Supporting Information

Chemoselective Electrophilic Oxidation of Heteroatoms by Hydroperoxy Sultams

Feyissa Gadissa Gelalcha, Bärbel Schulze*

Universität Leipzig, Institut für Organische Chemie, Johannisallee 29, D-04103 Leipzig,

Germany. E-mail: bschulze@organik.uni-leipzig.de

Table of contents

	Page
1 Synthesis and Experimental Data for 2b , 3c , 8b-d	S2-3
2 X-ray Crystal Structure Determination of 1c	S3
3 Additional references	S12
4 Figure S1	S13
5 Figure S2	S14
6 ¹ H NMR spectrum of 1b	S15
7 ¹³ C NMR spectrum of 1b	S16
8 ¹ H NMR spectrum of 1c	S17
9 ¹³ C NMR spectrum of 1c	S18
10 ¹ H NMR spectrum of 1d	S19
11 ¹³ C NMR spectrum of 1d	S20
12 ¹ H NMR spectrum of 2c	S21
13 ¹³ C NMR spectrum of 2c	S22
14 ¹ H NMR spectrum of 2d	S23
15 ¹³ C-NMR spectrum of 2d	S24
16 ¹ H NMR spectrum of 3c	S25
17 ¹³ C NMR spectrum of 3c	S26
18 ¹ H NMR spectrum of 3d	S27
19 ¹³ C NMR spectrum of 3d	S28
20 ¹ H NMR spectrum of 8c	S29
21 ¹³ C NMR spectrum of 8c	S30
22 ¹ H NMR spectrum of 8d	S31
23 ¹³ C NMR spectrum of 8d	S32

2(4-*t*-Butylphenyl)-3-hydroxy-2,3,4,5,6,7-hexahydro-1,2-benzisothiazole 1,1-dioxide (2b):

2b was obtained by sodium sulfite reduction³⁹ of 1.00 mmol **1b**. Yield 0.85 mmol, 85%. Mp 158-165°C. FT-IR (KBr, cm⁻¹) 1520, 1295, 1150. ¹H NMR (300 MHz, CDCl₃): δ 1.33 (s, 9H), 1.84 (m, 4H), 2.51 (m, 4H), 5.88 (s, 1H), 7.31-7.41 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 20.9, 21.21, 21.4, 23.0, 31.8, 34.9, 83.1, 123.4, 127.2, 132.6, 136.9, 139.4, 148.7.

2(2,5-Dichloro-4-isopropoxyphenyl)-4,5,6,7-tetrahydro-1,2-benzisothiazole-3(2H)-one

1,1-dioxide (3c): **3c** was prepared by refluxing an acidified ethanolic solution of 1 mmol **1c** analogous to the procedure described previously^{12a}. Yield: 0.37 mmol, 37 %. Mp 189-190°C. FT-IR (KBr) 1737, 1487, 1379, 1334, 1246, 1178, 1080 cm⁻¹. (EI) m/z 389.0 (M-1). ¹H NMR (200 MHz, DMSO-d₆): δ 1.35 (d, *J* = 5.86 Hz, 6H); 1.70-1.90 (m, br, 4H), 2.46 (m, 1H), 2.52 (m, 1H), 2.64 (m, 2H), 4.90 (m, 1H), 7.61 (s, 1H), 7.66 (s, 1H). ¹³C NMR (75 MHz, DMSO-d₆): δ 18.6, 19.98, 20.0, 20.3, 21.6, 72.4, 116.2, 118.0, 121.3, 132.8, 134.1, 136.2, 146.3, 155.2, 158.8.

Procedure for the Preparation of Salts 8b-d: **8b-d** were prepared from the respective compounds **6** and **7** analogous to the procedure described previously.^{12b}

2(4-*t*-Butylphenyl)-4,5,6,7-tetrahydro-1,2-benzisothiazolium perchlorate (8b): Yield 54%.

Mp (dec). 193-194°C (EtOH). Ir (KBr, cm⁻¹): 1460, 1100, 620. UV/VIS (EtOH) λ_{max} (lgε) 237 (3.98), 262 (3.89), 307 (3.95). ¹H NMR (dmso-d₆): δ 1.87 (m, 4H), 2.82 (m, 2H), 3.17 (m, 2H), 3.45 (s, 9H), 7.73 (m, 4H), 9.45 (s, 1H). ¹³C NMR (dmso-d₆): δ 20.8, 21.5, 22.7, 25.6, 31.1, 35.1, 123.1, 127.6, 134.7, 154.3, 155.4, 168.5. MS (EI, m/z): 271 ([M-HClO₄]⁺). C₁₇H₂₂ClNO₄S (371.9) calcd C 54.89 H 5.97, N 3.78, S 8.62, O 17.2, Cl 9.53. found C 54.73, H 5.86, N 3.82, S 9.19, O 17.4, Cl 9.54.

2(2,5-Dichloro-4-isopropoxyphenyl)-4,5,6,7-tetrahydro-1,2-benzisothiazolium

perchlorate (8c): Yield: 53 %. Mp (dec): 205-208 °C (EtOH). Ir (KBr, cm⁻¹): 1460, 1109, 625. UV/VIS (EtOH) λ_{max} (lgε) 238 (3.98), 272 (3.71), 314 (3.54), 458 (2.85). MS (EI, m/z): 341 ([M-HClO₄]⁺). ¹H (200 MHz, CDCl₃): δ 1.43 (d, *J* = 6.0 Hz, 6H); 1.95 (m, 4H), 2.94 (m, 2H), 3.25 (m, 2H), 4.67 (m, 1H), 7.08 (s, 1H), 7.79 (s, 1H), 8.66 (s, 1H). ¹³C NMR (50 MHz,

REVISED

CDCl₃): δ 21.2, 21.8, 22.2, 23.1, 25.3, 73.9, 115.9, 124.3, 126.1, 131.0, 130.6, 135.7, 157.3,

158.5, 172.1.

2(2,5-Dichloro-4-isopropoxyphenyl)-5,6,7,8-tetrahydro-4H-cyclohepta[d]-

benzothiazolium perchlorate (8d): Yield: 88 % Mp (dec): 185-187 °C (EtOH). MS (EI, m/z): 355 ([M-HClO₄])⁺. ¹H (200 MHz, CDCl₃): δ 1.42 (d, J = 6.0 Hz, 6H); 1.75 (m, 2H), 1.92 (m, 4H), 3.00 (m, 2H), 3.26 (m, 2H), 4.63 (m, 1H), 7.07 (s, 1H), 7.83 (s, 1H), 8.64 (s, 1H). ¹³C NMR (50 MHz, CDCl₃): δ 22.2, 26.7, 27.0, 28.2, 29.1, 31.9, 73.8, 115.9, 124.2, 125.8, 130.0, 130.1, 141.2, 157.3, 159.1, 176.3.

X-ray Crystal Structure Determination of 1c

Single crystals suitable for the x-ray crystal structure determination of **1c** were obtained from a solution of **1c** in acetone. Diffraction experiment was performed on an AXS-SMART area detector diffractometer system (ω rotation scans with narrow frames) equipped with graphite monochromated Mo- K α radiation (λ = 0.71073 Å). Data sets were corrected for Lorentz-Polarisation effects and for the effects of adsorption using the program SADABS.⁴⁰ The structure was solved by direct methods and refined using the program SHELXS and SHELXL.⁴¹ Non hydrogen atoms were refined anisotropically. Hydrogen atoms were located and refined isotropically except methyl hydrogens, which were calculated in idealized positions and allowed to ride on the atoms to which they were attached.

Table S1. Crystal data and structure refinement for **1c**.

Identification code	c1117fin	
Empirical formula	C16 H19 Cl2 N O5 S	
Formula weight	408.28	
Temperature	215(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	$a = 1091.42(16)$ pm	$\alpha = 90^\circ$.
	$b = 1432.4(2)$ pm	$\beta = 109.237(3)^\circ$.
	$c = 1243.36(18)$ pm	$\gamma = 90^\circ$.
Volume	1.8352(5) nm ³	
Z	4	

Density (calculated)	1.478 Mg/m ³
Absorption coefficient	0.494 mm ⁻¹
F(000)	848
Crystal size	0.38 x 0.20 x 0.08 mm ³
Theta range for data collection	2.16 to 28.89°.
Index ranges	-14<=h<=10, -19<=k<=18, -16<=l<=14
Reflections collected	11883
Independent reflections	4421 [R(int) = 0.0411]
Completeness to theta = 28.89°	91.5 %
Absorption correction	SADABS
Max. and min. transmission	0.9616 and 0.8345
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4421 / 0 / 280
Goodness-of-fit on F ²	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0447, wR2 = 0.1125
R indices (all data)	R1 = 0.0689, wR2 = 0.1225
Largest diff. peak and hole	0.674 and -0.439 e.Å ⁻³

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for **1c**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cl(1)	9465(1)	2588(1)	9448(1)	49(1)
Cl(2)	5977(1)	535(1)	11759(1)	47(1)
S(1)	6758(1)	1182(1)	7287(1)	30(1)
O(1)	5490(2)	839(1)	7174(1)	40(1)
O(2)	6811(2)	2168(1)	7100(2)	47(1)
O(3)	8790(2)	-606(1)	9041(1)	44(1)
O(4)	7511(2)	-1045(1)	8512(2)	56(1)
O(5)	7737(2)	2042(1)	12751(1)	50(1)
N(1)	7848(2)	896(1)	8501(1)	34(1)
C(1)	7502(2)	521(2)	6490(2)	31(1)
C(2)	6983(3)	475(2)	5216(2)	46(1)
C(3)	7995(4)	-17(3)	4799(3)	72(1)
C(4)	8588(3)	-841(2)	5494(2)	61(1)
C(5)	9286(3)	-619(2)	6732(2)	41(1)
C(6)	8512(2)	56(2)	7168(2)	32(1)
C(7)	8793(2)	214(2)	8422(2)	33(1)
C(8)	7789(2)	1234(1)	9564(2)	30(1)
C(9)	8517(2)	1999(2)	10099(2)	31(1)
C(10)	8505(2)	2299(2)	11151(2)	33(1)
C(11)	7738(2)	1846(1)	11685(2)	31(1)
C(12)	6975(2)	1091(2)	11128(2)	32(1)
C(13)	7012(2)	784(2)	10091(2)	33(1)
C(14)	7965(3)	2994(2)	13176(2)	46(1)
C(15)	6717(4)	3475(3)	12879(4)	97(1)
C(16)	8593(6)	2899(3)	14441(3)	132(2)

Table S3. Bond lengths [pm] and angles [°] for **1c**.

Cl(1)-C(9)	172.9(2)
Cl(2)-C(12)	173.1(2)
S(1)-O(1)	143.09(17)
S(1)-O(2)	143.53(17)
S(1)-N(1)	163.72(18)
S(1)-C(1)	175.1(2)
O(3)-C(7)	140.5(3)
O(3)-O(4)	147.4(3)
O(5)-C(11)	135.6(3)
O(5)-C(14)	145.4(3)
N(1)-C(8)	142.9(3)
N(1)-C(7)	144.7(3)
C(1)-C(6)	132.7(3)
C(1)-C(2)	149.8(3)
C(2)-C(3)	153.6(4)
C(3)-C(4)	148.0(5)
C(4)-C(5)	150.9(4)
C(5)-C(6)	149.9(3)
C(6)-C(7)	150.3(3)
C(8)-C(9)	138.7(3)
C(8)-C(13)	139.0(3)
C(9)-C(10)	138.1(3)
C(10)-C(11)	138.9(3)
C(11)-C(12)	140.1(3)
C(12)-C(13)	137.6(3)
C(14)-C(15)	146.1(5)
C(14)-C(16)	150.0(5)
O(1)-S(1)-O(2)	114.30(11)
O(1)-S(1)-N(1)	112.91(10)
O(2)-S(1)-N(1)	109.87(10)
O(1)-S(1)-C(1)	111.87(10)
O(2)-S(1)-C(1)	112.92(11)
N(1)-S(1)-C(1)	93.15(10)
C(7)-O(3)-O(4)	106.60(17)
C(11)-O(5)-C(14)	119.69(18)
C(8)-N(1)-C(7)	122.86(17)
C(8)-N(1)-S(1)	121.83(15)
C(7)-N(1)-S(1)	115.08(14)
C(6)-C(1)-C(2)	126.6(2)

C(6)-C(1)-S(1)	110.78(16)
C(2)-C(1)-S(1)	122.58(18)
C(1)-C(2)-C(3)	108.3(2)
C(4)-C(3)-C(2)	113.2(3)
C(3)-C(4)-C(5)	113.8(3)
C(6)-C(5)-C(4)	110.5(2)
C(1)-C(6)-C(5)	122.9(2)
C(1)-C(6)-C(7)	115.26(19)
C(5)-C(6)-C(7)	121.7(2)
O(3)-C(7)-N(1)	113.30(19)
O(3)-C(7)-C(6)	113.95(18)
N(1)-C(7)-C(6)	105.43(17)
C(9)-C(8)-C(13)	118.85(19)
C(9)-C(8)-N(1)	121.21(19)
C(13)-C(8)-N(1)	119.92(19)
C(10)-C(9)-C(8)	121.2(2)
C(10)-C(9)-Cl(1)	119.00(17)
C(8)-C(9)-Cl(1)	119.84(16)
C(9)-C(10)-C(11)	120.1(2)
O(5)-C(11)-C(10)	124.41(19)
O(5)-C(11)-C(12)	116.80(19)
C(10)-C(11)-C(12)	118.64(19)
C(13)-C(12)-C(11)	120.8(2)
C(13)-C(12)-Cl(2)	119.68(17)
C(11)-C(12)-Cl(2)	119.48(16)
C(12)-C(13)-C(8)	120.3(2)
O(5)-C(14)-C(15)	108.5(3)
O(5)-C(14)-C(16)	105.1(3)
C(15)-C(14)-C(16)	112.0(4)

Table S4. Anisotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for **1c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Cl(1)	52(1)	57(1)	45(1)	-10(1)	25(1)	-21(1)
Cl(2)	52(1)	50(1)	38(1)	2(1)	14(1)	-21(1)
S(1)	33(1)	26(1)	28(1)	3(1)	7(1)	3(1)
O(1)	35(1)	44(1)	41(1)	3(1)	15(1)	3(1)
O(2)	56(1)	27(1)	52(1)	10(1)	9(1)	6(1)
O(3)	57(1)	36(1)	37(1)	6(1)	13(1)	13(1)
O(4)	70(1)	35(1)	71(1)	-1(1)	35(1)	-2(1)
O(5)	79(1)	39(1)	41(1)	-15(1)	33(1)	-21(1)
N(1)	44(1)	30(1)	24(1)	-2(1)	5(1)	10(1)
C(1)	31(1)	34(1)	29(1)	-2(1)	10(1)	-1(1)
C(2)	42(2)	64(2)	30(1)	2(1)	11(1)	8(1)
C(3)	78(2)	106(3)	33(2)	0(2)	21(2)	33(2)
C(4)	55(2)	79(2)	46(2)	-21(2)	14(1)	15(2)
C(5)	39(1)	44(1)	41(1)	-5(1)	16(1)	6(1)
C(6)	33(1)	33(1)	30(1)	-2(1)	10(1)	-2(1)
C(7)	36(1)	31(1)	30(1)	0(1)	7(1)	5(1)
C(8)	36(1)	24(1)	26(1)	-2(1)	5(1)	3(1)
C(9)	33(1)	29(1)	33(1)	1(1)	13(1)	0(1)
C(10)	36(1)	27(1)	34(1)	-8(1)	11(1)	-7(1)
C(11)	36(1)	27(1)	30(1)	-3(1)	10(1)	0(1)
C(12)	36(1)	28(1)	31(1)	2(1)	7(1)	-4(1)
C(13)	41(1)	23(1)	29(1)	-1(1)	2(1)	-6(1)
C(14)	57(2)	40(1)	50(2)	-19(1)	29(1)	-14(1)
C(15)	80(3)	61(2)	155(4)	4(2)	45(3)	12(2)
C(16)	202(6)	64(2)	76(3)	-34(2)	-29(3)	14(3)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for **1c**.

	x	y	z	U(eq)
H(15A)	6271	3424	12066	146
H(15B)	6861	4129	13088	146
H(15C)	6192	3193	13287	146
H(16A)	8073	2491	14740	198
H(16B)	8658	3509	14794	198
H(16C)	9455	2636	14606	198
H(10A)	7640(40)	-1600(30)	8300(30)	92(13)
H(2A)	6250(40)	160(30)	4960(30)	81(12)
H(2B)	6840(30)	1020(30)	4920(30)	72(11)
H(3A)	7560(30)	-250(20)	4020(30)	68(9)
H(3B)	8740(50)	500(30)	4900(40)	130(18)
H(4A)	7730(40)	-1290(30)	5420(30)	92(12)
H(4B)	9140(40)	-1190(20)	5200(30)	83(11)
H(5A)	9370(30)	-1170(20)	7190(20)	51(8)
H(5B)	10140(30)	-350(20)	6840(30)	65(9)
H(7)	9690(30)	428(19)	8830(20)	50(8)
H(10)	8950(30)	2836(18)	11470(20)	40(7)
H(13)	6500(20)	278(16)	9718(19)	32(6)
H(14)	8520(40)	3280(30)	12940(30)	95(13)

Table S6. Torsion angles [°] for **1c**.

O(1)-S(1)-N(1)-C(8)	-64.6(2)
O(2)-S(1)-N(1)-C(8)	64.2(2)
C(1)-S(1)-N(1)-C(8)	179.99(19)
O(1)-S(1)-N(1)-C(7)	109.94(17)
O(2)-S(1)-N(1)-C(7)	-121.18(18)
C(1)-S(1)-N(1)-C(7)	-5.42(18)
O(1)-S(1)-C(1)-C(6)	-112.48(17)
O(2)-S(1)-C(1)-C(6)	116.89(18)
N(1)-S(1)-C(1)-C(6)	3.76(18)
O(1)-S(1)-C(1)-C(2)	64.6(2)
O(2)-S(1)-C(1)-C(2)	-66.0(2)
N(1)-S(1)-C(1)-C(2)	-179.2(2)
C(6)-C(1)-C(2)-C(3)	-13.3(4)
S(1)-C(1)-C(2)-C(3)	170.1(2)
C(1)-C(2)-C(3)-C(4)	42.3(4)
C(2)-C(3)-C(4)-C(5)	-59.9(4)
C(3)-C(4)-C(5)-C(6)	42.2(4)
C(2)-C(1)-C(6)-C(5)	-1.2(4)
S(1)-C(1)-C(6)-C(5)	175.76(19)
C(2)-C(1)-C(6)-C(7)	-178.1(2)
S(1)-C(1)-C(6)-C(7)	-1.2(3)
C(4)-C(5)-C(6)-C(1)	-12.5(4)
C(4)-C(5)-C(6)-C(7)	164.3(2)
O(4)-O(3)-C(7)-N(1)	64.0(2)
O(4)-O(3)-C(7)-C(6)	-56.5(2)
C(8)-N(1)-C(7)-O(3)	54.6(3)
S(1)-N(1)-C(7)-O(3)	-119.93(18)
C(8)-N(1)-C(7)-C(6)	179.87(19)
S(1)-N(1)-C(7)-C(6)	5.3(2)
C(1)-C(6)-C(7)-O(3)	122.4(2)
C(5)-C(6)-C(7)-O(3)	-54.6(3)
C(1)-C(6)-C(7)-N(1)	-2.4(3)
C(5)-C(6)-C(7)-N(1)	-179.4(2)
C(7)-N(1)-C(8)-C(9)	88.0(3)
S(1)-N(1)-C(8)-C(9)	-97.8(2)
C(7)-N(1)-C(8)-C(13)	-90.6(3)
S(1)-N(1)-C(8)-C(13)	83.6(2)
C(13)-C(8)-C(9)-C(10)	1.7(3)
N(1)-C(8)-C(9)-C(10)	-177.0(2)
C(13)-C(8)-C(9)-Cl(1)	-178.63(17)

N(1)-C(8)-C(9)-Cl(1)	2.7(3)
C(8)-C(9)-C(10)-C(11)	-1.2(3)
Cl(1)-C(9)-C(10)-C(11)	179.15(17)
C(14)-O(5)-C(11)-C(10)	32.8(4)
C(14)-O(5)-C(11)-C(12)	-151.7(2)
C(9)-C(10)-C(11)-O(5)	174.7(2)
C(9)-C(10)-C(11)-C(12)	-0.7(3)
O(5)-C(11)-C(12)-C(13)	-173.7(2)
C(10)-C(11)-C(12)-C(13)	2.1(3)
O(5)-C(11)-C(12)-Cl(2)	6.0(3)
C(10)-C(11)-C(12)-Cl(2)	-178.21(17)
C(11)-C(12)-C(13)-C(8)	-1.6(3)
Cl(2)-C(12)-C(13)-C(8)	178.72(17)
C(9)-C(8)-C(13)-C(12)	-0.3(3)
N(1)-C(8)-C(13)-C(12)	178.4(2)
C(11)-O(5)-C(14)-C(15)	89.7(3)
C(11)-O(5)-C(14)-C(16)	-150.4(3)

Additional References

- (39) Hoch, H.; Lang, S. *Chem. Ber.* **1943**, 76, 169-172. (b) Hoch, H.; Lang, S. *Chem. Ber.* **1944**, 77, 257-264.
- (40) Sheldrick, G. M. SADABS, Program for Scaling and Correction of Area Detector Data., University of Göttingen, 1997.
- (41) Sheldrick, G. M. SHELX-97, A Program for Crystal Structure Solution and Refinement, University of Göttingen, 1997.
-

S13

Figure S1. X-ray structure of **1c**. (a) ORTEP view; thermal ellipsoids are drawn at the 50% probability level. (b) intermolecular hydrogen bonding. Hydrogen atoms not involved in the H-bonding are omitted for clarity.

S14

Figure S2. Plot of $1/[1c]$ versus time showing the second order kinetics (methanol, 30°C).

¹H NMR spectrum of **1b**

S15

^{13}C NMR spectrum of **1b**

S16

S17

¹H NMR spectrum of **1c**

^{13}C NMR spectrum of **1c**

S18

¹H NMR spectrum of **1d**

S19

^{13}C NMR spectrum of **1d**

S20

¹H NMR spectrum of 2c

S21

^{13}C NMR spectrum of **2c**

S22

¹H NMR spectrum of **2d**

S23

S24

¹³C-NMR spectrum of 2d

¹H NMR spectrum of **3c**

S25

^{13}C NMR spectrum of **3c**

S26

¹H NMR spectrum of 3d

S27

S28

^{13}C NMR spectrum of **3d**

S29

^{13}H NMR spectrum of **8c**

S30

^{13}C NMR spectrum of **8c**

¹H NMR spectrum of **8d**

S31

S32

¹³C NMR spectrum of 8d