* rac-cis-**6a**

The oxidation of **4i**–**l** under the same reaction conditions (see *Exper. Part*) resulted in the starting material or partly in decomposition (**4j**). Increasing the reaction time to 24 h led to the formation of the sultams **8i**,**k**,**l** (see *Exper. Part*). Compound **8j** was obtained after 8 days at 5° (ice-bath). For **8a**–**h**, the reaction solution was stirred for 24 h at room temperature, without affording *rac-cis*-**6**. In this case, the sultams **8a**–**l** were isolated in moderate-to-good yield (40–76%).

The characteristic spectral data of *rac-cis*-**6a**–**h** are the chemical shifts of C(3) in ^{13}C-NMR ($CDCl_3$/acetone), which appear at 97.0–103.1 ppm, and the SO absorption band at 1055–1060 cm^{-1} in the IR spectra. The ^{13}C chemical shifts of the C(3) of the corresponding 3-hydroperoxy sultams **8a**–**h** are at higher field (90.7–95.1 ppm), and the typical symmetrical and antisymmetrical SO_2 absorption bands in the IR spectra are at 1130–1170 and 1250–1305 cm^{-1}.

The *cis*-configuration of *rac-cis*-**6a** was confirmed by X-ray crystal-structure analysis (*Fig.*). The isothiazole ring of *rac-cis*-**6a** is planar with a flat endocyclic N-atom attached to the SO group. This was also observed for a 3-hydroperoxy sultam [10], and *Oppolzer et al.* described this for 2,3-dihydro-3-methyl-1,2-benzisothiazole 1-oxide [15]. The distance of N(1) in *rac-cis*-**6a** from the plane C(7), C(8), C(9), and S(1)[1]) is −0.06 Å. The crystals of *rac-cis*-**6a** show an intermolecular H-bond between the sulfoxide O-atom and the H-atom of the HOO group of a second molecule *rac-cis*-**6a** (2.118 Å), but no intramolecular H-bond. The torsion angle between the isothiazole ring and the 2-aryl substituent is 93.2°.

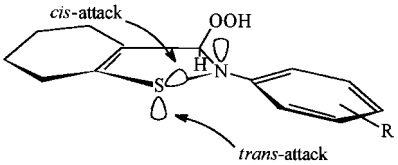
The course of oxidation of the salts **4** likely begins with nucleophilic attack of H_2O_2 at C(3) of the salts **4**. The electrostatic potentials of the isothiazolium salts **4** show a high positive charge at C(3), making it the preferred site for nucleophilic attack, whereas the S-atom displays a smaller electrostatic interaction with nucleophiles. The resulting intermediate **5** could not be isolated, but there is evidence by coupled HPLC-^{1}H-NMR for the existence of **5**. Being interested in intermediates of the oxidation of salts **4**, we investigated the oxidation of **4e** (R = 2-Cl): the reaction was monitored by HPLC to follow the conversion of **4e** to the oxidation products *rac-cis*-**6e**, *rac-cis*-**7e**, **8e**, 2-chloroaniline (decomposition product), and 3-oxo product **10e**, and an unkown product. For this peak (t_R 5.39 min), the corresponding ^{1}H-NMR spectrum was recorded immediately after on-line transfer to the HPLC-NMR probe head. For H−C(3), a chemical shift at 6.51 ppm was detected. The measurement was repeated after different time intervals. A new signal appeared at 5.48 ppm and increased continuously during the next 5 h, concurrent with disappearance of the signal at 6.51 ppm. The comparison with a reference spectrum of *rac-cis*-3-hydroxy sultim **7e** [11], where we observed, for H−C(3), a signal at 5.48 ppm, indicated that **7e** was a follow-up product of the unknown compound (t_R 5.39 min) formed in the absence of H_2O_2. We assume that this compound is the 3-hydroperoxy derivative of **5e**. The next step is the oxidation of sulfur, with formation of *rac-cis*- and *rac-trans*-3-hydroperoxy sultims **6**. The isolation of up to 70% of *rac-cis*-**6** points to a stereoselective reaction. We suppose that the lone-pair orbital of the N-atom together with the 3-hydroperoxy group influences the *cis/trans*-stereoselectivity. Donor substituents of the 2-aryl ring in the salts **4j**–**l** enhance the electron density in the isothiazole ring. This renders, first, C(3) less susceptible to the nucleophilic attack of H_2O_2 in **4** and intermediate **5**, observable in a low rate of reaction. Second, the *trans*-attack in **5** is preferred because of the stabilization of the formed pseudo-axial periplanar S−O bond due to the anomeric effect of the N lone pair which is situated in a plane through the N−C bond perpendicular to the plane of the isothiazole ring [16] (*Scheme 3*). The *rac-trans*-sultims **6** are more reactive than *rac-cis*-**6** and cannot be isolated. They are rapidly oxidized to give the sultams **8i**–**l**.

Acceptor substituents reduce the electron density in the lone-pair orbital of the N-atom. Hence, the nucleophilic attack at C(3) in **4a**–**h** and at the S-atom in **5a**–**h** is more convenient than with donor substituents. The smaller electron-density contribution of the lone pair of the N-atom prohibits the stabilization by the anomeric effect. Due to a H-bond between the HOO group and the oxidant on the *syn*-side of **5**, a *cis*-attack is

[1]) Arbitrary atom numbering in the *Figure*.

favored, and *rac-cis*-**6** is formed (*Scheme 3*). *rac-cis*-Sultims **6a**–**h** are stable and can be isolated. Keeping the sultims *rac-cis*-**6** in the reaction solution leads to oxidation to the corresponding sultams **8a**–**h**.

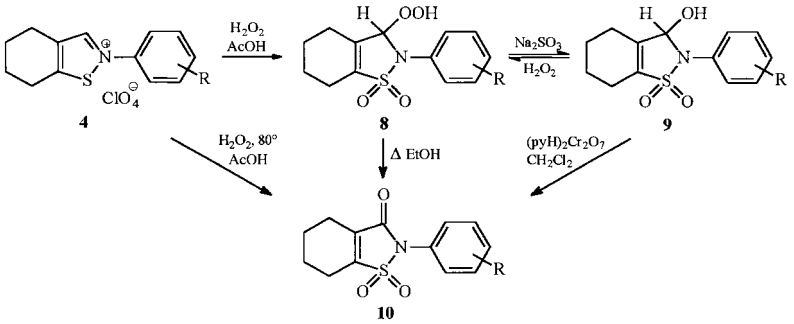
Scheme 3



Comparison of the isolated products, obtained by oxidation of salts **4**, with respect to the pK_a values of the anilines used for their preparation shows that, with increase of the pK_a value, the stereoselectivity of the formation of **6** changes.

We have reported the conversion of hydroperoxides **8** by thermolysis in EtOH into the 3-oxo products **10** *via* elimination of H_2O. Compound **10** was also obtained by oxidation of 3-hydroxy sultams **9** with pyridinium dichromate in CH_2Cl_2 [10]. We now report an improved procedure by direct oxidation of salts **4** with H_2O_2 in AcOH at 80° which enhances the yield of **10** up to 81% (*Scheme 4*). Furthermore, we found that 3-hydroxy sultams **9e** and **9i** produced by reduction of 3-hydroperoxy sultams **8e** and **8i**, respectively, with Na_2SO_3 [10] can be reoxidized with H_2O_2 (*Scheme 4*).

Scheme 4



First attempts to use the new sulfinamides as oxidizing agents were carried out. Heteroatoms such as S and P were successfully oxidized, but the reaction conditions should be optimized and other applications investigated.

Conclusion. – In summary, it has been shown that in contrast to our earlier report [10], oxidation of some isothiazolium salts **4** with H_2O_2 in AcOH leads to stable 3-hydroperoxy-2-phenylhexahydro-1,2-benzisothiazole 1-oxides *rac-cis*-**6**. This new class of cyclic sulfinamides could be isolated in fair-to-good yields. A mechanism for the formation of the oxidation products in dependence of the substituents in the 2-aryl ring is proposed.

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Experimental Part

General. M.p.: *Boetius* micro melting point apparatus; corrected. IR Spectra [cm^{-1}]: *Genesis FTIR Unicam Analytical System* (*ATI Mattson*); KBr pellets. ^{1}H-NMR Spectra: *Varian Gemini-200* (at 200 MHz) and *Varian Unity-400* (at 400 MHz); δ in ppm rel. to TMS as external standard, J in Hz. ^{13}C-NMR Spectra: at 50 MHz and 100 MHz on the same spectrometers. MS: *Quadrupol-MS VG 12-250* (*VG. Instruments GmbH, Manchester Analytical*) at 70 eV. Elemental analyses: *Heraeus* CHNO Rapid Analyzer.

1. *2-Aryl-4,5,6,7-tetrahydro-1,2-benzisothiazolium Perchlorates* (**4**). The salts **4a**, **e**, **f**, **j** were prepared according to [12]; **4i**, **l** according to [13]; the new salts **4** according to [12]. **4b**: 97%. Yellow crystals. M.p. 257–260°; **4c**: 96%. Beige crystals. M.p. 232–234°; **4d**: 72%. Beige crystals. M.p. 203–206°; **4g**: 51%. Yellow crystals. M.p. 240–242°; **4h**: 86%. Beige crystals. M.p.185–187°; **4k**: 76%. Colorless crystals. M.p. 124–126°.

2. *2-Aryl-2,3,4,5,6,7-hexahydro-3-hydroperoxy-1,2-benzisothiazole 1-Oxides* (*rac-cis*-**6**). *General Procedure.* H_2O_2 (0.7 ml, 30%) was added to a stirred suspension of **4** (0.26 mmol) in AcOH (0.7 ml) at r.t. After dissolvation of **4**, a colorless precipitate of *rac-cis*-**6** was obtained which was immediately isolated; otherwise oxidation to **8** occurred. The isolated compounds *rac-cis*-**6** were washed with H_2O and recrystallized from i-PrOH.

2-(2,6-Dichlorophenyl)-2,3,4,5,6,7-hexahydro-3-hydroperoxy-1,2-benzisothiazole 1-Oxide (*rac-cis*-**6a**): 42%. Colorless crystals. M.p. 131–134°. IR: 1060*s* (SO). ^{1}H-NMR ($CDCl_3$): 1.80 (*m*, 2 CH_2); 2.45 (*m*, 2 CH_2); 5.59 (*s*, H–C(3)); 7.29–7.49 (*m*, 3 arom. H); 8.87 (*s*, OOH). ^{13}C-NMR ($CDCl_3$): 21.5, 21.9, 22.5, 24.1 (C(4), C(5), C(6), C(7)); 103.1 (C(3)); 129.5 (2 arom. C); 131.0, 137.1 (3 arom. CH); 139.1 (arom. C); 140.7 (C(3a)); 144.4 (C(7a)). EI-MS: 334 ($M^{+\cdot}$). Anal. calc. for $C_{13}H_{13}Cl_2NO_3S$ (334.23): C 46.71, H 3.92, N 4.19, S 9.59, O 14.4; found: C 46.62, H 3.99, N 4.36, S 9.45, O 14.2.

2-(4-Carboxyphenyl)-2,3,4,5,6,7-hexahydro-3-hydroperoxy-1,2-benzisothiazole 1-Oxide (*rac-cis*-**6b**): 30%. Colorless crystals. M.p. 203–207°. IR: 1687*s* (CO), 1054*s* (SO). ^{1}H-NMR ((D$_6$)Acetone): 1.81 (*m*, 2 CH_2); 2.43 (*m*, 2 CH_2); 6.26 (*s*, H–C(3)); 7.40, 8.01 ($J_{AB} = 9.0$, 4 arom. H); 11.16 (*s*, OOH). ^{13}C-NMR ((D$_6$)Acetone): 21.1, 21.3, 22.2, 23.6 (C(4), C(5), C(6), C(7)); 96.8 (C(3)); 116.2 (2 arom. CH); 124.6 (arom. C); 131.6 (2 arom. CH); 141.3 (arom. C); 142.0 (C(3a)); 146.6 (C(7a)); 166.9 (CO). EI-MS: 309 ($M^{+\cdot}$). Anal. calc. for $C_{14}H_{15}NO_5S$ (309.37): C 54.35, H 4.90, N 4.53, S 10.36, O 25.9; found: C 54.11, H 4.87, N 4.42, S 10.59, O 26.1.

2,3,4,5,6,7-Hexahydro-3-hydroperoxy-2-[4-(methoxycarbonyl)phenyl]-1,2-benzisothiazole 1-Oxide (*rac-cis*-**6c**): 45%. Colorless crystals. M.p. 120–124°. IR: 1713*s* (CO), 1059*s* (SO). ^{1}H-NMR ((D$_6$)Acetone): 1.81 (*m*, 2 CH_2); 2.43 (*m*, 2 CH_2); 3.86 (*s*, Me); 6.26 (*s*, H–C(3)); 7.40, 7.99 ($J_{AB} = 8.6$, 4 arom. H); 11.29 (*s*, OOH). ^{13}C-NMR ((D$_6$)Acetone): 21.9, 22.2, 23.1, 24.5 (C(4), C(5), C(6), C(7)); 52.5 (Me); 97.8 (C(3)); 117.0 (2 arom. CH); 125.0 (arom. C); 132.1 (2 arom. CH); 142.1 (arom. C); 142.1 (C(3a)); 147.4 (C(7a)); 167.2 (CO). EI-MS: 323 ($M^{+\cdot}$). Anal. calc. for $C_{15}H_{17}NO_5S$ (323.39): C 55.71, H 5.31, N 4.33, S 9.91, O 24.7; found: C 55.30, H 5.35, N 4.32, S 9.94, O 24.9.

2-(2-Bromophenyl)-2,3,4,5,6,7-hexahydro-3-hydroperoxy-1,2-benzisothiazole 1-Oxide (*rac-cis*-**6d**): 60%. Colorless crystals. M.p. 138–140°. IR: 1060*s* (SO). ^{1}H-NMR ($CDCl_3$): 1.85 (*m*, 2 CH_2); 2.46 (*m*, 2 CH_2); 5.72 (*s*, H–C(3)); 7.30 (*m*, 2 arom. H); 7.67 (*m*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 21.6, 22.0, 22.5, 24.2 (C(4), C(5), C(6), C(7); 102.8 (C(3)); 125.2 (arom. C); 129.3, 130.8, 134.0, 134.6 (4 arom. CH); 139.1 (arom. C); 141.3 (C(3a)); 144.5 (C(7a)). EI-MS: 343/345 ($M^{+\cdot}$). Anal. calc. for $C_{13}H_{14}BrNO_3S$ (344.24): C 45.35, H 4.11, N 4.07, S 9.31, O 13.9; found: C 45.40, H 3.99, N 4.02, S 9.45, O 14.1.

2-(2-Chlorophenyl)-2,3,4,5,6,7-hexahydro-3-hydroperoxy-1,2-benzisothiazole 1-Oxide (*rac-cis*-**6e**): 70%. Colorless crystals. M.p. 134-137°. IR: 1060*s* (SO). ^{1}H-NMR ($CDCl_3$): 1.83 (*m*, 2 CH_2); 2.45 (*m*, 2 CH_2); 5.70 (*s*, H–C(3)); 7.31 (*m*, 2 arom. H); 7.45 (*m*, 1 arom. H); 7.75 (*m*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 21.5, 22.0, 22.5, 24.3 (C(4), C(5), C(6), C(7)); 102.5 (C(3)); 128.6 (arom. CH); 130.5 (arom. C); 130.7, 131.1, 134.6 (3 arom. CH); 137.2 (arom. C); 141.6 (C(3a)); 144.0 (C(7a)). EI-MS: 299 ($M^{+\cdot}$). Anal. calc. for $C_{13}H_{14}ClNO_3S$ (299.19): C 52.08, H 4.72, N 4.67, S 10.69, O 16.0; found: C 52.16, H 4.76, N 4.58, S 10.55, O 16.3.

2,3,4,5,6,7-Hexahydro-3-hydroperoxy-2-[2-(trifluoromethyl)phenyl]-1,2-benzisothiazole 1-Oxide (*rac-cis*-**6f**): 50%. Colorless crystals. M.p. 123–126°. IR: 1060*s* (SO). ^{1}H-NMR ($CDCl_3$): 1.82 (*m*, 2 CH_2); 2.46 (*m*, 2 CH_2); 5.63 (*s*, H–C(3)); 7.57 (*m*, 2 arom. H); 7.75 (*m*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 21.6, 22.1, 22.6, 24.2 (C(4), C(5), C(6), C(7)); 103.0 (C(3)); 121.1 (arom. CH); 123.2 (CF_3); 127.8 (arom. C); 129.6, 133.6, 136.2 (3 arom. CH); 136.5 (arom. C); 141.3 (C(3a)); 145.1 (C(7a)). EI-MS: 333 ($M^{+\cdot}$). Anal. calc. for $C_{14}H_{14}F_3NO_3S$ (333.35): C 50.44, H 4.24, N 4.20, S 9.62, O 14.0; found: C 50.28, H 4.09, N 4.14, S 9.71, O 14.2.

2-(2-Fluorophenyl)-2,3,4,5,6,7-hexahydro-3-hydroperoxy-1,2-benzisothiazole 1-Oxide (*rac-cis*-**6g**): 43%. Colorless crystals. M.p. 110–113°. IR: 1055*s* (SO). ^{1}H-NMR ((D$_6$)Acetone): 1.79 (*m*, 2 CH_2); 2.41 (*m*, 2 CH_2); 5.94 (*s*, H–C(3)); 7.19–7.35 (*m*, 3 arom. H); 7.65 (*m*, 1 arom. H). ^{13}C-NMR ((D$_6$)Acetone): 21.9, 22.3,

23.2, 24.7 (C(4), C(5), C(6), C(7)); 101.9 (C(3)); 117.3, 117.7, 126.1, 129.8 (4 arom. CH); 129.9, 131.7 (2 arom. C); 141.6 (C(3a)); 145.0 (C(7a)). EI-MS: 283 ($M^{+\cdot}$). Anal. calc. for $C_{13}H_{14}FNO_3S$ (283.34): C 55.10, H 4.99, N 4.94, S 11.31, O 16.9; found: C 55.24, H 4.86, N 5.04, S 11.55, O 16.8.

2-(3-Bromophenyl)-2,3,4,5,6,7-hexahydro-3-hydroperoxy-1,2-benzisothiazole 1-Oxide (*rac-cis*-**6h**): 44%. Colorless crystals. M.p. 116–120°. IR: 1059*s* (SO). ^{1}H-NMR ((D$_6$)Acetone): 1.80 (*m*, 2 CH$_2$); 2.42 (*m*, 2 CH$_2$); 6.20 (*s*, H–C(3)); 7.21–7.34 (*m*, 3 arom. H); 7.49 (br. *s*, 1 arom. H); 11.10 (*s*, OOH). ^{13}C-NMR ((D$_6$)Acetone): 21.6, 21.8, 22.7, 24.1 (C(4), C(5), C(6), C(7)); 97.6 (C(3)); 116.9, 120.7 (2 arom. CH); 123.3 (arom. C); 126.1, 131.7 (2 arom. CH); 141.4 (arom. C); 142.6 (C(3a)); 144.6 (C(7a)). EI-MS: 343/345 ($M^{+\cdot}$). Anal. calc. for $C_{13}H_{14}BrNO_3S$ (344.24): C 45.35, H 4.11, Br 23.18, N 4.07, S 9.31, O 13.9; found: C 45.11, H 4.12, Br 23.49, N 3.88, S 9.77, O 14.1.

3. *2-Aryl-2,3,4,5,6,7-hexahydro-3-hydroperoxy-1,2-benzisothiazole 1,1-Dioxides* (**8**). *General Procedure.* H_2O_2 (0.7 ml, 30%) was added at r.t. to a stirred suspension of **4a**–**l** (0.26 mmol) in AcOH (0.7 ml). Precipitates formed during the oxidations of **4a**–**h** were not isolated. After 24 h, colorless crystals of **8a**–**l** were obtained, isolated, and recrystallized from EtOH. Compound **8i** was described in [10].

2-(2,6-Dichlorophenyl)-2,3,4,5,6,7-hexahydro-3-hydroperoxy-1,2-benzisothiazole 1,1-Dioxide (**8a**): 55%. Colorless crystals. M.p. 180–183°. IR: 1250*s* (SO$_2$), 1170*s* (SO$_2$). ^{1}H-NMR (CDCl$_3$): 1.86 (*m*, 2 CH$_2$); 2.55 (*m*, 2 CH$_2$); 5.81 (*s*, H–C(3)); 7.27–7.52 (*m*, 3 arom. H). ^{13}C-NMR ((D$_6$)Acetone): 19.5, 21.4, 21.5, 23.5 (C(4), C(5), C(6), C(7)); 93.9 (C(3)); 129.7, 130.4 (3 arom. CH); 131.7 (2 arom. C); 137.6 (arom. C); 139.6 (C(3a)); 140.0 (C(7a)). EI-MS: 332 ([M – H$_2$O]$^{+\cdot}$). Anal. calc. for $C_{13}H_{13}O_4Cl_2NS$ (350.23): C 44.57, H 3.74, N 4.00, S 9.2; found C 44.58, H 3.66, N 4.11, S 9.3.

2-(4-Carboxyphenyl)-2,3,4,5,6,7-hexahydro-3-hydroperoxy-1,2-benzisothiazole 1,1-Dioxide (**8b**): 76%. Colorless crystals. M.p. 216–220°. IR: 1286*s* (SO$_2$), 1155*s* (SO$_2$). ^{1}H-NMR ((D$_6$)Acetone): 1.84 (*m*, 2 CH$_2$); 2.44 (*m*, 2 CH$_2$); 6.40 (*s*, H–C(3)); 7.51, 8.06 (J_{AB} = 9.0, 4 arom. H); 11.37 (*s*, OOH). ^{13}C-NMR ((D$_6$)Acetone): 19.2, 22.0, 22.2, 23.8 (C(4), C(5), C(6), C(7)); 90.8 (C(3)); 119.0 (2 arom. CH); 126.7 (arom. C); 132.1 (2 arom. CH); 136.5 (arom. C); 141.4 (C(3a)); 141.6 (C(7a)); 167.6 (CO). EI-MS: 307 ([M – H$_2$O]$^{+\cdot}$). Anal. calc. for $C_{14}H_{15}NO_6S$ (325.36): C 51.68, H 4.66, N 4.31, S 9.85, O 29.5; found: C 51.36, H 5.02, N 4.01, S 9.43, O 29.8.

2,3,4,5,6,7-Hexahydro-3-hydroperoxy-2-[4-(methoxycarbonyl)phenyl]-1,2-benzisothiazole 1,1-Dioxide (**8c**): 58%. Colorless crystals. M.p. 152–156°. IR: 1701*s* (CO), 1302*s* (SO$_2$), 1156*s* (SO$_2$). ^{1}H-NMR ((D$_6$)Acetone): 1.84 (*m*, 2 CH$_2$); 2.43 (*m*, 2 CH$_2$); 3.86 (*s*, Me); 6.39 (*s*, H–C(3)); 7.50, 8.03 (J_{AB} = 9.2, 4 arom. H); 11.49 (*s*, OOH). ^{13}C-NMR ((D$_6$)Acetone): 18.3, 21.2, 21.3, 22.9 (C(4), C(5), C(6), C(7)); 51.8 (Me); 89.9 (C(3)); 118.1 (2 arom. CH); 125.5 (arom. C); 131.1 (2 arom. CH); 135.8 (arom. C); 140.9 (C(3a)); 141.0 (C(7a)). EI-MS: 321 ([M – H$_2$O]$^{+\cdot}$). Anal. calc. for $C_{15}H_{17}NO_6S$ (339.39): C 53.08, H 5.06, N 4.13, S 9.45, O 28.3; found: C 52.95, H 5.12, N 4.13, S 9.38, O 28.0.

2-(2-Bromophenyl)-2,3,4,5,6,7-hexahydro-3-hydroperoxy-1,2-benzisothiazole 1,1-Dioxide (**8d**): 43%. Colorless crystals. M.p. 172–175°. IR: 1270*s* (SO$_2$), 1140*s* (SO$_2$). ^{1}H-NMR ((D$_6$)Acetone): 1.84 (*m*, 2 CH$_2$); 2.44 (*m*, 2 CH$_2$); 6.02 (*s*, H–C(3)); 7.36–7.54 (*m*, 2 arom. H); 7.74–7.80 (*m*, 2 arom. H); 11.05 (*s*, OOH). ^{13}C-NMR ((D$_6$)Acetone): 19.6, 22.2, 22.3, 24.1 (C(4), C(5), C(6), C(7)); 92.8 (C(3)); 127.2 (arom. C); 129.7, 130.2, 132.0, 133.4 (4 arom. CH); 135.0 (arom. C); 137.8 (C(3a)); 140.8 (C(7a)). EI-MS: 341/343 ([M – H$_2$O]$^{+\cdot}$). Anal. calc. for $C_{13}H_{14}BrNO_4S$ (360.24): C 43.35, H 3.92, N 3.89, S 8.90; found: C 43.21, H 3.89, N 3.97, S 8.81.

2-(2-Chlorophenyl)-2,3,4,5,6,7-hexahydro-3-hydroperoxy-1,2-benzisothiazole 1,1-Dioxide (**8e**): 61%. Colorless crystals. M.p. 154–157°. IR: 1250*s* (SO$_2$), 1130*s* (SO$_2$). ^{1}H-NMR (CDCl$_3$): 1.86 (*m*, 2 CH$_2$); 2.36 (*m*, 2 CH$_2$); 5.74 (*s*, H–C(3)); 7.33–7.60 (*m*, 4 arom. H); 8.78 (*s*, OOH). ^{13}C-NMR (CDCl$_3$): 19.3, 21.3, 21.4, 23.4 (C(4), C(5), C(6), C(7)); 94.6 (C(3)); 128.9, 131.3, 131.4 (3 arom. CH); 131.5 (arom. C); 133.7 (arom. CH); 136.2 (arom. C); 137.5 (C(3a)); 140.5 (C(7a)). EI-MS: 297 ([M – H$_2$O]$^{+\cdot}$). Anal. calc. for $C_{13}H_{14}ClNO_4S$ (315.79): C 49.44, H 4.47, N 4.44, S 10.16; found C 49.32, H 4.40, N 4.29, S 10.10.

2,3,4,5,6,7-Hexahydro-3-hydroperoxy-2-[2-(trifluoromethyl)phenyl]-1,2-benzisothiazole 1,1-Dioxide (**8f**): 40%. Colorless crystals. M.p. 132–135°. IR: 1270*s* (SO$_2$), 1160*s* (SO$_2$). ^{1}H-NMR (CDCl$_3$): 1.82 (*m*, 2 CH$_2$); 2.50 (*m*, 2 CH$_2$); 5.64 (*s*, H–C(3)); 7.62 (*m*, 3 arom. H); 7.80 (*d*, 1 arom. H); 8.68 (br. *s*, OOH). ^{13}C-NMR (CDCl$_3$): 19.4, 21.4, 21.5, 23.7 (C(4), C(5), C(6), C(7)); 91.9 (C(3)); 120.9 (CF$_3$); 126.4 (arom. CH); 128.2 (arom. C); 130.1, 133.7 (3 arom. CH); 133.8 (arom. C); 137.8 (C(3a)); 143.9 (C(7a)). EI-MS: 331 ([M – H$_2$O]$^{+\cdot}$). Anal. calc. for $C_{14}H_{14}F_3NO_4S$ (349.35): C 48.13, H 4.04, N 4.01, S 9.2; found: C 48.13, H 4.02, N 4.30, S 9.3.

2-(2-Fluorophenyl)-2,3,4,5,6,7-hexahydro-3-hydroperoxy-1,2-benzisothiazole 1,1-Dioxide (**8g**): 45%. Colorless crystals. M.p. 132–134°. IR: 1290*s* (SO$_2$), 1160s (SO$_2$). ^{1}H-NMR ((D$_6$)Acetone): 1.83 (*m*, 2 CH$_2$); 2.43 (*m*, 2 CH$_2$); 5.98 (*s*, H–C(3)); 7.23–7.34 (*m*, 2 arom. H); 7.42–7.53 (*m*, 1 arom. H); 7.64–7.72 (*m*, 1 arom. H).

^{13}C-NMR ((D$_6$)Acetone): 18.8, 21.3, 21.4, 23.1 (C(4), C(5), C(6), C(7)); 93.2 (C(3)); 117.1 (arom. CH); 122.7 (arom. C); 125.3, 130.7, 132.6 (3 arom. CH); 136.7 (C(3a)); 140.6 (C(7a)); 160.2 (arom. C). EI-MS: 281 ([M – H$_2$O]$^{+\cdot}$). Anal. calc. for $C_{13}H_{14}FNO_4S$ (299.34): C 52.19, H 4.72, N 4.68, S 10.72; found: C 52.16, H 4.62, N 4.60, S 10.51.

2-(3-Bromophenyl)-2,3,4,5,6,7-hexahydro-3-hydroperoxy-1,2-benzisothiazole 1,1-Dioxide (**8h**): 56%. Colorless crystals. M.p. 160–163°. IR: 1305*s* (SO$_2$), 1157*s* (SO$_2$). ^{1}H-NMR ((D$_6$)Acetone): 1.84 (*m*, 2 CH$_2$); 2.42 (*m*, 2 CH$_2$); 6.29 (*s*, H–C(3)); 7.34–7.51 (*m*, 3 arom. H); 7.64 (*s*, 1 arom. H); 11.40 (*s*, OOH). ^{13}C-NMR ((D$_6$)Acetone): 19.3, 22.1, 22.2, 23.8 (C(4), C(5), C(6), C(7)); 91.3 (C(3)); 120.9 (arom. C); 123.4 (arom. C); 124.8, 128.7, 132.1 (3 arom. CH); 136.6 (arom. C); 138.8 (C(3a)); 141.6 (C(7a)). EI-MS: 341/343 ([M – H$_2$O]$^{+\cdot}$). Anal. calc. for $C_{13}H_{14}BrNO_4S$ (360.24): C 43.34, H 3.93, Br 22.18, N 3.89, S 8.90, O 17.8; found: C 43.64, H 3.86, Br 22.39, N 3.97, S 8.58, O 17.6.

2,3,4,5,6,7-Hexahydro-3-hydroperoxy-2-(3-methylphenyl)-1,2-benzisothiazole 1,1-Dioxide (**8j**): 42%. Colorless crystals. M.p. 167–170°. IR: 1280*s* (SO$_2$), 1160*s* (SO$_2$). ^{1}H-NMR ((D$_6$)Acetone): 1.72–1.90 (*m*, 2 CH$_2$); 2.34 (*s*, Me); 2.31–2.49 (*m*, 2 CH$_2$); 6.18 (*s*, H–C(3)); 7.01–7.10 (*m*, 1 arom. H); 7.20–7.35 (*m*, 3 arom. H). ^{13}C-NMR ((D$_6$)Acetone): 19.4, 21.9, 22.1, 22.3 (C(4), C(5), C(6), C(7)); 23.8 (Me); 92.1 (C(3)); 120.6, 124.0, 127.2, 130.2 (4 arom. CH); 136.8, 137.0 (2 arom. C); 140.2 (C(3a)); 141.5 (C(7a)). EI-MS: 277 ([M – H$_2$O]$^{+\cdot}$). Anal. calc. for $C_{14}H_{17}NO_4S$ (295.38): C 56.92, H 5.81, N 4.74, S 10.85, O 21.7; found: C 56.80, H 5.76, N 4.99, S 10.83, O 21.6.

2,3,4,5,6,7-Hexahydro-3-hydroperoxy-2-(4-methylphenyl)-1,2-benzisothiazole 1,1-Dioxide (**8k**): 63%. Colorless crystals. M.p. 165–168°. IR: 1270*s* (SO$_2$), 1160*s* (SO$_2$). ^{1}H-NMR (CDCl$_3$): 1.82 (*m*, 2 CH$_2$); 2.35 (*s*, Me); 2.49 (*m*, 2 CH$_2$); 5.79 (*s*, H–C(3)); 7.20, 7.32 (J_{AB} = 8.2, 4 arom. H); 9.16 (br. *s*, OOH). ^{13}C-NMR (CDCl$_3$): 19.1, 21.3, 21.4, 21.5, 23.4 (C(4), C(5), C(6), C(7), Me); 92.8 (C(3)); 124.5, 130.8 (4 arom. CH); 132.2, 137.0 (2 arom. C); 137.3 (C(3a)); 140.4 (C(7a)). EI-MS: 277 ([M – H$_2$O]$^{+\cdot}$). Anal. calc. for $C_{14}H_{17}NO_4S$ (295.38): C 56.92, H 5.81, N 4.74, S 10.85, O 21.7; found: C 56.87, H 5.44, N 4.62, S 10.24, O 22.0.

2,3,4,5,6,7-Hexahydro-3-hydroperoxy-2-(4-methoxyphenyl)-1,2-benzisothiazole 1,1-Dioxide (**8l**): 50%. Colorless crystals. M.p. 142–144°. IR: 1280*s* (SO$_2$), 1160*s* (SO$_2$). ^{1}H-NMR (CDCl$_3$): 1.82 (*m*, 2 CH$_2$); 2.50 (*m*, 2 CH$_2$); 3.80 (*s*, Me); 5.67 (*s*, H–C(3)); 6.93 (*m*, 2 arom. H); 7.36 (*m*, 2 arom. H). ^{13}C-NMR (CDCl$_3$): 19.2, 21.4, 21.5, 23.5 (C(4), C(5), C(6), C(7)); 56.0 (Me); 93.9 (C(3)); 115.5 (2 arom. CH); 127.3 (arom. C); 128.7 (2 arom. CH); 137.2 (C(3a)); 140.4 (C(7a)); 159.7 (arom. C). EI-MS: 293 ([M – H$_2$O]$^{+\cdot}$). Anal. calc. for $C_{14}H_{17}NO_5S$ (311.38): C 54.00, H 5.51, N 4.50, S 10.29; found C 54.01, H 5.79, N 4.56, S 9.99.

4. *2-Aryl-2,3,4,5,6,7-hexahydro-3-hydroxy-1,2-benzisothiazole 1,1-Dioxides* (**9**). Compounds **9e** and **9i** were synthesized by reduction of **8e** and **8i** with Na_2SO_3 in H_2O according to [10].

2-(2-Chlorophenyl)-2,3,4,5,6,7-hexahydro-3-hydroxy-1,2-benzisothiazole 1,1-Dioxide (**9e**): 59%. Colorless crystals. M.p. 129–133°. IR: 1290*s* (SO$_2$), 1180*s* (SO$_2$). ^{1}H-NMR (CDCl$_3$): 1.84 (*m*, 2 CH$_2$); 2.49 (*m*, 2 CH$_2$); 3.21 (*d*, J = 10, OH); 5.61 (*d*, J = 10, H–C(3)); 7.38 (*m*, 2 arom. H); 7.54 (*m*, 2 arom. H). ^{13}C-NMR (CDCl$_3$): 19.1, 21.5, 21.6, 23.5 (C(4), C(5), C(6), C(7)); 84.4 (C(3)); 128.4 (arom. CH); 130.7 (arom. C); 131.1, 131.4, 134.4 (3 arom. CH); 135.2 (arom. C); 136.2 (C(3a)); 143.3 (C(7a)). EI-MS: 299 ($M^{+\cdot}$). Anal. calc. for $C_{13}H_{14}ClNO_3S$ (299.79): C 52.08, H 4.71, N 4.67, S 10.70; found: C 51.70, H 4.69, N 4.89, S 10.62.

2,3,4,5,6,7-Hexahydro-3-hydroxy-2-phenyl-1,2-benzisothiazole 1,1-Dioxide (**9i**): 52%. Colorless crystals. M.p. 143–145°. IR: 1280*s* (SO$_2$), 1140*s* (SO$_2$). ^{1}H-NMR ((D$_6$)Acetone): 1.82 (*m*, 2 CH$_2$); 2.44 (*m*, 2 CH$_2$); 5.90 (*s*, H–C(3)); 7.18–7.25 (*m*, 2 arom. H); 7.37–7.49 (*m*, 2 arom. H). ^{13}C-NMR ((D$_6$)Acetone): 19.3, 22.1, 22.4, 23.8 (C(4), C(5), C(6), C(7)); 83.1 (C(3)); 122.3, 123.0, 130.4 (5 arom. CH); 134.5 (arom. C); 137.2 (C(3a)); 144.5 (C(7a)). EI-MS: 265 ($M^{+\cdot}$). Anal. calc. for $C_{13}H_{15}NO_3S$ (265.35): C 58.85, H 5.70, N 5.28, S 12.09; found: C 58.78, H 5.64, N 5.12, S 12.17.

5. *2-Aryl-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxides* (**10**). *General Procedure.* H_2O_2 (3 ml, 30%) was added to a suspension of **4** (0.86 mmol) in AcOH (8 ml). The soln. was stirred for 2 to 3 h at 80°. After cooling, crystals were isolated and recrystallized from EtOH. Compounds **10i** and **10l** are described in [10].

*2-(2,6-Dichlorophenyl)-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide* (**10a**): 67%. Colorless crystals. M.p. 185–188°. IR: 1740*s* (CO), 1310*s* (SO$_2$), 1170*s* (SO$_2$). ^{1}H-NMR ((D$_6$)Acetone): 1.92 (*m*, 2 CH$_2$); 2.56 (*m*, CH$_2$); 2.68 (*m*, CH$_2$); 7.63–7.69 (*m*, 3 arom. H). ^{13}C-NMR ((D$_6$)Acetone): 20.1, 21.4, 21.5, 21.8 (C(4), C(5), C(6), C(7)); 130.8 (2 arom. C); 131.5, 134.0 (3 arom. CH); 137.0 (arom. C); 138.6 (C(3a)); 149.3 (C(7a)); 160.4 (C(3)). EI-MS: 332 ($M^{+\cdot}$). Anal. calc. for $C_{13}H_{11}Cl_2NO_3S$ (332.21): C 47.00, H 3.34, N 4.21, O 14.4; found: C 47.31, H 3.50, N 4.44, O 14.5.

*2-(4-Carboxyphenyl)-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide* (**10b**): 81%. Colorless crystals. M.p. 225–228°. IR: 1739*s* (CO), 1694*s* (CO), 1307*s* (SO$_2$), 1175*s* (SO$_2$). ^{1}H-NMR ((D$_6$)Acetone): 1.90

(*m*, 2 CH_2); 2.52 (*m*, CH_2); 2.65 (*m*, CH_2); 7.66, 8.21 (J_{AB} = 8.6, 4 arom. H). ^{13}C-NMR ((D$_6$)Acetone): 18.9, 20.5, 20.7, 21.0 (C(4), C(5), C(6), C(7)); 124.1 (arom. C); 127.4, 131.5 (4 arom. CH); 134.9 (arom. C); 137.1 (C(3a)); 146.5 (C(7a)); 160.0 (C(3)); 166.5 (CO). EI-MS: 307 ($M^{+\cdot}$). Anal. calc. for $C_{14}H_{13}NO_5S$ (307.34): C 54.71, H 4.27, N 4.56, S 10.43, O 26.0; found: C 54.54, H 4.36, N 4.49, S 10.61, O 26.1.

*4,5,6,7-Tetrahydro-2-(4-methoxycarbonyl)-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide* (**10c**): 55%. Colorless crystals. M.p. 163–165°. IR: 1737*s* (CO), 1722*s* (CO), 1307*s* (SO_2), 1183*s* (SO_2). ^{1}H-NMR ((D$_6$)Acetone): 1.92 (*m*, 2 CH_2); 2.53 (*m*, CH_2); 2.66 (*m*, CH_2); 3.92 (*s*, Me); 7.67, 8.18 (J_{AB} = 8.7, 4 arom. H). ^{13}C-NMR ((D$_6$)Acetone): 19.8, 21.4, 21.5, 21.9 (C(4), C(5), C(6), C(7)); 53.0 (Me); 128.1 (2 arom. CH); 131.8 (arom. C); 131.9 (2 arom. CH); 135.7 (arom. C); 137.8 (C(3a)), 147.2 (C(7a)); 160.6 (C(3)); 166.7 (CO). EI-MS: 321 ($M^{+\cdot}$). Anal. calc. for $C_{15}H_{15}NO_5S$ (321.37): C 56.06, H 4.71, N 4.36, S 9.98, O 24.9; found: C 55.53, H 4.74, N 4.35, S 10.13, O 25.2.

*2-(2-Bromophenyl)-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide* (**10d**): 52%. Colorless crystals. M.p. 170–173°. IR: 1740*s* (CO), 1330*s* (SO_2), 1170*s* (SO_2). ^{1}H-NMR ($CDCl_3$): 1.89 (*m*, 2 CH_2); 2.54 (*m*, CH_2); 2.68 (*m*, CH_2); 7.44 (*m*, 3 arom. H); 7.76 (*m*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 19.7, 21.0, 21.3, 22.0 (C(4), C(5), C(6), C(7)); 125.6 (arom. C); 128.7, 129.2, 132.4, 132.6 (4 arom. CH); 134.8 (arom. C); 136.6 (C(3a)); 147.0 (C(7a)); 159.3 (C(3)). EI-MS: 341/343 ($M^{+\cdot}$). Anal. calc. for $C_{13}H_{12}BrNO_3S$ (342.22): C 45.62, H 3.54, N 4.09, S 9.37, O 14.0; found: C 45.76, H 3.38, N 4.20, S 10.12, O 14.1.

*2-(2-Chlorophenyl)-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide* (**10e**): 71%. Colorless crystals. M.p. 139–142°. IR: 1740*s* (CO), 1330*s* (SO_2), 1170*s* (SO_2). ^{1}H-NMR ($CDCl_3$): 1.89 (*m*, 2 CH_2); 2.53 (*m*, CH_2); 2.67 (*m*, CH_2); 7.39–7.60 (*m*, 4 arom. H). ^{13}C-NMR ($CDCl_3$): 19.7, 21.0, 21.2, 21.3 (C(4), C(5), C(6), C(7)); 126.9, 128.5 (2 arom. CH); 131.5 (arom. C); 132.2, 132.5 (2 arom. CH); 135.6 (arom. C); 136.6 (C(3a)); 147.5 (C(7a)); 159.4 (C(3)). EI-MS: 297 ($M^{+\cdot}$). Anal. calc. for $C_{13}H_{12}ClNO_3S$ (297.77): C 52.43, H 4.07, N 4.70, O 16.1; found: C 52.66, H 3.57, N 4.73, O 16.2.

*4,5,6,7-Tetrahydro-2-[2-(trifluoromethyl)phenyl]-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide* (**10f**): 67%. Colorless crystals. M.p. 167–170°. IR: 1740*s* (CO), 1320*s* (SO_2), 1160*s* (SO_2). ^{1}H-NMR ($CDCl_3$): 1.89 (*m*, 2 CH_2); 2.52 (*m*, CH_2); 2.69 (*m*, CH_2); 7.54 (*m*, 1 arom. H); 7.68 (*m*, 2 arom. H); 7.84 (*m*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 19.7, 20.9, 21.3, 21.6 (C(4), C(5), C(6), C(7)); 120.4 (CF_3); 125.8 (arom. CH); 129.0 (arom. C); 131.4, 131.5, 133.4 (3 arom. CH); 133.7 (arom. C); 136.6 (C(3a)); 147.9 (C(7a)); 160.6 (C(3)). EI-MS: 331 ($M^{+\cdot}$). Anal. calc. for $C_{14}H_{12}F_3NO_3S$ (331.33): C 50.75, H 3.65, N 4.23, S 9.68; found: C 50.41, H 3.62, N 4.30, S 9.49.

*2-(2-Fluorophenyl)-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide* (**10g**): 50%. Colorless crystals. M.p. 136–140°. IR: 1732*s* (CO), 1336*s* (SO_2), 1180*s* (SO_2). ^{1}H-NMR ($CDCl_3$): 1.86 (*m*, 2 CH_2); 2.53 (*m*, CH_2); 2.65 (*m*, CH_2); 7.31 (*m*, 2 arom. H); 7.44 (*m*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 19.6, 20.9, 21.1, 21.2 (C(4), C(5), C(6), C(7)); 117.5, 117.9, 125.6, 131.9 (4 arom. CH); 132.7 (arom. C); 136.8 (C(3a)); 147.7 (C(7a)); 159.8 (C(3)); 161.2 (arom. C). MS: 281 ($M^{+\cdot}$). Anal. calc. for $C_{13}H_{12}FNO_3S$ (281.32): C 55.50, H 4.30, N 4.98, S 11.40; found: C 55.31, H 4.19, N 4.76, S 11.23.

*2-(3-Bromophenyl)-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide* (**10h**): 50%. Colorless crystals. M.p. 120–122°. IR: 1735*s* (CO), 1325*s* (SO_2), 1181*s* (SO_2). ^{1}H-NMR ((D$_6$)Acetone): 1.91 (*m*, 2 CH_2); 2.52 (*m*, CH_2); 2.65 (*m*, CH_2); 7.50–7.56 (*m*, 2 arom. H); 7.68–7.76 (*m*, 2 arom. H). ^{13}C-NMR ((D$_6$)Acetone): 19.8, 21.4, 21.6, 21.9 (C(4), C(5), C(6), C(7)); 123.4 (arom. C); 127.9, 131.8, 132.6 (3 arom. CH); 132.7 (arom. C); 133.6 (arom. CH); 137.8 (C(3a)); 147.2 (C(7a)); 160.7 (C(3)). EI-MS: 341/343 ($M^{+\cdot}$). Anal. calc. for $C_{13}H_{12}BrNO_3S$ (342.22): C 45.62, H 3.54, Br 23.35, N 4.09, S 9.37, O 14.0; found: C 45.36, H 3.63, Br 23.06, N 4.04, S 9.58, O 14.3.

*2-(3-Methylphenyl)-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide* (**10j**): 72%. Colorless crystals. M.p. 159–160°. IR: 1731*s* (CO), 1321*s* (SO_2), 1180*s* (SO_2). ^{1}H-NMR ((D$_6$)Acetone): 1.91 (*m*, CH_2); 2.39 (*s*, Me); 2.50 (*m*, CH_2); 2.64 (*m*, CH_2); 7.24–7.44 (*m*, 4 arom. H). ^{13}C-NMR ((D$_6$)Acetone): 19.5, 20.9, 21.0, 21.3 (C(4), C(5), C(6), C(7)); 21.8 (Me); 125.6, 129.2 (2 arom. CH); 129.4 (arom. C); 130.0, 131.0 (2 arom. CH); 136.7 (arom. C); 140.4 (C(3a)); 146.6 (C(7a)); 160.3 (C(3)). EI-MS: 277 ($M^{+\cdot}$). Anal. calc. for $C_{14}H_{15}NO_3S$ (277.37): C 60.62, H 5.46, N 5.05, S 11.56, O 17.3; found: C 60.71, H 5.52, N 5.23, S 11.98, O 17.5.

*2-(4-Methylphenyl)-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide* (**10k**): 51%. Colorless crystals. M.p. 175–177°. IR: 1730*s* (CO), 1330*s* (SO_2), 1180*s* (SO_2). ^{1}H-NMR ((D$_6$)Acetone): 1.90 (*m*, 2 CH_2); 2.40 (*s*, Me); 2.50 (*m*, CH_2); 2.63 (*m*, CH_2); 7.32, 7.37 (J_{AB} = 8.6, 4 arom. H). ^{13}C-NMR ((D$_6$)Acetone): 18.9, 20.5, 20.7, 20.8, 21.0 (C(4), C(5), C(6), C(7), Me); 127.5 (arom. C); 128.7, 130.7 (4 arom. CH); 136.8 (arom. C); 140.2 (C(3a)); 146.5 (C(7a)); 160.2 (C(3)). EI-MS: 277 ($M^{+\cdot}$). Anal. calc. for $C_{14}H_{15}NO_3S$ (277.34): C 60.63, H 5.45, N 5.05, S 11.56; found: C 60.29, H 5.72, N 5.82, S 11.29.

6. *HPLC-^{1}H-NMR Measurements:* A *Merck-Hitachi LiChrograph L-6200A* gradient pump was fitted with a *Bruker DRX 500* NMR spectrometer (4-mm inverse-detection LC probe head, detection volume 120 µl).

^{1}H-NMR Spectra were measured at 500.13 MHz. Suppression of MeCN and residual HDO signals was performed by presaturation. For calibration, the suppressed signal of MeCN was set to 2.0 ppm. Column: *Knaur LiChrospher 100 RP-18* (5 μm); 250 × 4 mm. Eluent: D_2O/MeCN 1 : 1, each solvent contains 0.1% of TFA. UV: 210 nm, 0.8 ml min^{-1}, stopped-flow mode.

7. *X-Ray Crystal-Structure Determination of* **6a**[2]) Crystals were obtained from EtOH. The intensities were collected on a *STADI 4* diffractometer (*Stoe*). Data collection and refinement parameters are listed in *Table 2*. The structure was solved by direct methods with SHELXS86 [17], the refinement was performed with SHELXL93 [18].

Table 2. *Crystallographic Data for Compound* **6a**

	6a
Empirical formula	$C_{13}H_{13}Cl_2NO_3S$
Formula weight	334.20
Crystal color, habit	colorless, prism
Crystal temp. [K]	293
Radiation, wavelength [Å]	MoK_α, 0.71069
Crystal dimensions [mm]	0.29 × 0.26 × 0.18
Crystal system	triclinic
Space group	$P\bar{1}$
Z	2
Reflections for cell determination	80
2θ range for cell determination [°]	$20 < 2\theta < 46$
Unit cell parameters a [Å]	8.080(2) α [°] 76.54(2)
b [Å]	9.451(2) β [°] 87.06(2)
c [Å]	9.947(3) γ [°] 84.77(2)
V [Å^3]	735.3(3)
D [Mg/m^3]	1.509
Absorption coefficient μ [mm^{-1}]	0.588
Transmission factors (min, max)	0.90; 0.85
Scan type	$\omega/2\theta$
2θ (max) [°]	50
Total reflections measured	3631
Symmetry-independent reflections	2605
Reflections observed ($I > 2\sigma(I)$)	2111
Variables	218
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0416$ $\omega R_2 = 0.1147$
R indices (all data)	$R_1 = 0.555$ $\omega R_2 = 0.1245$
$\Delta\rho$ (max, min) [e Å^{-3}]	0.698, −0.377
Goodness of fit s	1.071

REFERENCES

[1] M. Carmen Carreño, *Chem. Rev.* **1995**, *95*, 1717.
[2] R. J. Butlin, I. D. Linney, D. J. Critcher, M. F. Mahon, K. C. Molloy, M. Wills, *J. Chem Soc.*, *Perkin Trans. 1* **1993**, 1581.
[3] M. Wills, R. J. Butlin, I. D. Linney, R. W. Gibson, *J. Chem. Soc.*, *Perkin Trans. 1* **1991**, 3383.
[4] D. R. J. Hose, T. Raynham, M. Wills, *Tetrahedron: Asymmetry* **1993**, *4*, 2159.
[5] A. Waldner, *Tetrahedron Lett.* **1989**, *30*, 3061.
[6] A. Waldner, A. De Mesmaeker, P. Hoffmann, T. Mindt, T. Winkler, *Synlett* **1991**, 101.
[7] D. P. Curran, L. Huang Kuo, *J. Org. Chem.* **1994**, *59*, 3259.

[2]) Further details are available upon request from the *Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH*, D-76344 Eggenstein Leopoldshafen, on quoting the deposition No. 406998, the names of the authors, and journal citation.

[8] F. A. Davis, J. C. Towson, D. B. Vashi, R. ThimmaReddy, J. P. McCauley, M. E. Harakal, D. J. Gosciniak, *J. Org. Chem.* **1990**, *55*, 1254.
[9] F. A. Franklin, R. Thimma Reddy, J. P. McCauley, R. M. Przeslawski, M. E. Harakal, P. J. Carroll, *J. Org. Chem.* **1991**, *56*, 809.
[10] B. Schulze, S. Kirrbach, K. Illgen, P. Fuhrmann, *Tetrahedron* **1996**, *52*, 783.
[11] K. Illgen, Ch. Hartung, R. Herzschuh, B. Schulze, *Molecules* **1996**, *1*, 139.
[12] B. Schulze, B. Friedrich, S. Wagner, P. Fuhrmann, *J. Prakt. Chem.* **1996**, *338*, 424.
[13] B. Schulze, U. Obst, G. Zahn, B. Friedrich, R. Cimiraglia, H.-J. Hofmann, *J. Prakt. Chem.* **1995**, *337*, 175.
[14] 'Handbook of Chemistry and Physics', Ed. D. R. Lide, CRC-Press, Boca Raton, Ann Arbor, Boston, 1990 – 1991, Kap. 8, pp. 33 – 35.
[15] W. Oppolzer, M. Wills, C. Starkemann, G. Bernardinelli, *Tetrahedron Lett.* **1990**, *31*, 4117.
[16] C. Chapuis, J.-Y. de Saint Laumer, M. Marty, *Helv. Chim. Acta* **1997**, *80*, 146.
[17] Sheldrick, G. M. SHELXS-86, Program for the solution of crystal structures, Göttingen 1986.
[18] Sheldrick, G. M. SHELXL-93, Program for the refinement of crystal structures, Göttingen 1993.

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