92. Efficient Preparation and X-Ray Structure Analyses of (2*R*)-*N*-Pyruvoyl- and (2*R*)-*N*-(Phenylglyoxyloyl)bornane-10,2-sultam

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Dedicated to Prof. *Vladimir Prelog* on the occasion of his 90th birthday

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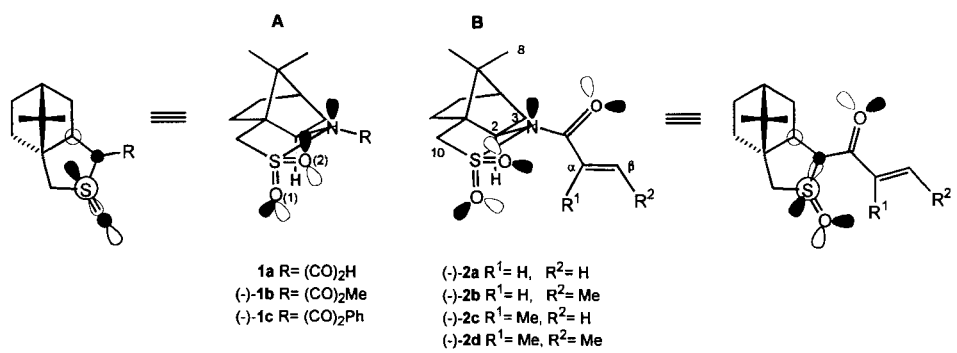
An efficient synthesis of the two title compounds is reported, as well as their X-ray crystal-structure analyses. A discussion based on stereoelectronic considerations rationalizes the first example of a crystalline $SO_2/C(O)$ *syn*-periplanar conformer of a *N*-acylbornane-10,2-sultam.

We have recently reported the diastereoselective [4 + 2] cycloaddition of 1-methoxybuta-1,3-diene to (2*R*)-*N*-glyoxyloylbornane-10,2-sultam (**1a**)[2]) under high pressure and/or in the presence of catalytic amounts of [Eu(fod)$_3$] [6]. To study the scope and limitation of this kind of hetero-*Diels-Alder* reaction[3]), we prepared the homologous dienophiles (−)-**1b**, **c**[4]) which are also important chiral precursors for nucleophilic additions[5]).

Scheme



1a R= $(CO)_2H$
(-)-**1b** R= $(CO)_2Me$
(-)-**1c** R= $(CO)_2Ph$

(-)-**2a** R^1= H, R^2= H
(-)-**2b** R^1= H, R^2= Me
(-)-**2c** R^1= Me, R^2= H
(-)-**2d** R^1= Me, R^2= Me

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[2]) For an efficient synthesis of **1a**, see [1]. For the spirocyclization of 2-substituted tryptamines, *Pictet-Spengler* cyclization, and formal syntheses of compactin and purpurosamine C, see [2], [3], [4], and [5], respectively.
[3]) For a recent review on asymmetric intermolecular homo- and hetero-*Diels-Alder* reactions, see [7].
[4]) For an independent and recent synthesis of (−)-**1b**, isolated as a gum and presented without chiroptical data, see [8].
[5]) For the diastereoselective reduction of *N*-pyruvoyl- and *N*-(phenylglyoxyloyl)amides, see [9].

Pure (−)-**1b**, recrystallized from Et_2O, was obtained in 72% yield after deprotonation of the commercially available (2*R*)-bornane-10,2-sultam [10] with NaH (1.0 equiv.) in toluene, followed by acylation with pyruvaloyl chloride [11]. Similarly, using phenylglyoxyloyl chloride [12] (NaH (1.5 equiv.), toluene, $Ph(CO)_2Cl$ (1.2 equiv.), −20° to room temperature), the unknown (−)-**1c** was synthesized and isolated in 71% yield after recrystallization from AcOEt.

The X-ray crystal-structure analysis of (−)-**1b** (see below, *Fig. 1*) shows an astonishing $SO_2/C(O)$ *syn*-periplanar conformation which is, to the best of our knowledge, the first example of a crystalline uncomplexed conformer of *N*-acylbornane-10,2-sultam recognized as such in the literature[6]). The X-ray structures reported up to date for such derivatives systematically have an *anti*-periplanar $SO_2/C(O)$ conformation[7]), initially rationalized on the basis of dipole-dipole interactions [13], and more recently [16] on the basis of stereoelectronic considerations associated with the generalized anomeric effect of the N lone pair [17]. Indeed, pyramidalization of the N-atom in camphor-derived sultams is another common and well documented feature [18], initially attributed to a possible pinching effect of the five-membered sultam ring minimizing the steric and ring constraints [19]. More recently, a careful examination of the *Cambridge Structural Data Base*

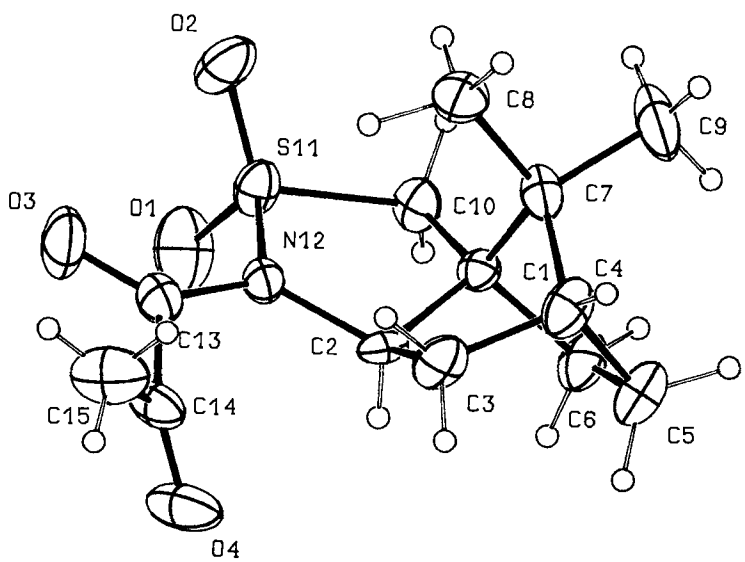

Fig. 1. *ORTEP Diagram of (−)-***1b**. Arbitrary numbering.

[6]) For a $SO_2/C(O)$ *syn*-periplanar conformation of (−)-**2b** chelated by $TiCl_4$, see [13]; $\Delta hN = 0.150$ (6) Å, torsional angle S–N–C=O −25.6 (7)°.

[7]) For an *anti*-periplanar S–N–C=N conformation, see [14]; this characteristic conformation was also observed for toluene-sultams derived from saccharine (= 1,2-benzoisothiazol-3(2*H*)-one 1,1-dioxide) [15].

(1995) showed that this pyramidalization is generally dependent on the S–N–C=O torsional angle [16][6][8][9]), and that the N pyramid tends to planarity for a pure *syn*- or *anti*-periplanar conformation of the SO_2/C(O) groups, thus favoring the electronic delocalization and, therefore, the chemical reactivity[10]).

Considering first the most common SO_2/C(O) *anti*-periplanar case ((–)-**1c**, (–)-**2a–d**) and assuming a possible anomeric effect between the N lone pair and the *quasi anti*-periplanar S–O(1) σ-bond[11]), it became important to define the orientation of all O lone pairs. With respect to the SO_2 molecular orbitals, this is not an obvious task, and we retained two working hypotheses *A* and *B*. To reach maximum stabilization, the most evident is, according to hypothesis *A*, to place the four O lone pairs in the O(1)=S=O(2) plane, thus allowing two *anti*-periplanar σ^* anomeric stabilizations with the most electronegative O substituents. This symmetric representation, possessing four parallel lone pairs (see *A*), does not need more explanation. Hypothesis *B* considers the polarizable S–N(acyl) bond with staggered lone pairs and merits a more detailed discussion (see *B*). In that case, the O(1) lone pairs are orientated in the O(1)=S–N plane. One lone pair is *anti*-periplanar to the S–N bond, while the second, *syn*-periplanar to this bond, is pointing below the N pyramid[12]). Consequently, the O(2) lone pairs are preferably oriented in the C(10)–S=O(2) plane[13]), minimizing electrostatic repulsion between the N and S–N O(2) *syn*-periplanar lone pairs, and thus directing the π-orbitals of the pseudoequatorial O(2) atom[14]) for favorable N electronic delocalization. In both hypotheses, and in supplement to the dipole-dipole interaction, the *anti*-periplanarity of the SO_2/C(O) groups may also be rationalized by a *Coulomb* repulsion between the SO_2 and C(O) lone pairs.

The roles of the O(1) and O(2) atoms in hypothesis *B* could be inverse, *i.e.*, the lone pairs of O(2) would direct in the O(2)=S–N plane, while the C(10)–S=O(1) plane would contain the lone pairs of O(1). However, this inversion is only possible either at the price of a destabilizing electrostatic repulsion between the N and the S–N *syn*-periplanar O(2)

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[8]) Selected ΔhN, and S–N–C=O and O=C–C=X torsional angles are as follows: (–)-**1b**: 0.083 (6) Å, –9.3 (8)°, +121.2 (5)°; (–)-**1c**: 0.228 (5) Å, +150.6 (5)°, +102.8 (6)°; (–)-**2a** [19]: 0.226 (5) Å, +153.9 (4)°, +1.0 (9)°; (–)-**2b** [10]: 0.230 (5) Å, +150.8 (4)°, –6.1 (8)°; (–)-**2c** [20]: 0.304 (7) Å, +134.8 (6)°, +140.2 (8)°; (–)-**2d** [18]: 0.308 (4) Å, +140.2 (4)°, +134.0 (5)°.

[9]) For a detailed discussion of the steric, electronic, and electrostatic influences of pseudoaxial substituents in the five-membered ring of camphorsultam- and toluenesultam-derived dienophiles on π-facial stereoselectivity, see [16]. For a preliminary attempt to put in evidence a stereoelectronic influence, see [21].

[10]) Sultam (–)-**1b** has the most planar N reported up to date for a *N*-acylbornane-10,2-sultam derivative. For the most extreme *anti*-periplanar example reported (ΔhN = 0.164 Å, S–N–C=O +172.4°), see [22]. For a different point of view concerning the chemical reactivity of *syn*- and *anti*-periplanar conformers, see [23].

[11]) The N lone pair (lp) position is defined as in [13] and is also *anti*-periplanar to the H–C(2) σ-bond; dihedral angle lp–N–S=O(1) for (–)-**1b** –162.9 (4)°, and for (–)-**1c** –177.2 (4)°. This postulated anomeric effect may be the result rather than the cause of the observed geometry.

[12]) A possible electrostatic assistance to the N pyramidalization is not excluded.

[13]) For a practically *anti*-periplanar complexation of Ti at O(2) with respect to C(10) (torsional angle C(10)–S=O(2)–Ti –157.4 (3)°), see [13]. For a similar intramolecular H-bonding (C(10)–S=O(2)–H –167.9 (1)°), see [24].

[14]) Due to intrinsic properties of the camphor skeleton as well as to steric effect of the Me(8) group, the C(3) and O(2) atoms are systematically pseudoequatorial with respect to the five-membered sultam ring (see *Table 1*). Due to *gauche* effects, these atoms are often pseudoaxial in toluene-sultams [15].

lone pairs or by loss of the N lone pair S=O(1) anomeric stabilization under conditions of predominant steric or ring constraints [15] [25]. This alternative, which entails a favorable orientation of the O(1) π-orbitals with respect to the N lone pair, can also be envisaged in case of *quasi*-planarity of the N-atom[15]).

The conformation of the enoyl side chain may be understood as a result of steric interactions [18] either between the C(β)-atom and the SO_2 moiety for (−)-**2a, b**, which force the C=C bond into a s-*cis* conformation with respect to the C=O bond, or between the sterically more demanding Me group at C(α) and SO_2 for (−)-**2c, d** thus now forcing, in the crystalline state, the C=C bond into an *anti*-clinal conformation[8]).

An identical stereoelectronic situation (hypothesis *A* or *B*) explains the exceptional SO_2/C(O) *syn*-periplanar conformation of (−)-**1b**, but now directed by the final side-chain heteroatom. The X-ray structure analysis of (−)-**1b** shows several noteworthy features (*Fig. 1*). Indeed, the C(13) atom perfectly bisects the O(1)=S=O(2) angle, directing O(3) slightly further from O(1) than from O(2)[16]). The electrostatic and steric repulsion is geometrically minimized by the *quasi*-planarity of the N-atom[8]), accentuated by the *syn*-planarity of the S–N–C(13)=O(3) moiety[8])[17]). As already observed for the (2*R*)-*N*-(methacryloyl)bornane-10,2-sultam ((−)-**2c**), the sterically more demanding Me(15) group now directs the conformation of the side chain by preferring to avoid the C(3) atom, thereby minimizing simultaneously the electrostatic and dipole-dipole interactions of both carbonyls groups which adopt an *anti*-clinal conformation[8]). We wondered why (−)-**1b** could not adopt an *anti*-periplanar s-*transoid* arrangement such as (−)-**2c** [20]. A MM2 calculation [26] simulating this conformation[16])[18]) confirmed that it would be sterically unfavorable due to a much shorter distance between the O(4)···O(2) atoms, resulting in a higher electrostatic repulsion between their lone pairs.

The situation in (−)-**1c** is slightly different (see *Fig. 2*). With respect to the steric demand of a Ph substituent as compared to (−)-**1a, b**, the two carbonyl groups of (−)-**1c** cannot easily gain an electron-delocalizing stabilization by a pure or *quasi* C(O)/C=O s-*cis* or s-*trans* conformation and are obliged to adopt an orthogonal conformation[8]), where the C=O(4) group is conjugated with the aromatic π-system[19]). The benzene ring is directed towards the lower face of the camphor moiety to minimize the destabilizing O(4)/O(1) lone-pair interactions and the C(8)/Ph steric repulsion. This conformation also has the advantage that it minimizes the O(4)/O(2) repulsion and thus does not oblige the C=O(3) to adopt a less satisfying SO_2 *syn*-periplanar arrangement.

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[15]) Although semi-empirical calculations [16] did not permit the unequivocal determination of the orientation of the SO_2 lone pairs, they nevertheless suggest a symmetric orientation according to hypothesis *A* for non-chelated *syn*-periplanar s-*cis* (−)-**2a** and an orientation according to hypothesis *B* for its *anti*-periplanar s-*cis* conformer.

[16]) C(13)···O(1) 3.134 (8) Å; C(13)···O(2) 3.129 (8) Å; O(3)···O(1) 3.178 (7) Å; O(3)···O(2) 3.016 (7) Å.

[17]) An angle of 4.1(3)° is measured between the lone pair on the N and the $2p_z$ orbital of the adjacent carbonyl group. In comparison, the *anti*-periplanar (−)-**1c** (14.5 (4)°) and (−)-**2b** (18.1 (2)° [13]) have higher values.

[18]) *Syn*-periplanar s-*trans* conformer: S–N–C=O −8.5°, O=C–C=O +123.1°, O(3)···O(1) 2.96 Å, and O(3)···O(2) 2.95 Å; *anti*-periplanar s-*trans* conformer: S–N–C=O +165.0°, O=C–C=O +155.7°, O(4)···O(1) 3.03 Å, and O(4)···O(2) 2.73 Å.

[19]) Torsional angle O(4)=C(14)–C(15)=C(16) +172.4 (6)°.

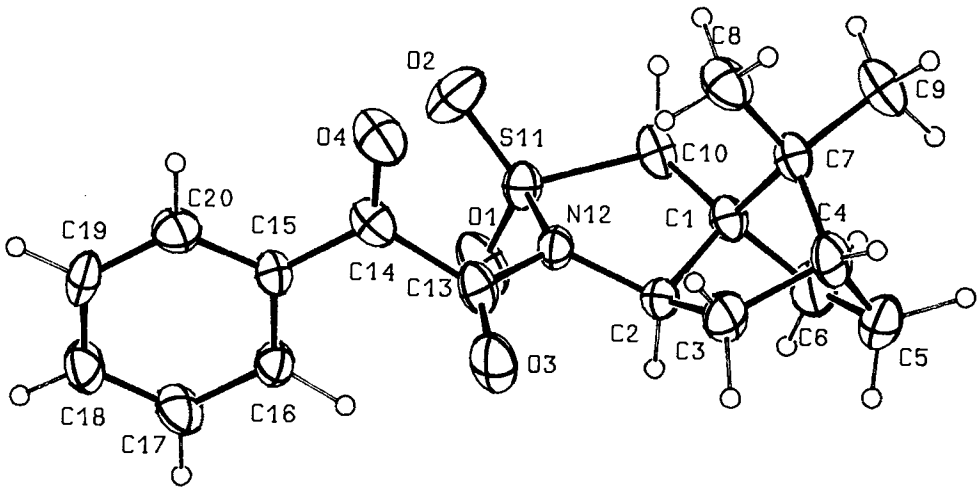

Fig. 2. *ORTEP Diagram of (–)-***1c**. Arbitrary numbering.

An anomeric effect between the N lone pair and the S=O(1) bond would theoretically lead to an elongation of this bond and a shortening of the S–N bond [17]. Comparison of the S=O(1) *vs.* S=O(2) bond lengths in more than forty *N*-acylbornane-10,2-sultam derivatives did not reveal any obvious or systematic correlation. This is certainly due to the competing S=O(2) (hypothesis *A*) or S–N *anti*-periplanar O(1) lone-pair anomeric effect (hypothesis *B*) which tends to shorten the S=O(1) bond length and to lengthen the S=O(2) or S–N bond, respectively.

Table 1. *Selected Bond Lengths* [Å] *and Angles* [°] *for (–)-***1b** *and (–)-***1c**

	(–)-**1b**	(–)-**1c**		(–)-**1b**	(–)-**1c**
C(1)–C(10)	1.502 (7)	1.518 (7)	C(10)–C(1)–C(2)	109.2 (4)	110.0 (4)
C(1)–C(2)	1.530 (7)	1.551 (7)	N(12)–C(2)–C(1)	106.8 (4)	105.4 (4)
C(2)–N(12)	1.478 (6)	1.466 (6)	C(1)–C(10)–S(11)	107.3 (4)	106.7 (4)
C(10)–S(11)	1.783 (6)	1.775 (5)	O(2)–S(11)–O(1)	119.1 (3)	116.3 (3)
S(11)–O(2)	1.407 (5)	1.415 (4)	O(2)–S(11)–N(12)	109.8 (3)	111.0 (2)
S(11)–O(1)	1.425 (4)	1.415 (4)	O(1)–S(11)–N(12)	108.0 (3)	107.7 (3)
S(11)–N(12)	1.705 (4)	1.686 (4)	O(2)–S(11)–C(10)	112.6 (3)	114.4 (3)
N(12)–C(13)	1.344 (7)	1.392 (6)	O(1)–S(11)–C(10)	109.4 (3)	110.2 (3)
C(13)–O(3)	1.210 (7)	1.196 (6)	N(12)–S(11)–C(10)	95.3 (2)	95.1 (2)
C(13)–C(14)	1.524 (9)	1.541 (8)	C(13)–N(12)–C(2)	128.1 (4)	121.9 (4)
C(14)–O(4)	1.204 (7)	1.206 (6)	C(13)–N(12)–S(11)	119.0 (4)	122.5 (4)
			C(2)–N(12)–S(11)	112.0 (3)	109.3 (3)
			O(3)–C(13)–N(12)	124.1 (6)	122.1 (5)
			O(3)–C(13)–C(14)	117.2 (5)	119.3 (5)
			N(12)–C(13)–C(14)	118.5 (5)	118.2 (5)
			O(1)–S(11)–N(12)–C(2)	102.3 (4)	80.9 (4)
			O(2)–S(11)–N(12)–C(2)	–126.4 (4)	–150.8 (4)
			S(11)–N(12)–C(2)–C(3)	141.4 (4)	153.9 (4)

In conclusion, the X-ray analysis of (−)-**1b** illustrates the crucial function of the specific electronic situation in *N*-acylbornane-10,2-sultams in controlling both the conformational equilibrium and chemical reactivity. This is consistent with a recent rationalization based on the high reactivity of the SO_2/C(O) *syn*-periplanar conformers of **1** and **2** which may also contribute to the course of their stereochemical transformations [6b] [16][20]).

Cycloadditions and nucleophilic additions of (−)-**1b, c** will soon be reported.

Financial support from the *Polish Academy of Sciences* and from the University of Warsaw (BST/18/95) is gratefully acknowledged. We are also indebted to Prof. *N. Harada* for supplying the fractional coordinates of the diastereoisomer (−)-*S*-**6b**; one of the three compounds for which X-ray crystal-structure analyses are reported in [27].

Experimental Part

General. MS: *AMD-604* spectrometer; EI = electron ionization, LSI = liquid secondary ionization; *m/z* (rel. %). M.p.'s: *Kofler*-type (*Boetius*) hot-stage apparatus; not corrected. Optical rotations: *Perkin-Elmer-241* polarimeter at 22°. IR Spectra: *Nicolet-FT-IR Magna-500* spectrometer; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: in $CDCl_3$ using $SiMe_4$ as internal standard, *Varian-Gemini-200* and *Varian-Unity Plus-500* spectrometers; δ in ppm, *J* in Hz.

X-Ray Structure Determination of (−)-**1b** *and* (−)-**1c**: Suitable crystals were grown from a MeOH/hexane soln. The measurements were run on an *Enraf-Nonius-MACH3* diffractometer using *Express* software, without absorption corrections. *Table 2* shows details of the data collection and refinement. In the final steps of the least-squares procedure, all but Me group H-atoms were kept fixed at their calculated positions. The known configuration of the asymmetric centers of the sultam unit has been confirmed by the *Flack* parameter refinement [28]. The structure

Table 2. *Crystal Data and Structure Refinement for (−)-***1b** *and (−)-***1c**

	(−)-**1b**	(−)-**1c**		(−)-**1b**	(−)-**1c**
Empirical formula	$C_{13}H_{19}NO_4S$	$C_{18}H_{21}NO_4S$	$F(000)$	608	736
Formula weight	285.35	347.42	Crystal size [mm]	0.28 × 0.14 × 0.10	0.70 × 0.14 × 0.14
Temperature [K]	293 (2)	293 (2)	Range for data coll. [°]	4.82 to 74.15	4.40 to 73.48
Wavelength [Å]	1.54178	1.54178	Reflections collected	1251	1395
Crystal system	Orthorhombic	Orthorhombic	Independent reflections	1251	1395
Space group	$P2_12_12_1$	$P2_12_12_1$	Refinement method	Full-matrix least-squares on F^2	
Unit cell dimensions [Å]	a = 8.1942 (6)	a = 7.651 (1)	Data/restr./param.	1251/0/236	1395/0/242
	b = 11.8701 (2)	b = 11.789 (1)	Goodness-of-fit on F^2	1.082	1.066
	c = 14.4680 (2)	c = 19.144 (3)	Final R [$I > 2\sigma(I)$]	$R1$ = 0.0486, $wR2$ = 0.1236	$R1$ = 0.0470, $wR2$ = 0.1080
Volume [Å^3]	1407.2 (1)	1726.7 (4)			
Z	4	4	R indices (all data)	$R1$ = 0.0486, $wR2$ = 0.1236	$R1$ = 0.0485 $wR2$ = 0.1096
Density (calculated) [Mg/m^{-3}]	1.347	1.336	Absolute struct. param.	0.05 (5)	−0.01 (5)
Absorption coefficient [mm^{-1}]	2.143	1.851	Extinction coefficient	0.0075 (9)	0.0013 (4)

[20]) Publication of [16b] has been postponed for several months due to strong disagreements between semi-empirical transition-state calculations [16a] and expected results. This discrepancy has been recently rationalized [16b] on the basis of the results from a stereoelectronically assisted selective hydrolysis under cycloaddition conditions of *N*-(2-oxa-3-azabicyclo[2.2.1]hept-5-ene-3-carbonyl)-derived diastereoisomer mixtures.

was solved by the SHELXS86 [29] and refined with the SHELXL93 [30] programs. Lists of the fractional atomic coordinates, isotropic thermal parameters, and bond lengths and angles have been deposited at the *Cambridge Crystallographic Data Centre*[21]).

(2R)-N-Pyruvoylbornane-10,2-sultam (= *(3aS,6R,7aR)-1-(1,2-Dioxopropyl)-1,4,5,6,7,7a-hexahydro-8,8-dimethyl-3H-3a,6-methano[2,1]benzoisothiazole 2,2-Dioxide*; (−)-**1b**). NaH (50% in mineral oil; 0.44 g, 9.2 mmol) was washed with dry toluene and suspended in toluene (5 ml). The suspension was cooled to 0° under Ar, and a soln. of (2*R*)-bornane-10,2-sultam (1.98 g, 9.2 mmol) in dry toluene (25 ml) was added during 10 min. The mixture was stirred at r.t. for 1 h, cooled to −20° and pyruvoyl chloride (= 2-oxopropanoyl chloride; 1.29 g, 12.1 mmol) was added dropwise within 15 min. The mixture was allowed to reach r.t. and stirred for an additional 22 h. H_2O (10 ml) was added, the mixture stirred for 10 min, the aq. phase extracted with toluene (2 × 50 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the crude product recrystallized from Et_2O: (−)-**1b** (1.89 g, 72%). M.p. 103–104°. $[\alpha]_D = -189.5$ ($c = 1.0$, $CHCl_3$). IR (KBr): 1720, 1675. ^{1}H-NMR (500 MHz): 1.00 (*s*, 3 H); 1.20 (*s*, 3 H); 1.35–1.46 (*m*, 2 H); 1.86–2.12 (*m*, 5 H); 2.45 (*s*, 3 H); 3.47 (*AB*, J = 87, 14, 2 H); 4.02 (br. *t*, J = 6.4, 1 H). ^{13}C-NMR (500 MHz): 19.89 (C(9)); 21.38 (C(8)); 26.13 (C(15)); 26.24 (C(5)); 33.34 (C(6)); 38.34 (C(3)); 45.31 (C(4)); 47.83 (C(7)); 49.57 (C(1)); 53.02 (C(10)); 65.22 (C(2)); 194.12 (C(14)). EI-MS: 242 (23, $[M - COMe]^+$); 135 (100). LSI-MS: 308 (30, $[M + Na]^+$), 286 (58, $[M + H]^+$), 216 (100). Anal. calc. for $C_{13}H_{19}NO_4S$: C 54.7, H 6.7, N 4.9; found: C 54.7, H 6.9, N 4.7.

(2R)-N-(Phenylglyoxyloyl)bornane-10,2-sultam (= *(3aS,6R,7aR)-1,4,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(2-phenyl-1,2-dioxoethyl)-3H-3a,6-methano[2,1]benzoisothiazole 2,2-Dioxide*; (−)-**1c**). As described for **1b**, with NaH (60% in mineral oil; 0.29 g, 7.2 mmol) in toluene (5 ml), (2*R*)-bornane-10,2-sultam (1.03 g, 4.7 mmol) in toluene (10 ml), and phenylglyoxyloyl chloride (= 2-phenyl-3-oxoacetyl chloride; 0.97 g, 5.8 mmol); stirring at r.t. overnight). Workup with sat. aq. NH_4Cl soln. (10 ml; instead of H_2O) and toluene (2 × 30 ml) and recrystallization from AcOEt gave (−)-**1c** (1.15 g, 71%). M.p. 172–173°. $[\alpha]_D = -234.4$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3100, 1680, 1600, 1120, 570. ^{1}H-NMR (200 MHz): 0.98 (*s*, 3 H); 1.21 (*s*, 3 H); 1.25–2.20 (*m*, 7 H); 3.45 (*AB*, J = 85, 13.9, 2 H); 4.08 (*dd*, J = 7.8, 4.8, 1 H); 7.45–8.05 (*m*, 5 H). ^{13}C-NMR (500 MHz): 19.87 (C(9)); 20.91 (C(8)); 26.28 (C(5)); 32.89 (C(6)); 38.17 (C(3)); 45.07 (C(4)); 47.98 (C(7)); 49.97 (C(1)); 52.54 (C(10)); 64.39 (C(2)); 128.96 (C(17), C(19)); 130.15 (C(16), C(20)); 132.29 (C(15)); 134.29 (C(18)); 186.83 (C(14)). EI-MS: 347 (0.2, M^+), 105 (100). Anal. calc. for $C_{18}H_{21}NO_4S$: C 62.2, H 6.1, N 4.0; found: C 62.34, H 6.2, N 4.0.

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