

Arne Kolberg, Joachim Sieler and Bärbel Schulze*

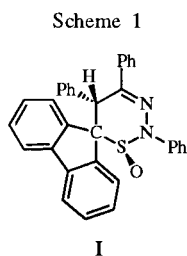
Department of Organic Chemistry, Faculty of Chemistry and Mineralogy, University of Leipzig,
 Talstr. 35, 04103 Leipzig, Germany
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Dedicated to Prof. Mühlstädt on the occasion of his 70th birthday

Oxidation of 2-benzenesulfonylaminoisothiazolium salts **1**, **2** and their imines **3**, **4** with hydrogen peroxide gave 1,2,3-thiadiazine 1-oxides **5**, **6**, which were converted into the corresponding 1,2,3-thiadiazine 1,1-dioxides **7**, **8** using *m*-chloroperoxybenzoic acid. Oxidation of **5**, **6** with hydrogen peroxide furnished isothiazol-3(2*H*)-one 1,1-dioxides **9**, **10** as ring contraction products.

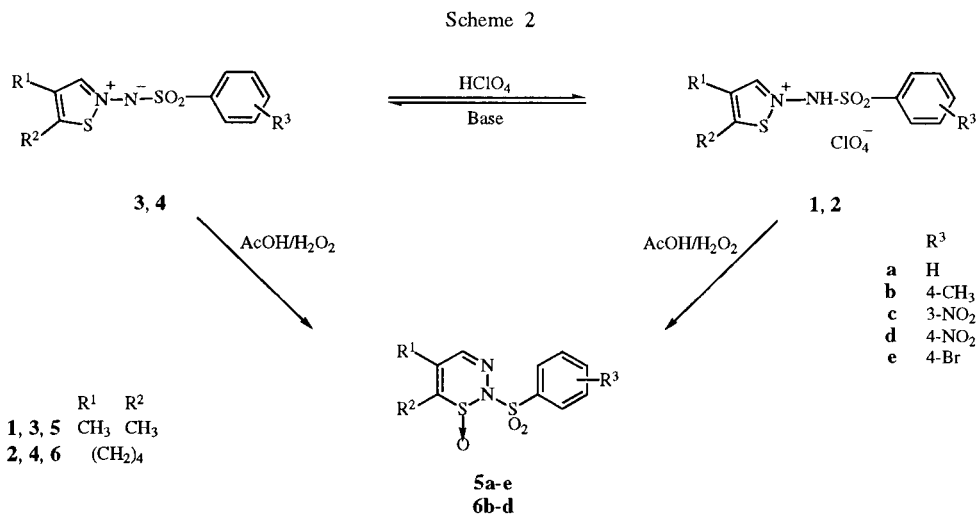
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Relatively little is known about synthesis and use of 1,2,3-thiadiazine heterocycles [1,2]. Herein we report a new approach to these systems in their 1-oxide and 1,1-dioxide forms, respectively. The only isolation of a 1,2,3-thiadiazine 1-oxide **I** is described by Bonini [3] (Scheme 1).



In our investigations of oxidation reactions non-benzo fused isothiazoles were used. 1,2,3-Thiadiazine 1-oxides **5**, **6** were produced in moderate yields by oxidation of 2-benzenesulfonylaminoisothiazolium salts **1**, **2** or the corresponding imines **3**, **4** with hydrogen peroxide at 0° (Scheme 2). The precursors **1-4** for the synthesis of 1,2,3-thiadiazine 1-oxides **5**, **6** were easily synthesized by reaction of β-thiocyanatovinylaldehydes with benzene sulfonylhydrazides [4,5]. The surprising point is the lack of stable 3-hydroperoxyisothiazole 1-oxides or 1,1-dioxides as one might expect based on the reaction of 2-phenyl- and 2-benzoylamino-substituted isothiazolium salts with hydrogen peroxide [6,7,8].

Structure of cyclic sulfanylhydrazides **5** was proved by X-ray analysis of **5e** (Figure 1) [9].



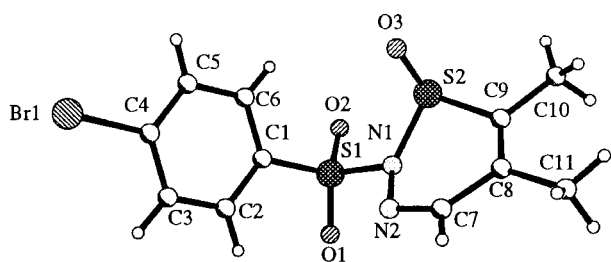


Figure 1. Structure of molecule 5e.

Table 1
Crystal Data and Bond Distances [Å] of 5e

Monoclinic	C2/c
a = 17.282 (15)	$\alpha = 90^\circ$
b = 7.4862 (6) Å	$\beta = 98.93 (2)^\circ$
c = 21.501 (2) Å	$\gamma = 90^\circ$
V = 2748.0 (4) Å ³	Z = 8
D _x = 1.756 Mg/m ³	T = 293 (2) K
R (int) = 0.0465	
N-1—N-2 1.389 (3)	S-2—O-3 1.469 (2)
S-2—N-1 1.714 (3)	S-1—N-1 1.704 (2)
N-2—C-7 1.292 (4)	S-2—C-9 1.777 (3)

In the ir spectra of **5**, **6** the typical sulfoxide absorption is at 1104–1109 cm⁻¹. A singlet appears in the ¹H nmr for H-C-4 at 7.49–7.92 ppm and ¹³C signals were observed at 144.8–145.5 ppm for C-4, 124.4–126.3 ppm (C-5) and 138.7–140.0 ppm for C-6.

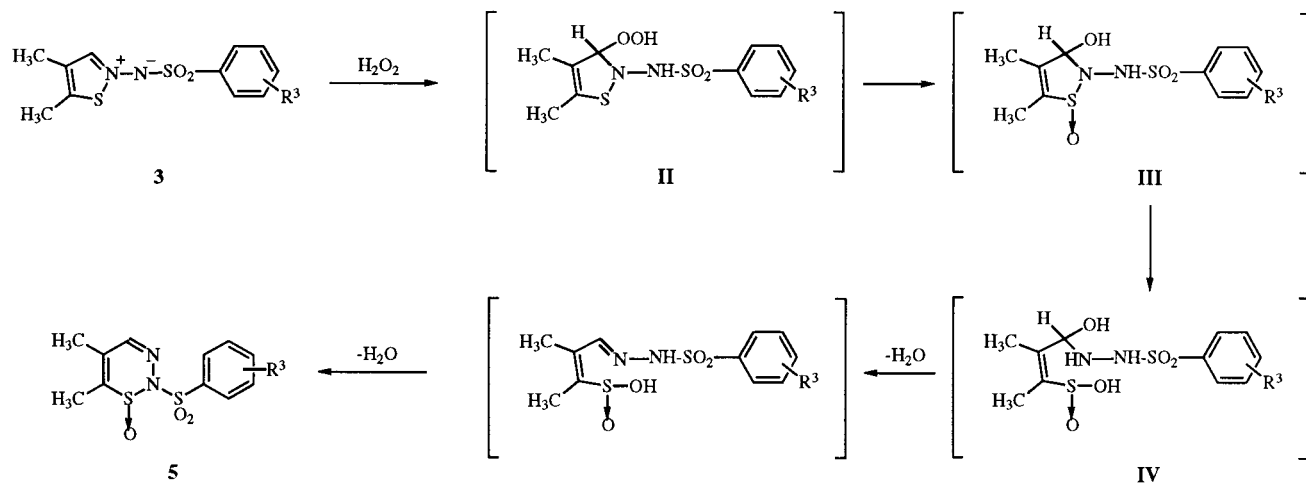
A proposed mechanism for the oxidation is that nucleophilic attack of hydrogen peroxide on the C-3 atom in the imine **3** occurs. This forms 3-hydroperoxyisothiazole **II** followed by redoxreaction resulting in 3-hydroxyisothiazole **III** (Scheme 3).

The intermediates **II** and **III** could not be isolated, but evidence of existence is given by hplc-nmr coupling in the oxidation of the 2-aryl derivatives of **3**, **4** [10]. Water attack on the S-N bond results in cleavage giving the acyclic intermediate **IV**, followed by repeated elimination of water to form 1,2,3-thiadiazine **5**. Conversion of **5**, **6** into the more common 1,2,3-thiadiazine 1,1-dioxides **7**, **8** succeed by reaction with *m*-chloroperoxybenzoic acid (Scheme 4). In contrast, the oxidation of **5**, **6** with hydrogen peroxide at room temperature proceeds with ring contraction to isothiazol-3(2*H*)-one 1,1-dioxides **9**, **10** (method A). Compounds **9** and **10** are also available by oxidation of **3**, **4** without isolation of the 1,2,3-thiadiazine 1-oxides **5**, **6** (method B). This hydroperoxide induced ring contraction proceeds by attack of hydrogen peroxide at C-4, followed by *S,N*-bond cleavage forms the acyclic sulfenic acid and recyclization to the 3-oxo-compounds **9**, **10**. Attempts to functionalize the cyclic sulfonylhydrazides **7**, **8** with hydrogen peroxide to hydroperoxides or rearrangement products **9**, **10** failed.

The structure of **8c** as well as of **9c** was established by X-ray analyses (Figure 2) [9]. Until now synthesis of 1,2,3-thiadiazine 1,1-dioxides has been accomplished by the reaction of hydrazine with *o*-substituted benzoic acid derivatives or ring conversion from saccharin derivatives [1,2], but they are limited to benzo-fused 1,2,3-thiadiazines.

Doubled bands for SO₂ absorption are characteristic for the 1,2,3-thiadiazine 1,1-dioxides **7**, **8** at 1330–1390 and 1165–1200 cm⁻¹ for asymmetric and symmetric vibrations, respectively. In the ¹H nmr the H-C-4 absorption is about 7.49–7.38 ppm, in the ¹³C spectra of **7**, **8** signals at 144.8–145.5 ppm (C-4), 124.4–126.3 ppm (C-5) and 138.7–140.0 ppm (C-6) are typical. The isothiazol-3(2*H*)-one 1,1-dioxides **9**, **10** (saccharin derivatives) are char-

Scheme 3



5,6-Dimethyl-2-(benzenesulfonyl)-2*H*-1,2,3-thiadiazine 1-Oxide (**5a**).

The yield was 31% from ethanol as colorless prisms, mp 158-159° dec; ir: 1371 (SO₂), 1182 (SO₂), 1106 (S→O), 725, 619, 572 cm⁻¹.

Anal. Calcd. for C₁₁H₁₂N₂O₃S₂ (284.36): C, 46.46; H, 4.25; N, 9.85. Found: C, 46.68; H, 4.29; N, 9.86.

5,6-Dimethyl-2-(4-toluenesulfonyl)-2*H*-1,2,3-thiadiazine 1-Oxide (**5b**).

The yield was 48% from ethanol as colorless prisms, mp 151-155° dec; ir: 1367 (SO₂), 1172 (SO₂), 1106 (S→O), 668, 615, 545 cm⁻¹.

Anal. Calcd. for C₁₂H₁₄N₂O₃S₂ (298.38): C, 48.30; H, 4.73; N, 9.39. Found: C, 48.53; H, 4.52; N, 9.33.

5,6-Dimethyl-2-(3-nitrobenzenesulfonyl)-2*H*-1,2,3-thiadiazine 1-Oxide (**5c**).

The yield was 45% from ethanol as colorless needles, mp 148-149° dec; ir: 1535 (NO₂), 1370 (SO₂), 1350 (NO₂), 1185 (SO₂), 1100 (S→O) cm⁻¹.

Anal. Calcd. for C₁₁H₁₁N₃O₅S₂ (329.36): C, 40.11; H, 3.37; N, 12.76. Found: C, 40.22; H, 3.52; N, 13.02.

5,6-Dimethyl-2-(4-nitrobenzenesulfonyl)-2*H*-1,2,3-thiadiazine 1-Oxide (**5d**).

The yield was 45% from ethanol as colorless needles, mp 142-144° dec; ir: 1535 (NO₂), 1370 (SO₂), 1350 (NO₂), 1185 (SO₂), 1095 (S→O) cm⁻¹.

Anal. Calcd. for C₁₁H₁₁N₃O₅S₂ (329.36): C, 40.11; H, 3.37; N, 12.76. Found: C, 39.86; H, 3.66; N, 12.52.

2-(4-Brombenzenesulfonyl)-5,6-dimethyl-2*H*-1,2,3-thiadiazine 1-Oxide (**5e**).

The yield was 44% from ethanol as colorless needles, mp 158-160° dec; ir: 1375 (SO₂), 1180 (SO₂), 1095 (S→O) cm⁻¹; ¹H nmr (deuteriochloroform): 7.96/7.68 (4H, arom. J_{AB} = 8.50 Hz), 7.26 (s, 1H, H-C-4), 2.39 (s, 3H, CH₃), 2.08 (s, 3H, CH₃); ¹³C nmr (deuteriochloroform): 145.0 (C-4), 139.4 (C-6), 136.8 (C-1'), 133.1 (C-3'/5'), 131.0 (C-2'/6'), 130.6 (C-4), 124.7 (C-5), 17.8 (CH₃), 17.1 (CH₃); ms: m/z 363 (2, M⁺), 143 (15), 127 (40), 115 (55), 75 (32), 67 (55), 59 (65).

Anal. Calcd. for C₁₁H₁₁N₂O₃S₂Br (363.26): C, 36.37; H, 3.05; N, 7.71. Found: C, 36.58; H, 3.16; N, 7.78.

2-(4-Toluenesulfonyl)-5,6,7,8-tetrahydro-2*H*-1,2,3-benzothiadiazine 1-Oxide (**6b**).

The yield was 26% from ethanol as colorless prisms, mp 178-179° dec; ir: 1396 (SO₂), 1172 (SO₂), 1105 (S→O), 1018, 667, 611, 546 cm⁻¹.

Anal. Calcd. for C₁₄H₁₆N₂O₃S₂ (324.42): C, 51.83; H, 4.97; N, 8.64. Found: C, 51.69; H, 5.18; N, 8.87.

2-(3-Nitrobenzenesulfonyl)-5,6,7,8-tetrahydro-2*H*-1,2,3-benzothiadiazine 1-Oxide (**6c**).

The yield was 52% from ethanol as colorless needles, mp 160-162° dec; ir: 1534 (NO₂), 1377 (SO₂), 1354 (NO₂), 1183 (SO₂), 1109 (S→O) cm⁻¹; ¹H nmr (deuteriochloroform): 8.97 (s, 1H, H-C-2'), 8.49 (d, 1H, H-C-4'), J = 8.24 Hz), 8.43 (d, 1H, H-C-6'), J = 7.97 Hz); 7.77 (t, 1H, H-C-5'), J = 8.08 Hz); 7.58 (s, 1H, H-C-4), 2.87 (m, 2H, CH₂), 2.68 (m, 2H, CH₂), 2.45 (m,

4H, 2 x CH₂); ¹³C nmr (deuteriochloroform): 148.7 (C-3'), 144.7 (C-4), 142.5 (C-6), 140.0 (C-1'), 134.8 (C-6'), 131.1 (C-5'), 129.4 (C-4'), 126.3 (C-5), 125.2 (C-2'), 27.6 (CH₂), 27.3 (CH₂), 22.1 (CH₂), 21.9 (CH₂); ms: m/z 355 (0.5, M⁺), 308 (17), 307 (10, M⁺-SO), 186 (6, SO₂Ar⁺), 171 (6), 155 (22), 141 (15), 123 (77), 109 (15), 81 (15), 76 (63), 65 (50), 59 (55), 51 (100).

Anal. Calcd. for C₁₃H₁₃N₃O₅S₂ (355.33): C, 43.94; H, 3.68; N, 11.82. Found: C, 44.12; H, 3.50; N, 11.75.

2-(4-Nitrobenzenesulfonyl)-5,6,7,8-tetrahydro-2*H*-1,2,3-benzothiadiazine 1-Oxide (**6d**).

The yield was 47% from ethanol as colorless prisms, mp 163-164° dec; ir: 1530 (NO₂), 1370 (SO₂), 1350 (NO₂), 1181 (SO₂), 1107 (S→O), 740, 621 cm⁻¹.

Anal. Calcd. for C₁₃H₁₃N₃O₅S₂ (355.39): C, 43.94; H, 3.68; N, 11.82. Found: C, 43.66; H, 3.56; N, 11.74.

2-Benzenesulfonyl-1,2,3-thiadiazine 1,1-Dioxides **7, 8**.

General Procedure.

1,2,3-Thiadiazine 1-oxide **5** or **6** (0.2 mmole) was dissolved in 40 ml of dichloromethane and 70 mg of 50% *m*-chloroperbenzoic acid in 20 ml of dichloromethane was added. After stirring under air exclusion for 8 hours, the organic phase was separated, the solvent was removed *in vacuo* and residue was washed five times with ether. Recrystallization was accomplished from ethanol.

5,6-Dimethyl-2-(4-toluenesulfonyl)-2*H*-1,2,3-thiadiazine 1,1-Dioxide (**7b**).

The yield was 24% from ethanol as colorless prisms, mp 161-162°; ir: 1378 (SO₂), 1334 (SO₂), 1193 (SO₂), 1171 (SO₂), 671, 544 cm⁻¹; ¹H nmr (acetone-d₆): 7.95/7.50 (4H, arom. J_{AB} = 8.30 Hz), 7.49 (s, 1H, H-C-4), 2.47 (s, 3H, CH₃), 2.22 (s, 3H, CH₃), 2.06 (s, 3H, CH₃); ¹³C nmr (acetone-d₆): 147.9 (C-1'), 143.5 (C-4), 139.1 (C-6), 136.3 (C-5), 135.1 (C-4'), 131.3 (C-2'/6'), 130.4 (C-3'/5'), 22.3 (4'-CH₃), 17.1 (CH₃), 11.2 (CH₃); ms: m/z 314 (2, M⁺), 250 (1), 186 (2), 155 (18), 115 (81), 91 (100), 67 (44), 39 (38).

Anal. Calcd. for C₁₂H₁₄N₂O₄S₂ (314.38): C, 45.85; H, 4.48; N, 8.91. Found: C, 46.06; H, 4.37; N, 9.12.

2-(4-Toluenesulfonyl)-5,6,7,8-tetrahydro-2*H*-1,2,3-benzothiadiazine 1,1-Dioxide (**8b**).

The yield was 62% from ethanol as colorless prisms, mp 161-162°; ir: 1382 (SO₂), 1330 (SO₂), 1189 (SO₂), 1164 (SO₂), 670, 542 cm⁻¹.

Anal. Calcd. for C₁₄H₁₆N₂O₄S₂ (340.42): C, 49.40; H, 4.74; N, 8.23. Found: C, 49.56; H, 5.02; N, 8.22.

2-(3-Nitrobenzenesulfonyl)-5,6,7,8-tetrahydro-2*H*-1,2,3-benzothiadiazine 1,1-Dioxide (**8c**).

The yield was 90% from ethanol as colorless prisms, mp 168°; ir: 1538 (NO₂), 1391 (SO₂), 1348 (NO₂), 1334 (SO₂), 1196 (SO₂), 1166 (SO₂), 935, 742, 667 cm⁻¹; ¹H nmr (acetone-d₆): 8.81 (s, 1H, H-C-2'), 8.67 (d, 1H, H-C-4'), 8.49 (d, 1H, H-C-6'), 8.47 (m, 1H, H-C-5'), 7.48 (s, 1H, H-C-4), 2.61 (m, 2H, CH₂), 2.50 (m, 2H, CH₂), 1.82 (m, 2H, CH₂), 1.75 (m, 2H, CH₂); ¹³C nmr (acetone-d₆): 149.8 (C-3'), 143.6 (C-4), 141.2 (C-6), 140.4 (C-5), 136.9 (C-1'), 136.1 (C-6'), 132.9 (C-4'), 130.9 (C-5'), 125.3 (C-2'), 27.5 (CH₂), 22.1 (CH₂), 22.0 (CH₂), 21.6 (CH₂); ms: m/z 371 (8, M⁺), 307 (4, M⁺-SO₂), 243 (5,

M⁺-2 SO₂), 186 (4), 157 (4), 141 (100), 122 (11), 91 (40), 77 (80), 65 (21), 52 (18).

Anal. Calcd. for C₁₃H₁₃N₃O₆S₂ (371.39): C, 42.04; H, 3.53; N, 11.31. Found: C, 42.08; H, 3.54; N, 11.25.

2-(4-Nitrobenzenesulfonyl)-5,6,7,8-tetrahydro-2*H*-1,2,3-benzothiadiazine 1,1-Dioxide (**8d**).

The yield was 39% from ethanol as colorless prisms, mp 209-210°; ir: 1530 (NO₂), 1386 (SO₂), 1341 (NO₂), 1313 (SO₂), 1195 (SO₂), 1164 (SO₂), 742 cm⁻¹.

Anal. Calcd. for C₁₃H₁₃N₃O₆S₂ (371.39): C, 42.04; H, 3.53; N, 11.31. Found: C, 42.08; H, 3.62; N, 11.16.

2-Benzenesulfonylaminoisothiazol-3(2*H*)-one 1,1-Dioxides **9**, **10**.

General Procedure.

Method A.

1,2,3-Thiadiazine 1-oxide **5**, **6** (1 mmole) was suspended in 8 ml of acetic acid, 5 ml of 30% hydrogen peroxide was added and stirred at room temperature. After 3-4 days of evaporation of the solvent, the precipitate was collected and recrystallized from ethanol.

Method B.

To a stirred suspension of **3** or **4** (1 mmole) and 3 ml of acetic acid, 3 ml of hydrogen peroxide (30%) was added dropwise and just enough acetic anhydride until the solution became clear at room temperature. The colorless crystals formed after 12-20 hours. They were then filtered and recrystallized from ethanol.

2-Benzenesulfonylamino-4,5-dimethylisothiazol-3(2*H*)-one 1,1-Dioxide (**9a**).

The yield was 20% (A), 58% (B) from ethanol as colorless needles, mp 195-196°; ir: 1760 (CO), 1350 (SO₂), 1195 (SO₂), 1170 (SO₂) 550 cm⁻¹; ¹H nmr (dimethyl-d₆ sulfoxide): 10.96 (s, 1H, NH), 7.89/7.86 (d, 2H, arom.), 7.54 (m, 3H, arom.), 2.16 (s, 3H, CH₃), 1.90 (s, 3H, CH₃).

Anal. Calcd. for C₁₁H₁₂N₂O₅S₂ (316.29): C, 41.77; H, 3.82; N, 8.86. Found: C, 41.95; H, 3.70; N, 9.02.

4,5-Dimethyl-2-(4-toluenesulfonylamino)-isothiazol-3(2*H*)-one 1,1-Dioxide (**9b**).

The yield was 23% (A), 61% (B) from ethanol as colorless needles, mp 183-185°; ir: 1755 (CO), 1355 (SO₂), 1190 (SO₂), 1170 (SO₂), 550 cm⁻¹.

Anal. Calcd. for C₁₂H₁₄N₂O₅S₂ (330.38): C, 43.62; H, 4.27; N, 8.48. Found: C, 43.43; H, 4.01; N, 8.29.

4,5-Dimethyl-2-(3-nitrobenzenesulfonylamino)-isothiazol-3(2*H*)-one 1,1-Dioxide (**9c**).

The yield was 27% (A) from ethanol as colorless needles, mp 208-213°; ir: 1755 (C=O), 1535 (NO₂), 1355 (NO₂/SO₂), 1190 (SO₂), 585 cm⁻¹; ¹H nmr (dimethyl-d₆ sulfoxide): 11.86 (s, 1H, NH), 8.55 (m, 2H, H-C-2'/4'), 8.29 (m, 1H, H-C-6'), 7.92 (m, 1H, H-C-5'), 2.22 (s, 3H, CH₃), 1.90 (s, 3H, CH₃); ¹³C nmr (dimethyl-d₆ sulfoxide): 159.8 (C-3), 147.6 (C-3'), 143.1 (C-5), 140.7 (C-1'), 133.6 (C-4), 132.9 (C-6'), 128.3 (C-4'), 122.4 (C-2'), 9.1 (CH₃), 8.2 (CH₃); ms: m/z 361 (M⁺, 28), 186 (12), 175 (92), 147 (33), 129 (30), 122 (22), 101 (33), 76 (55), 59 (48), 55 (100), 43 (62), 39 (68).

Anal. Calcd. for C₁₁H₁₁N₃O₇S₂ (361.29): C, 36.57; H, 3.07; N, 11.63. Found: C, 36.86; H, 3.11; N, 11.87.

4,5-Dimethyl-2-(4-nitrobenzenesulfonylamino)-isothiazol-3(2*H*)-one 1,1-Dioxides (**9d**).

The yield was 30% (A) from ethanol as colorless crystals, mp 248-251°; ir: 1755 (CO), 1535 (NO₂), 1360 (SO₂), 1350 (NO₂), 1190 (SO₂), 745, 545 cm⁻¹.

Anal. Calcd. for C₁₁H₁₁N₃O₇S₂ (361.29): C, 36.57; H, 3.07; N, 11.63. Found: C, 36.71; H, 3.19; N, 11.79.

2-(4-Bromobenzenesulfonylamino)-4,5-dimethyl-isothiazol-3(2*H*)-one 1,1-Dioxide (**9e**).

The yield was 13% (A) from ethanol as colorless needles, mp 227-228°; ir: 1750 (CO), 1360 (SO₂), 1190 (SO₂), 545 cm⁻¹.

Anal. Calcd. for C₁₁H₁₁N₂O₅S₂Br (395.25): C, 33.43; H, 2.80; N, 7.09. Found: C, 33.47; H, 2.95; N, 7.29.

2-Benzenesulfonylamino-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide (**10a**).

The yield was 17% (A), 35% (B) from ethanol as colorless crystals, mp 215-217°; ir: 3340, 1700 (C=O), 1350 (SO₂), 1180 (SO₂) cm⁻¹.

Anal. Calcd. for C₁₃H₁₄N₂O₅S₂ (342.39): C, 45.60; H, 4.12; N, 8.18. Found: C, 45.41; H, 4.21; N, 8.01.

2-(3-Nitrobenzenesulfonylamino)-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide (**10c**).

The yield was 42% (A) from ethanol as colorless needles, mp 239-240°; ir: 3222 (NH), 1758 (C=O), 1537 (NO₂), 1355 (NO₂), 1340 (SO₂), 1189 (SO₂), 669 cm⁻¹; ¹H nmr (acetone-d₆): 8.72 (s, 1H, H-C-2'), 8.60 (m, 1H, H-C-4'), 8.38 (m, 1H, H-C-6'), 8.00 (m, 1H, H-C-5'), 2.57 (m, 2H, CH₂), 2.36 (t, 2H, CH₂), 1.89 (m, 2H, CH₂), 1.87 (m, 2H, CH₂); ¹³C nmr (acetone-d₆): 159.7 (C=O), 148.6 (C-3'), 147.3 (C-5), 141.5 (C-1'), 136.1 (C-6'), 134.2 (C-4), 131.5 (C-5'), 128.6 (C-4'), 123.5 (C-2'), 20.7, 20.5, 20.3, 19.2 (4 x CH₂); ms: m/z 387 (8, M⁺), 186 (5), 173 (33), 154 (15), 128 (18), 109 (25), 80 (100), 65 (25), 53 (20).

Anal. Calcd. for C₁₃H₁₃N₃O₇S₂ (387.39): C, 40.31; H, 3.38; N, 10.85. Found: C, 40.47; H, 9.49; N, 10.59.

X-Ray Crystal Structure Determination of **5e**, **8c** and **9c** [9].

Crystals of compounds **5e**, **8c** and **9c** suitable for X-ray investigations were obtained by slow evaporation of an ethanol solution. The cell parameters and intensities were measured on a diffractometer: CCD (AXS, Bruker) or STADI 4 (Fa. Stoe). The structure was solved by direct methods using SHELXS 93 program [11]; the refinement was performed using SHELX 97 [12].

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[9] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbh, D-76344

Eggenstein Leopoldshafen 2; o quoting the depository numbers CSD-410668 for **5e**, CSD-410669 for **8c** and CSD-410670 for **9c**, the names of the authors and journal citation.

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