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Synthesis of Stable Hydroperoxides of Sultams by Oxidation of Isothiazolium Salts*

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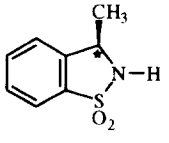
Abstract: In this paper the first synthesis of stable 3-hydroperoxy-sultams **3a-d** as well as the corresponding isothiazol-3(2H)-one 1,1-dioxides **8a-e** by oxidation of isothiazolium salts **6a-e** is reported. The 3-hydroxy-sultams **7b-d** are obtained by reduction of hydroperoxides **3b-d**.

Sultams have aquired great importance as chiral auxiliaries in asymmetric syntheses since Oppolzer's discovery of camphor sultam.[1] Apart from camphor sultam, also toluene-2,α-sultam **1** and the corresponding oxaziridines **2**, which can be synthesized from saccharin, have been applied as a chiral auxiliary and as asymmetric oxidants, respectively.[2-4]

In this paper, we report the synthesis of stable 3-hydroperoxy-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1,1-dioxides **3** as a new class of sultams with oxidizing properties.



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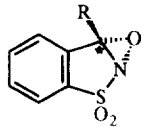

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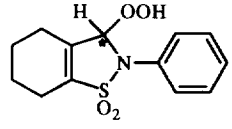


3

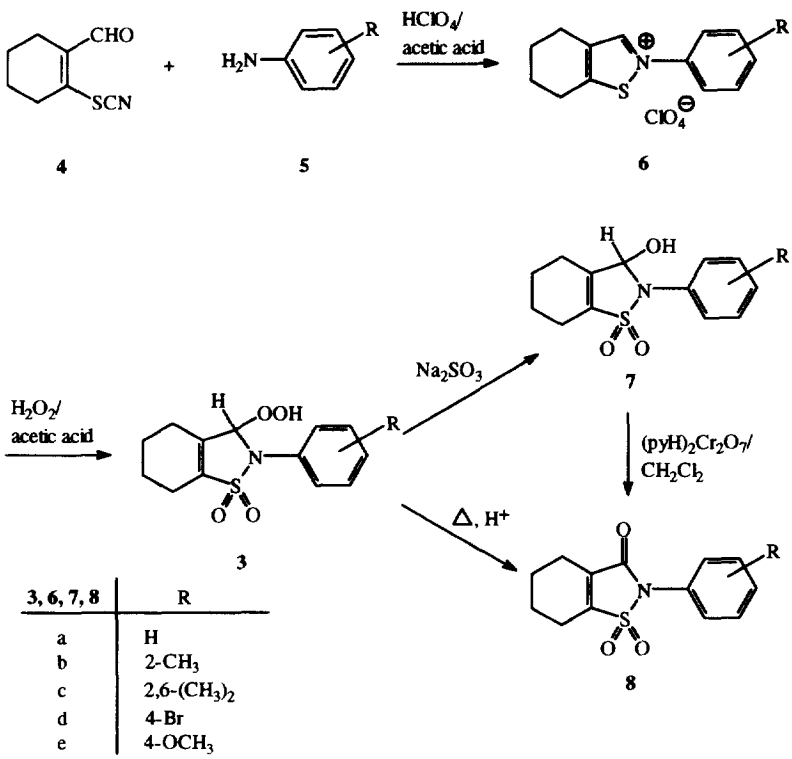
As educts for **3**, bicyclic isothiazolium salts **6**, which were prepared by cyclocondensation of thiocyanates **4** with substituted anilines **5**,[5,6] are employed. Recently, we investigated the preparation of isothiazolium salts and their reactions with N- and C-nucleophiles.[5-7] In the present paper we describe for the first time oxidation reactions of isothiazolium salts **6** in which the heterocyclic ring system is retained.

RESULTS AND DISCUSSION

We have investigated the reaction of compounds **6a-d** with hydrogen peroxide in acetic acid at room

*Dedicated to Prof. Dr. H. Suschitzky on the occasion of his 80th birthday.

temperature, yielding colourless crystals. In contrast to expectation, these stable compounds were identified by spectroscopic methods as 3-hydroperoxy-isothiazole 1,1-dioxides **3a-d** (Scheme 1). The derivative **3a** crystallized together with **8a**, while **3b-d** were obtained as pure compounds. Under the same oxidation conditions, the isothiazoles unsubstituted in the 3-position provided only isothiazol-3(2H)-one 1,1-dioxides.[8]



3, 6, 7, 8	R
a	H
b	2-CH_3
c	2,6-$(CH_3)_2$
d	4-Br
e	4-OCH_3

Scheme 1

The characteristics of the hydroperoxides **3a-d** are the ^{13}C chemical shifts of the C-3 atoms in $CDCl_3$, which appear at 91.8-95.1 ppm, and SO_2 absorption bands (1150-1170 cm^{-1} and 1260-1290 cm^{-1}) in the infrared. The hydroperoxide **3e** could not be isolated from reaction of **6e**; instead the 3-oxo product **8e** was obtained in 49% yield. The hydroperoxides **3b-d** are converted by thermolysis in ethanol into 1,1-dioxides **8b-d** by elimination of water. The reaction takes place also by acidic catalysis. Until now 1,1-dioxides of type **8** have been synthesized by oxidation of isothiazol-3(2H)-ones, which were prepared by multistep reactions.[9,10]

On reduction with Na_2SO_3 in water, the hydroperoxides **3b-d** are converted into the novel 3-hydroxy-sultams **7b-d**. The ^1H NMR spectra of **7b-d** show the typical 3-H proton at 5.37-5.99 ppm. The ^{13}C chemical shift of the C-3 atoms appears between 82.9 and 85.6 ppm in $CDCl_3$ and DMSO-d_6. The reduction also proceeds in DMSO-d_6, where it could be followed by NMR.

The hydroxy-sultams **7** are oxidized to the oxo-products **8** by pyridinium dichromate in CH_2Cl_2. The compounds **8** were identified by spectroscopic methods. In particular, the IR spectra of the 1,1-dioxides **8** show a carbonyl absorption band in the 1730 cm^{-1} region and absorptions for the SO_2 group at 1150-1170 cm^{-1} and 1280-1330 cm^{-1}. The signals of the C-3 atoms in the ^{13}C-spectra are found at 156.5-160.0 ppm.

Table 1 Yield and melting point data of sultams 3, 7 and isothiazolones 8

compounds	3		7		8	
	yield [%]	mp [°C]	yield [%]	mp [°C]	yield [%]	mp [°C]
a	22	157-162 d.	-	-	47[a]	177-180
b	68	148-152 d.	52	135-138	43[b]/63[c]	127-130
c	57	159-167 d.	49	167-171	46[b]/43[c]	143-145
d	75	169-172 d.	86	156-158	14[b]/55[c]	106-107
e	-	-	-	-	49[a]	143-145

[a] method A, [b] method B, [c] method C

The structure of the hydroperoxide **3d** was confirmed by an X-ray structure analysis (Fig. 1). **3d** shows two crystallographically distinct conformers **A** and **B** in a 1 : 1 ratio (Fig. 1), which correspond to different conformations of the phenyl group. In conformer **B** the phenyl group is 52.85° out of plane of the isothiazole ring, in the other (**A**) it is only 31.55°. The isothiazole ring of **3d** is approximately planar with a flat endocyclic nitrogen attached to the SO_2 group. The distance of N(8) in **B** from plane C(9), C(12), C(17), S(18) is -0.02(2) Å and that of N(28) in conformer **A** is -0.075(2) Å. The bond lengths and bond angles are listed in Table 2 only for conformer **B**, because the data for **A** are very similar, except for C(29) - O(30), which is 1.343(1) Å in **A**.

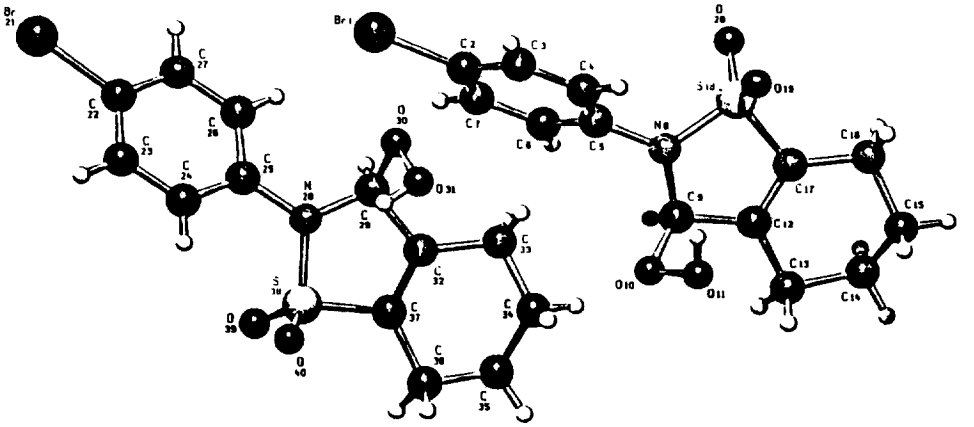


Fig. 1 Crystal structure of 2(4'-bromophenyl)-3-hydroperoxy-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1,1-dioxide (**3d**) with crystallographic numbering

Table 2 Selected bond lengths (Å) and bond angles (°) of 2(4'-bromophenyl)-3-hydroperoxy-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1,1-dioxide (3d)

Br(1) - C(2) 1.870(8)	C(9) - O(10) 1.405(1)	C(17) - S(18) 1.733(9)
C(5) - N(8) 1.437(1)	C(9) - C(12) 1.485(1)	S(18) - O(19) 1.424(6)
N(8) - C(9) 1.430(1)	O(10) - O(11) 1.496(1)	S(18) - O(20) 1.413(5)
N(8) - S(18) 1.643(7)	C(12) - C(17) 1.317(1)	

N(8) - C(9) - C(12)	106.9(7)	N(8) - S(18) - C(17) 92.9 (4)	O(20) - S(18) - C(17) 111.5(4)
O(19) - S(18) - N(8)	112.2(4)	C(9) - O(10) - O(11) 105.9(7)	O(10) - C(9) - C(12) 114.5(8)
O(20) - S(18) - O(19)	115.3(3)	C(5) - N(8) - S(18) 121.8(5)	O(10) - C(9) - N(8) 112.9(7)

CONCLUSION

In summary, it is shown that under certain reaction conditions isothiazolium salts, in contrast to earlier reports,[11] are oxidized to retain the isothiazole ring system. A simple method has been developed to form stable hydroperoxides of sultams **3**.

Furthermore, a new efficient synthetic route to 2-aryl-isothiazol-3(2H)-one 1,1-dioxides **8**, which are versatile dienophiles, has been found.

EXPERIMENTAL SECTION

All melting points were determined on a Boëtius micro melting point apparatus. The IR spectra (potassium bromide) were recorded on a Spekord M 80 spectrophotometer, Carl Zeiss, Jena. NMR spectra were determined with the Varian Gemini-200 (^{1}H NMR: 200 MHz, ^{13}C NMR: 50 MHz) spectrometer. The chemical shifts given in ppm are referenced to the deuterated solvent. Mass spectra were measured with the V6 12-250 mass spectrometer of Analytical Instruments Manchester. The elemental analyses were performed using the CHN-Rapid Heraeus Elemental Analyzer.

2-Aryl-4,5,6,7-tetrahydro-1,2-benzisothiazolium perchlorates (6)

The salts **6a, d, e** were prepared according to literature procedure[6]; the salts **6b** and **6c** also;

6b: yield 82%, mp 225-226 °C; **6c**: yield 74%, mp 238-240 °C.

2-Aryl-3-hydroperoxy-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1,1-dioxides (3)

General procedure:

To a stirred suspension of **6** (1 mmol) in 6 ml acetic acid was added 4 ml hydrogen peroxide (30%) at room temperature. After standing for 1 or 2 days, colourless crystals were obtained and recrystallized from ethanol.

3-Hydroperoxy-2-phenyl-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1,1-dioxide (3a):

I.R. ν (cm^{-1}): 1270(SO_2), 1155(SO_2); ^1H NMR ($CDCl_3$): δ = 1.82(m, 4H, CH_2);2.41(m, 4H, $2CH_2$); 6.21(s, 1H, H-3); 7.22(m, 2H, o-H); 7.49-7.40(m, 3H, m/p-H); ^{13}C NMR ($CDCl_3$): δ = 19.3; 22.2; 23.8(t, C-4,5,6,7); 91.9(d, C-3); 122.1(d, p-C); 123.0(d, o-C); 130.4(d, m-C); 134.5(s, C-3a); 136.8(s, i-C); 141.4(s, C-7a); MS (m/z): 281(M^+); Anal. Calcd for $C_{13}H_{15}NO_4S$: C, 55.49; H, 5.38; N, 4.98. Found C, 55.79; H, 5.45; N, 4.98.

3-Hydroperoxy-2(2'-methylphenyl)-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1,1-dioxide (3b):

I.R. ν (cm^{-1}): 1280(SO_2), 1150(SO_2); ^1H NMR ($CDCl_3$): δ = 1.85(m, 4H, $2CH_2$); 2.46(s, 3H, CH_3); 2.54(m, 4H, $2CH_2$); 5.52(s, 1H, H-3); 7.31(m, 4H, o/m/p-H); ^{13}C NMR ($CDCl_3$): δ = 18.8(q, CH_3); 19.4; 21.5; 21.6; 23.6(t, C-4,5,6,7); 95.1(d, C-3); 127.7(d, o-C); 130.0(d, p-C); 131.7(s, o-C); 132.0(d, m-C); 137.8(s, C-3a); 140.1(s, i-C); 140.3(s, C-7a);); MS (m/z): 295(M^+), 277(M^+-H_2O); Anal. Calcd for $C_{14}H_{17}NO_4S$: C, 56.93; H, 5.81; N, 4.74. Found C, 56.76; H, 6.01; N, 4.80.

3-Hydroperoxy-2(2',6'-dimethylphenyl)-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1,1-dioxide (3c):

I.R. ν (cm^{-1}): 1290(SO_2), 1150(SO_2); ^1H NMR ($CDCl_3$): δ = 1.85(m, 4H, $2CH_2$); 2.21(s, 3H, CH_3); 2.52(m, 4H, $2CH_2$); 2.60(s, 3H, CH_3); 5.54(s, 1H, H-3); 7.12-7.27(m, 3H, m/p-H); ^{13}C NMR($CDCl_3$): δ = 18.8(q, $2CH_3$); 19.4; 19.8; 21.5; 23.7(t, C-4,5,6,7); 94.8(d, C-3); 129.5(d, p-C); 129.8(s, o-C); 130.0(d, m-C); 138.2(s, C-3a); 139.5(s, i-C); 142.0(s, C-7a); MS (m/z): 291(M^+-H_2O); Anal. Calcd for $C_{15}H_{19}NO_4S$: C, 58.22; H, 6.20; N, 4.53. Found C, 57.92; H, 5.95; N, 4.70.

2(4'-Bromophenyl)-3-hydroperoxy-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1,1-dioxide (3d):

I.R. ν (cm^{-1}): 1260(SO_2), 1160(SO_2); ^1H NMR ($CDCl_3$): δ = 1.83(M, 4H, $2CH_2$); 2.27(m, 2H, CH_2); 2.50(m, 2H, CH_2); 5.83(s, 1H, H-3); 7.30; 7.52(4H, Ph, J_{AB}= 8.9 Hz); ^{13}C NMR ($CDCl_3$): δ = 19.0; 21.4; 21.5; 23.4(t, C-4,5,6,7); 91.8(d, C-3); 124.0(d, m-C); 133.0(s, p-C); 133.3(d, o-C); 134.3(s, i-C); 137.1(s, C-3a); 140.0(s, C-7a); MS (m/z): 343/341(M^+-H_2O); Anal. Calcd for $C_{13}H_{14}BrNO_4S$: C, 43.35; H, 3.92; N, 3.89. Found C, 43.72; H, 3.79; N, 4.01.

X-ray diffraction analysis of ***3d***[12]: Crystals were obtained from ethanol. $C_{13}H_{14}O_4BrNS$ (360.2), colourless prism, size 0.80x0.73x0.40 mm, a = 14.406 (3), b = 12.270(3), c = 8.315(3) Å, α = 88.95(3), β = 104.23(3), γ = 89.04(3), V = 1424.1(7) $Å^3$, Z = 4, space group triclinic P1, absorption coefficient m = 5.431 mm^{-1}. The measurements were performed with STOE, radiation CuK_α; unique reflections 2929, measured 3195, observed with $F > 3\sigma(F)$, $3° < \theta < 50°$; structure solution direct methods (SHELXS)[13] refinement (SHELXL)[14], R_{int} = 0,0111, number of refined parameters 362, R = 0.0491.

2-Aryl-3-hydroxy-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1,1-dioxides (7)

General procedure:

Na_2SO_3 x $7H_2O$(4 mmol) was dissolved in 12 ml water and added to **3**. The suspension was stirred for 24 hours at room temperature. The mixture was extracted with ether. The combined organic phases was washed with saturated NaCl solution and dried over anhydrous Na_2SO_4. After slow removal of the solvent, colourless crystals were isolated and recrystallized from ethanol.

3-Hydroxy-2(2'-methylphenyl)-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1,1-dioxide (7b):

I.R. ν (cm^{-1}): 3500(OH), 1280(SO_2), 1150(SO_2); ^1H NMR ($CDCl_3$): δ = 1.82(m, 4H, $2CH_2$); 2.41(s, 3H, CH_3); 2.46(m, 4H, $2CH_2$); 3.09(d, 1H, OH); 5.37(d, 1H, H-3); 7.27-7.33(m, 4H, o/m/p-H); ^{13}C NMR ($CDCl_3$): δ = 18.8(q, CH_3); 19.1; 21.6; 23.4(t, C-4,5,6,7); 85.6(d, C-3); 127.5(d, o-C); 130.0(d, p-C); 131.9(d, m-C); 132.1(s, o-C); 132.3(d, m-C); 135.6(s, C-3a); 141.1(s, i-C); 143.2(s, C-7a);); MS (m/z): 279(M^+); Anal. Calcd for $C_{14}H_{17}NO_3S$: C, 60.18; H, 6.19; N, 5.01. Found C, 60.51; H, 6.27; N, 4.86.

3-Hydroxy-2(2',6'-dimethylphenyl)-2,3,4,5,6,7-hexahydo-1,2-benzisothiazole 1,1-dioxide (7c):

I.R. ν (cm^{-1}): 3500(OH), 1280(SO_2), 1150(SO_2); ^1H NMR ($CDCl_3$): δ = 1.84(m, 4H, $2CH_2$); 2.25(s, 3H, CH_3); 2.49(m, 4H, $2CH_2$); 2.51(s, 3H, CH_3); 5.37(s, 1H, H-3), 7.13-7.17(m, m/p-H); ^{13}C NMR ($CDCl_3$): δ = 19.1(q, $2CH_3$); 20.0; 21.0; 21.6; 23.4(t, C-4,5,6,7); 84.9(d, C-3); 129.5(d, p-C); 129.8(d, m-C); 136.0(s, o-C); 140.3(s, C-3a); 142.4(s, i-C); 142.7(s, C-7a); MS (m/z): 293(M^+); Anal. Calcd for $C_{15}H_{19}NO_3S$: C, 61.40; H, 6.54; N, 4.77. Found C, 60.93; H, 6.38; N, 4.72

2(4'-Bromophenyl)-3-hydroxy-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1,1-dioxide (7d):

I.R. ν (cm^{-1}): 3420(OH), 1280(SO_2), 1150(SO_2); ^1H NMR ($CDCl_3$): δ = 1.77(m, 4H, $2CH_2$); 2.43(m, 4H, $2CH_2$); 5.99(s, 1H, H-3); 7.32; 7.51(4H, Ph, J_{AB}= 8.9 Hz); ^{13}C NMR ($CDCl_3$): δ = 18.8; 21.5; 23.2(t, C-4,5,6,7); 82.9(d, C-3); 119.1(s, p-C); 123.4(d, o-C); 133.1(d, m-C); 134.5(s, i-C); 134.7(s, C-3a); 143.3(s, C-7a); MS (m/z): 345/343(M^+); Anal. Calcd for $C_{13}H_{14}BrNO_3S$: C, 45.35; H, 4.11; N, 4.07. Found C, 45.71; H, 4.15; N, 3.99

2-Aryl-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2H)-one 1,1-dioxides (8)

General procedure:

Method A: To a stirred suspension of isothiazolium salt **6** (1 mmol) in 6 ml acetic acid is added dropwise 5 ml hydrogen peroxide at room temperature. The obtained colourless crystals were filtrated and recrystallized from ethanol.

Method B: Hydroperoxide **3** (1 mmol) was refluxed for 6 hours in 5 ml ethanol. Colourless crystals were obtained and recrystallized from ethanol. The addition of 1.5 ml conc. HCl catalysed the reaction.

Method C: Sultam **7** is dissolved in 3 ml CH_2Cl_2. To the stirred solution is added $(pyH)_2Cr_2O_7$ (2.5 mmol) at room temperature. The mixture is stirred for 8 hours. Purification by Al_2O_3 chromatography with 3x10 ml ethyl

acetate. The combined organic layer was washed with 10% Na_2CO_3 and saturated NaCl solution, dried over anhydrous Na_2SO_4. After removal of the solvent, colourless crystals were isolated, which were purified by recrystallisation from ethanol.

2-Phenyl-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2H)-one 1,1-dioxide (8a):

I.R. ν (cm^{-1}): 1730(C=O), 1325(SO_2), 1180(SO_2); ^{1}H NMR (acetone-d_6): δ = 1.88(m, 4H, $2CH_2$); 2.52(m, 2H, CH_2); 2.64(m, 2H, CH_2); 7.44-7.58(m, 5H, o/m/p-H); ^{13}C NMR (acetone-d_6): δ = 19.8; 21.3; 21.6; 21.9(t, C-4,5,6,7); 129.4(d, o-C); 130.6(d, p-C); 130.9(d, m-C); 131.1(s, i-C); 137.6(s, C-3a); 147.2(s, C-7a); 161.0(s, C-3); MS (m/z): 263(M^+); Anal. Calcd for $C_{13}H_{13}NO_3S$: C, 59.29; H, 4.98; N, 5.32. Found C, 58.96; H, 5.21; N, 5.53

2(2'-Methylphenyl)-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2H)-one 1,1-dioxide (8b):

I.R. ν (cm^{-1}):1730(C=O), 1320(SO_2), 1170(SO_2); ^{1}H NMR ($CDCl_3$): δ = 1.91(m, 4H, $2CH_2$); 2.28(s, 3H, CH_3); 2.53(m, 2H, CH_2); 2.67(m, 2H, CH_2); 7.36(m, 4H, o/m/p-H); ^{13}C NMR ($CDCl_3$): δ = 18.5(q, CH_3); 19.6; 20.9; 21.1; 21.4(t, C-4,5,6,7); 127.7(d, o-C); 127.8(d, p-C); 131.0(d, m-C); 131.1(d, m-C); 132.1(s, o-C); 136.5(s, C-3a); 139.8(s, i-C); 147.8(s, C-7a); 159.9(s, C-3); MS (m/z): 277(M^+); Anal. Calcd for $C_{14}H_{15}NO_3S$: C, 60.62; H, 5.46; N, 5.05. Found C, 60.33; H, 5.35; N, 5.16.

2(2',6'-Dimethylphenyl)-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2H)-one 1,1-dioxide (8c):

I.R. ν (cm^{-1}): 1725(C=O), 1310(SO_2), 1160(SO_2); ^{1}H NMR ($CDCl_3$): δ = 1.89(m, 4H, $2CH_2$); 2.29(s, 6H, $2CH_3$); 2.53(m, 2H, CH_2); 2.66(m, 2H, CH_2); 7.19(m, 3H, m/p-H); ^{13}C NMR ($CDCl_3$): δ = 19.0(q, $2CH_3$); 19.6; 20.9; 21.0; 21.3(t, C-4,5,6,7); 127.0(d, p-C); 129.5(d, m-C); 130.8(s, o-C); 136.3(s, C-3a); 140.4(s, i-C); 147.7(s, C-7a); 160.0(s, C-3); MS (m/z): 291(M^+); Anal. Calcd for $C_{15}H_{17}NO_3S$: C, 61.82; H, 5.89; N, 4.81. Found C, 61.65; H, 5.51; N, 4.71.

2(4'-Bromophenyl)-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2H)-one 1,1-dioxide (8d):

I.R. ν (cm^{-1}): 1730(C=O), 1330(SO_2), 1170(SO_2); ^{1}H NMR ($CDCl_3$): δ = 1.88(m, 4H, $2CH_2$); 2.51(m, 2H, CH_2); 2.66(m, 2H, CH_2); 7.63; 7.34(4H, J_{AB}= 8.9 Hz); ^{13}C NMR ($CDCl_3$): δ = 19.6; 20.9; 21.0; 21.3(t, C-4,5,6,7); 124.2(s, p-C); 129.8(d, o-C); 133.6(m-C); 133.9(s, i-C); 136.8(s, C-3a); 146.8(s, C-7a); 160.0(s, C-3); MS (m/z): 343/341(M^+); Anal. Calcd for $C_{13}H_{12}BrNO_3S$: C, 45.62; H, 3.54; N, 4.09. Found C, 45.72; H, 3.50; N, 3.98.

2(4'-Methoxyphenyl)-4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2H)-one 1,1-dioxide (8e):

I.R. ν (cm^{-1}): 1740(C=O), 1370(SO_2), 1170(SO_2); ^{1}H NMR (DMSO-d_6): δ = 1.88(m, 4H, $2CH_2$); 2.52(m, 2H, $2CH_2$), 2.65(m, 2H, $2CH_2$); 3.95(s, 3H, OCH_3); 7.05; 7.36(4H, J_{AB}= 8.8 Hz, o/m-H); ^{13}C NMR (DMSO-d_6): δ = 19.6; 20.9; 21.4(t, C-4,5,6,7); 56.9(q, OCH_3); 115.7(d, m-C); 124.1(d, o-C); 128.7(s, i-C); 131.0(s, C-3a); 146.8(s, C-7a); 156.5(s, p-C); 161.5(s, C=O);); MS (m/z): 293(M^+); Anal. Calcd for $C_{14}H_{15}NO_4S$: C, 57.32; H, 5.15; N, 4.77. Found C, 56.99; H, 4.98; N, 4.98.

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REFERENCES AND NOTES

1. Kim, B.H.; Curran, D.P. *Tetrahedron* **1993**, *49*, 293-318.
2. Davis, A.; Sheppard, A.C. *Tetrahedron* **1989**, *45*, 5703-5742.
3. Oppolzer, W.; Lienard, P. *Helv. Chim. Acta* **1992**, *75*, 2572-2582.
4. Davis, F.A.; ThimmaReddy, R.; McCauley, Jr., J.P.; Przeslawski, R.M.; Harakal, M.E. *J. Org. Chem.* **1991**, *56*, 809-815.
5. Schulze, B.; Rosenbaum, K.; Hilbig, J.; Weber, L. *J. Prakt. Chem., Chem. Ztg.* **1992**, 334, 25-33.
6. Schulze, B.; Obst, U.; Zahn, G.; Friedrich, B.; Cimiraglia, R.; Hofmann, H.-J. *J. Prakt. Chem., Chem. Ztg.* **1995**, *337*, 175-183.
7. Schulze, B.; Selke, D.; Kirrbach, S.; Kempe, R. *J. Prakt. Chem., Chem. Ztg.* **1994**, *336*, 115-120.
8. Schulze, B.; Kirsten, G.; Kirrbach, S.; Rahm, A.; Heimgartner, H. *Helv. Chim. Acta* **1991**, *74*, 1059-1070.
9. Lewis, S.N.; Miller, G.A.; Hausman, M.; Szamborski, E.C. *J. Heterocycl. Chem.* **1971**, *8*, 571-580.
10. Waldner, A. *Helv. Chim. Acta* **1989**, *72*, 1435-1443.
11. Sykes, P.; Ullah,H. *J. Chem. Soc., Perkin Trans 1* **1972**, 2305-2315.
12. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein Leopoldshafen 2; on quoting the depository number CSD-401637, the names of the authors and journal citation.
13. Sheldrick, G.M. SHELXS-86, Program for the solution of crystal structures, Göttingen 1986.
14. Sheldrick, G.M. SHELXL-93, Program for the solution determination, Göttingen 1993.

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