Fluorinated Diazo Diketones in Rhodium(II)-Catalyzed Reactions with Sultams: Chemoselective *O*-Functionalization of Amide Carbonyl Groups

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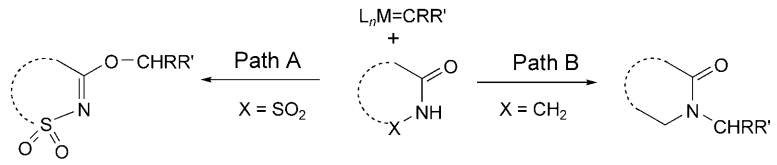
Dedicated to Professor *Rolf Huisgen* on the occasion of his 85th birthday

Rhodium(II)-catalyzed decomposition of fluorinated diazo diketones in the presence of isothiazole-3(2*H*)-one 1,1-dioxides offers a chemoselective and useful tool for *O*-functionalization of their C=O groups by interaction with transient fluorine-containing Rh^{II}-diketocarbenoids. The resulting *O*-alkylimidates of isothiazole 1,1-dioxides, bearing (trifluoromethyl)acetyl groups, easily react with traces of H_2O giving rise to stable hydrates of the perfluoroacetyl groups. No $O \rightarrow N$ isomerization of *O*-alkylimidates (similar to the *Lander–Chapman* rearrangement) was observed under the reaction conditions studied.

Introduction. – Recently, it has been found that catalytic decomposition of diazocarbonyl compounds in the presence of 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide and analogues results in *O*-alkylation of the C=O group of isothiazol-3(2*H*)-one 1,1-dioxides and in the exclusive formation of the corresponding *O*-alkylimidates, (*Scheme 1*, *Path A*) [1], while in similar reactions of amides and lactams with diketo- and closely related carbenoids, according to the literature data, essentially only *N*-alkylation products of the starting compounds have been isolated (*Path B*) [2–5]. The reason for such considerable differences in the ketocarbenoid reactivity with amides, lactams, and sultams investigated by us as yet remains unclear.

Scheme 1



The amide moiety (O=C–NH) of 3-oxosultam 1,1-dioxides is an ambident system [6][7] that is able to interact with electrophilic reagents at the N- or O-atom. In view of their amide character, *N*-substituted sulfonamides should be thermodynamically more stable than the isomeric *O*-substituted derivatives related to the structure of imidates [6][8]. This conclusion is corroborated by numerous examples of irreversible thermal isomerization of *O*-substituted imidates into their associated *N*-substituted derivatives

[6] [9–12], known as the *Lander–Chapman* rearrangement [10] [13]. The trend toward this rearrangement increases substantially with 'accumulation' of multiple bonds and electron-withdrawing groups in the migrating fragment of the imidate molecule [6].

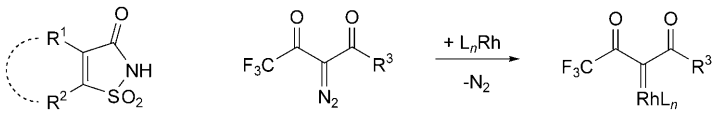
Based on the aforesaid, it could be concluded that, in the course of reactions of amides and lactams with diketocarbenoids, initially *O*-alkylation products also occur, but they then spontaneously experience $O \rightarrow N$ migration of the diketocarbene fragment, and as the final products of the process, *N*-alkyl derivatives are produced.

Thus, one might expect that the increasing electrophilicity of the carbenoid C-atom in the molecule of *O*-alkyl derivatives of isothiazole 1,1-dioxides could also facilitate $O \rightarrow N$ rearrangements. Basically, this could be attained by incorporation of strongly electronegative atoms or groups into the 'carbenoid fragment' of the molecule of *O*-alkylimidate. To test the validity of this assumption and the possibility of a *Lander–Chapman* rearrangement with *O*-alkylimidates of isothiazole 1,1-dioxides and related systems, we compared the reactivity of carbenoids with perfluorinated and non-fluorinated acyl groups bonded to carbenoid center [14].

Herein, we present the results of our research dealing with catalytic decomposition of a series of fluorine-containing diazo diketones by $Rh_2(OAc)_4$ in the presence of **1a** and its analogs.

Results and Discussion. – Three sultams of different structure were selected for this research: the parent 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide (**1a**), its hydrogenated analog 4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide (**1b**), and a monocyclic representative of this series, 5-methyl-4-phenylisothiazol-3(2*H*)-one 1,1-dioxide (**1c**; *Scheme 2*) Except for **1a**, the two other isothiazole 1,1-dioxides were prepared by a three-step synthesis from the corresponding ketones involving, as the final stage, the oxidation of the relevant isothiazoles with H_2O_2 in glacial AcOH [15].

Scheme 2



1 **2** **2'a–c**

1a R^1–R^2 = –$(CH)_4$–
1b R^1–R^2 = –$(CH_2)_4$–
1c R^1 = Ph, R^2 = Me

2a R^3 = Me
2b R^3 = *t*-Bu
2c R^3 = *p*-BrC_6H_4

Fluorine-containing diketocarbenoids **2′a–c** were generated *via* catalytic decomposition of the associated fluorinated 2-diazo-1,3-diketones **2a–c** ('*F*-diazodiketones') having one perfluoroacetyl group in their structure and various other acyl groups (R^3 = Me, *t*-Bu, *p*-BrC_6H_4), namely 3-diazo-1,1,1-trifluoropentane-2,4-dione (**2a**), 3-diazo-1,1,1-trifluoro-5,5-dimethylhexane-2,4-dione (**2b**), and 1-(4-bromophenyl)-2-diazo-4,4,4-trifluorobutane-1,3-dione (**2c**, *Scheme 2*). The fluorinated diazo diketones **2a–c** were prepared by a new diazo-transfer protocol developed recently in our laboratory [16].

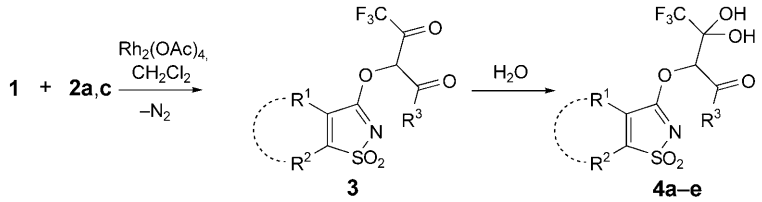
The reaction of **1** with **2** was carried out in the presence of $[Rh_2(OAc)_4]$ in anhydrous CH_2Cl_2 at room temperature. After completion of the decomposition process (TLC), the mixture was separated on a column with neutral silica gel, and the isolated compounds were analyzed using ^{1}H- and ^{13}C-NMR spectroscopy, mass spectrometry, and X-ray crystal-structure analysis.

It was found that fluorinated diazo diketones **2** are rather stable in decomposition reactions with $[Rh_2(OAc)_4]$. Unlike their nonfluorinated analogues [1], *F*-diazo diketones **2** under usual reaction conditions decompose very slowly, and, furthermore, attempts to carry out the Rh^{II}-catalyzed reaction with the crowded *F*-diazodiketone **2b** failed completely. In the case of the arylsubstituted *F*-diazodiketone **2c**, to increase the yield of final product, the catalytic reaction was performed with 25% excess of starting diazo compound.

As a result of the Rh^{II}-catalyzed decomposition of **2a**,**c** in the presence of sultams **1a**–**c** and subsequent workup, adducts of these sulfonimidic substrates **1** and the respective fluorinated diketocarbenes in a 1:1 ratio, were isolated.

Spectroscopic investigations revealed that the obtained compounds are *O*-alkylimidates **4**; products of a formal insertion of the relevant diketocarbenes into the O–H bond of the enol form of **1** (*Scheme 3*). The yields of the isolated products were not very good (17–63%), but at this point, we did not try to optimize them.

Scheme 3



	R^1	R^2	R^3
3a	–(CH)$_4$–		Me
3b	–(CH)$_4$–		*p*-BrC$_6$H$_4$
3c	–(CH$_2$)$_4$–		Me
3d	–(CH$_2$)$_4$–		*p*-BrC$_6$H$_4$
3e	Ph	Me	Me

According to the ^{1}H-NMR spectra of the 'crude' reaction mixtures, formation of the isomeric *N*-alkyl derivatives of sultams **1** did not occur under these conditions. We also established that, initially only *O*-alkylimidates **3** were present in the mixture, which, after chromatography on silica gel, turned into hydrates **4**.

The structures of the novel *O*-alkylimidates **4a**–**e** were established by means of NMR spectra (^{1}H, ^{13}C, and ^{19}F), mass-spectrometry studies, and confirmed by IR and UV spectra, and elemental analysis (see *Exper. Part*). The molecular structure of one of the adducts, 3-[(1,1-dioxido-1,2-benzisothiazol-3-yl)oxy]-5,5,5-trifluoro-4,4-dihydroxypentan-2-one (**4a**), has been determined by X-ray crystallography. The main crystallographic data for this molecule are given in the *Table* (see *Exper. Part*), the molecular structure is presented in *Fig. 1*. These data corroborated the 3-*O*-alkylimidate structure of the obtained compounds with the hydrated perfluoroacetyl carbonyl groups.

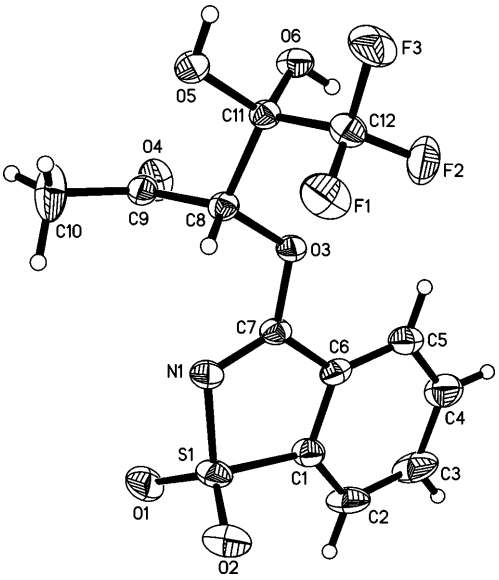


Fig. 1. *Crystal structure of* **4a**

The X-ray analysis show that the molecules of *O*-alkylimidate **4a** are linked into an extended network by the intermolecular association between O(5)–H of the hydrate function and O(1) of the SO_2 group (2.833 Å), and, between O(6)–H of the hydrate function with O(4) of the C=O group (2.724 Å) (*Fig. 2*). Thus, each molecule of **4a** forms four H-bonds with neighboring molecules, and along the crystallographic *b*-axis, there is stacking of the benzisothiazole units through π/π-interaction leading to a

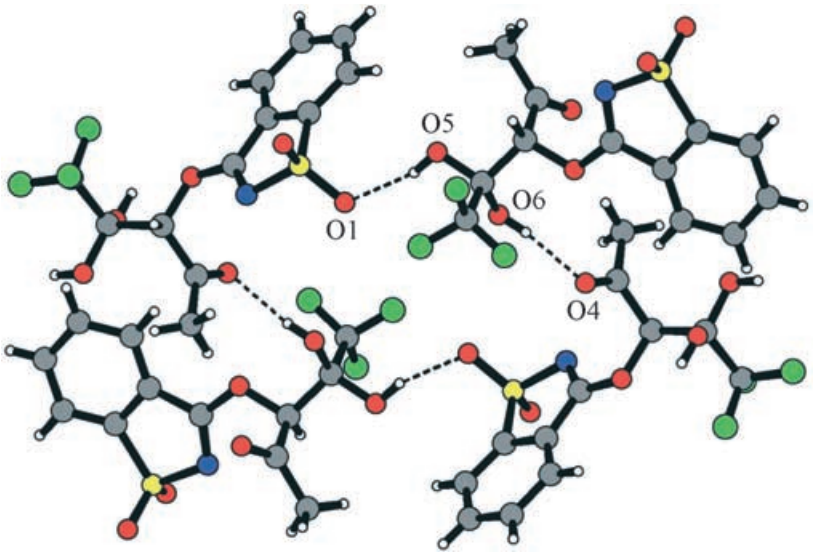


Fig. 2. *Cyclic 'square' pattern by H-bonds of four molecules of* **4a**

complex three-dimensional network structure. In *Fig. 2*, one can see the cyclic 'square' pattern formed by four molecules, and *Fig. 3* shows the topology of the corrugated (4,4)-network (without F- and H- atoms).

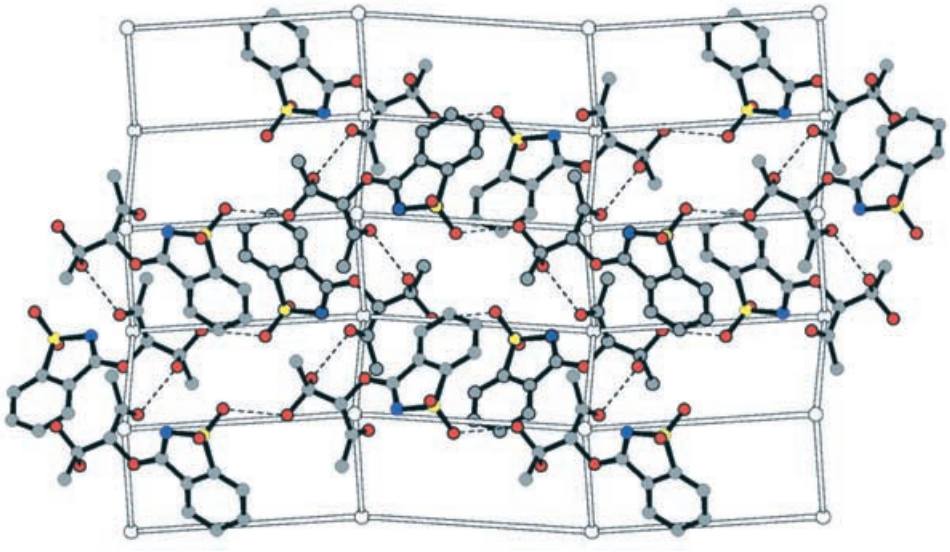


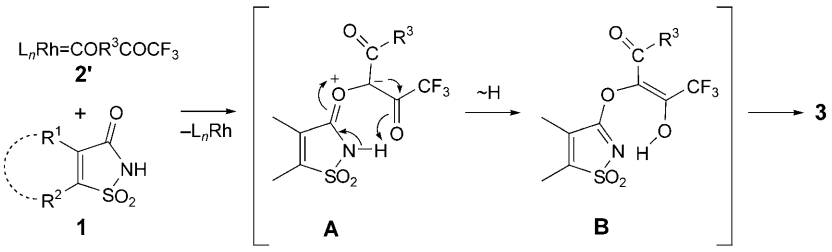
Fig. 3. *The schematic representation of the corrugated (4,4)-network*

The NMR spectra of the obtained adducts show the H-, C- and F-signals in the appropriate ranges, corresponding to the structure of hydrated *O*-alkylimidates **4a**–**e**. The chemical shifts of these signals are very close to the corresponding parameters of the NMR spectra of the initial sultams **1a**–**c** and *F*-diazodiketones **2a**,**c**. The main changes in the ^{1}H-NMR spectra of compounds **4a**–**e**, as compared with those of the starting reagents, consist in the appearance of a *singlet* from the OCH group in the region of 5.5–6.7 ppm, and two *singlets* from the OH groups of the $C(OH)_2$ moiety at 7.12–7.37 and 7.21–7.42 ppm, respectively. Simultaneously, in the ^{13}C-NMR spectra of **4**, a strong signal of the OCH group appears in the region of 80.4–85.0 ppm, and *quadruplets* at 92.7–94.5 ppm are attributed to the C-atoms of the hydrated perfluoroacetyl groups, $CF_3C(OH)_2$.

In the IR spectra of each imidate **4a**–**e**, several strong absorption bands are observed at 1667–1729 cm^{-1} (C=O), 1559–1573 cm^{-1} (C=N), 1317–1336 cm^{-1} and 1157–1177 cm^{-1} (SO_2), which are typical for the other *O*-alkylimidates isolated from similar reactions with nonfluorinated diazo diketones/diketocarbenoids [1].

The most-likely mechanism for the formation of *O*-alkylimidates **3**, which are formally the insertion products of the appropriate fluorine-containing dioxocarbenes into O–H bond of the enol form of isothiazole 1,1-dioxides **1**, apparently involves the generation of the intermediate carbonyl ylide **A** due to the initial attack of the carbonyl O-atom by the electrophilic diketocarbenoid **2′** (*Scheme 4*) [17]. The subsequent stabilization of the ylide **A** into *O*-alkylimidates **3** may occur by intramolecular NH-proton transfer *via* either a 1,4-sigmatropic hydrogen shift [17c,e] or a formal 1,6-

Scheme 4



migration of the H-atom to the anionic center of the carbonyl ylide through the enol intermediate **B**. The formation of O-H insertion products **3** *via* the 'oxonium' pathway, that is involving enol form of sultams **1** and then oxonium ylides, seems unlikely [1a].

Thus, Rh-catalyzed reactions of fluorine-containing diazo diketones **2** with isothiazole 1,1-dioxides **1** apparently occur just in the same manner as with their nonfluorinated counterparts [1], and, at this stage of our research, we have no experimental arguments in favor of a facile $O \rightarrow N$ isomerization of fluorine-containing *O*-alkylimidates **3** under the reaction conditions studied. Presumably, *O*-to-*N* rearrangement of *O*-alkylimidates **3a**–**e** is hindered owing to the bulky and highly electronegative SO_2 group adjacent to the end point of migration, which can strongly reduce the electronic density at the α-N-atom. In addition, by steric reasons prevent migration of likewise bulky *O*-alkyl substituents to the N-atom. This gives rise to the occurrence of *O*-alkylimidates **3** in a catalytic reaction, which then easily reacts with H_2O on silica gel or in air to produce, as the final products, stable hydrates of fluorine-containing *O*-alkyl derivatives **4** of sultams.

Conclusions. – It has been established that the Rh^{II}-catalyzed decomposition of fluorinated diazo diketones in the presence of 3-oxoisothiazole 1,1-dioxides provides a chemoselective and useful tool for the *O*-functionalization of their C=O groups by the reaction with the transient fluorine-containing Rh^{II}-diketocarbenoids. No $O \rightarrow N$ isomerization of the final products was observed under the reaction conditions studied. Instead, the resulting *O*-alkylimidates, which possess a trifluoroacetyl group in their structure, easily react with traces of H_2O during workup on silica gel to give stable hydrates.

Experimental Part

General. All solvents were dried by standard methods and, after reactions and chromatographic workup were evaporated in a rotatory evaporator. Thin-layer chromatography (TLC; reaction monitoring): *Silufol UV/VIS* 254 nm (*Kavalier*) using UV light and I_2 as visualizing agents. Column chromatography (CC): silica gel *60* (0.063–0.200 mm, 70–230 mesh ASTM; *Merck*). M.p.: *Boetius* micro-melting-point apparatus; corrected. UV/VIS Spectra: *Beckman DU650*; λ_{max} in nm (log ε). IR Spectra: *Genesis FTIR Unicam Analytical System* (*ATI Mattson*); KBr pellets, cm^{-1}. ^1H- (200 or 300 MHz), ^{13}C- (50 or 75 MHz), ^{19}F- (188 MHz) Spectra: *Varian Gemini-200* or *Varian Gemini-300* spectrometers; δ in ppm rel. to Me_4Si and $CFCl_3$ as internal standards, *J* in Hz. MS: *Quadrupole-MS VG 12-250*; 70 eV. Elemental analysis: *Heraeus CHNO Rapid Analyser*.

General Procedure for the Preparation of O-*Alkylimidates* **4a**–**e**. To a stirred soln. of diazo diketone **2a**–**c** (3.0 mmol of **2a**,**b** and 3.75 mmol of **2c**) and isothiazole dioxide **1a**–**c** (3.0 mmol) in CH_2Cl_2 (10 ml) $Rh_2(OAc)_4$

(0.003 mmol for **1a**,**b** or 0.00375 mmol for **1c**) was added in one portion. The mixture was stirred at r.t. until completion of the reaction (TLC monitoring) and was charged on a small column with silica gel (6 g); the gradient elution was performed with petroleum ether and Et_2O mixture. On removing the solvents and recrystallization of the main product from $CHCl_3$, the adducts **4a**–**e** were obtained.

3-[(1,1-Dioxido-1,2-benzisothiazol-3-yl)oxy]-5,5,5-trifluoro-4,4-dihydroxypentan-2-one (**4a**). Yield: 63%. White solid. M.p. 123–125°. UV (EtOH): 201 (4.48), 206 (4.49), 214 (4.48), 275 (3.56), 327 (2.95), 376 (2.64). IR: 1726*s* (C=O), 1559*s* (C=N), 1333*s* (SO_2), 1173*s* (SO_2). ^{1}H-NMR (300 MHz, (D_6)acetone): 2.53 (*s*, Me); 5.76 (*s*, CH); 7.37 (*s*, OH); 7.42 (*s*, OH); 7.97–8.09 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, (D_6)acetone): 28.6 (Me); 84.0 (CH); 93.0 (*q*, ^2J(C,F) = 32.6, C(OH)$_2$); 122.2 (arom. CH); 123.1 (*q*, ^1J(C,F) = 289.1, CF_3); 124.2 (arom. CH); 134.5 (arom. CH); 126.0 (C(3a)); 135.5 (arom. CH); 143.9 (C(7a)); 168.5 (C(3)); 198.0 (C=O). ^{19}F-NMR (188 MHz, (D_6)acetone): −82.88. ESI-MS: 354 ([M + H]$^+$). Anal. calc. for $C_{12}H_{10}F_3NO_6S$ (353.27): C 40.80, H 2.85, N 3.96; found: C 40.64, H 2.89, N 4.20.

X-Ray Crystal-Structure Analysis of **4a**. Crystals were obtained from $CHCl_3$. The intensities were measured on a *Siemens SMART CCD* diffractometer. Data collection and cell-refinement parameters are listed in the *Table*. The structure was solved by direct methods, and refinement was performed with SHELX-97 [18]. Crystallographic data have been deposited with *The Cambridge Crystallographic Data Centre*, CCDC No. 265902. These data can be obtained free of charge from *CCDC via* http://www.ccdc.cam.ac.uk/data_request/cif.

Table. *Crystallographic Data of* **4a**

Empirical formula		$C_{12}H_{10}F_3NO_6S$	
Formula weight [g mol^{-1}]		353.24	
Crystal dimensions [mm]		0.2 × 0.2 × 0.2	
Temperature [K]		213(2)	
Crystal system		monoclinic	
Space group		$P2_1/n$	
Radiation, wavelength [Å]		MoK_α, 0.71073	
2θ Range for cell determination [°]		4–56	
Unit-cell parameters	a [Å]	9.7730(17)	α [°] 90
	b [Å]	8.2506(14)	β [°] 96.696(3)
	c [Å]	18.539(3)	γ [°] 90
	V [Å^3]	1484.7	
D [g cm^{-3}]		1.494	
Absorption coefficient μ [mm^{-1}]		0.464	
Scan type		ω	
$2\theta_{max}$ [°]		58	
Total reflections measured		10528	
Symmetry-independent reflections		10528	
Reflections observed with $I > 2\sigma(I)$		8448	
Variables		249	
Final R indices ($I > 2\sigma$ (I))		$R_1 = 0.0717$ $\omega R_2 = 0.1181$	
R indices (all data)		$R_1 = 0.0948$ $\omega R_2 = 0.1252$	
$\Delta\rho$ (max, min) [e Å^{-3}]		0.563, −0.469	
Goodness-of-fit		1.193	

1-(4-Bromophenyl)-2-[(1,1-dioxido-1,2-benzisothiazol-3-yl)oxy]-4,4,4-trifluoro-3,3-dihydroxybutan-1-one (**4b**). Yield: 45%. White solid. M.p. 101–103°. UV (EtOH): 204 (4.37), 257 (4.03), 328 (2.84), 334 (2.47), 378 (2.30). IR: 1684*s* (C=O), 1560*s* (C=N), 1336*s* (SO_2), 1177*s* (SO_2). ^{1}H-NMR (300 MHz, (D_6)acetone): 6.71 (*s*, CH); 7.28 (*s*, OH); 7.39 (*s*, OH); 7.82–8.16 (*m*, 8 arom. H). ^{13}C-NMR (75 MHz, (D_6)acetone): 80.6 (CH); 94.5 (*q*, ^2J(C,F) = 33.2, C(OH)$_2$); 123.4 (arom. CH); 124.3 (*q*, ^1J(C,F) = 289.7, CF_3); 125.5 (arom. CH); 127.0 (C(3a)); 129.9 (arom. C); 132.5 (2 arom. CH); 133.3 (2 arom. CH); 135.7 (arom. CH); 136.7 (arom. CH); 137.0 (arom. C); 145.1 (C(7a)); 169.5 (C(3)); 191.8 (C=O). ^{19}F-NMR (188 MHz, (D_6)acetone): −83.19. FAB-MS: 494/496 (M^+). Anal. calc. for $C_{17}H_{11}BrF_3NO_6S$ (494.24): C 41.31, H 2.24, N 2.83; found: C 37.72, H 2.25, N 2.23.

3-[(4,5,6,7-Tetrahydro-1,1-dioxido-1,2-benzisothiazol-3-yl)oxy]-5,5,5-trifluoro-4,4-dihydroxypentan-2-one (**4c**). Yield: 35%. White solid. M.p. 131–133°. UV (EtOH): 219 (3.53), 285 (3.03). IR: 1729*s* (C=O), 1565*s* (C=N), 1322*s* (SO_2), 1159*s* (SO_2). ^{1}H-NMR (200 MHz, (D_6)acetone): 1.81 (*m*, 2 CH_2); 2.40 (*s*, Me); 2.51 (*m*, 2 CH_2); 5.48 (*s*, CH); 7.16 (*s*, OH); 7.21 (*s*, OH). ^{13}C-NMR (50 MHz, (D_6)acetone): 20.7, 20.9, 21.2, 21.4 ((CH_2)$_4$); 84.2 (CH); 92.8 (*q*, ^2J(C,F) = 32.0, $C(OH)_2$); 122.9 (*q*, ^1J(C,F) = 288.8, CF_3); 132.8 (C(3a)); 155.2 (C(7a)); 171. 3 (C(3)); 198.5 (C=O). ^{19}F-NMR (188 MHz, (D_6)acetone): −83.02. ESI-MS: 358 ([*M* + H]$^+$). Anal. calc. for $C_{12}H_{14}F_3NO_6S$ (357.30): C 40.34, H 3.95, N 3.92; found: C 39.49, H 4.02, N 3.82.

1-(4-Bromophenyl)-2-[(4,5,6,7-tetrahydro-1,1-dioxido-1,2-benzisothiazol-3-yl)oxy]-4,4,4-trifluoro-3,3-dihydroxybutan-1-one (**4d**). Yield: 17%. White solid. M.p. 87–89°. UV (CH_3CN): 197 (4.24), 199 (4.22), 211 (4.05), 266 (4.21). IR: 1687*s* (C=O), 1586*s* (C=N), 1317*s* (SO_2), 1157*s* (SO_2). ^{1}H-NMR (300 MHz, (D_6)acetone): 1.88 (*m*, 2 CH_2); 2.55 (*m*, 2 CH_2); 6.47 (*s*, CH); 7.12 (*s*, OH); 7.30 (*s*, OH); 7.81, 8.08 (*AA′BB′*, *J* = 8.7, 4 arom. H). ^{13}C-NMR (75 MHz, (D_6)acetone): 21.6, 21.4, 21.9, 22.1 ((CH_2)$_4$); 80.4 (CH); 94.4 (*q*, ^2J(C,F) = 32.7, $C(OH)_2$); 124.3 (*q*, ^1J(C,F) = 284.7, CF_3); 129.9 (arom. C)); 132.5 (2 arom. CH); 133.0 (C(3a)); 133.3 (2 arom. CH); 137.1 (arom. C); 156.2 (C(7a)); 171. 8 (C(3)); 191.9 (C=O). ^{19}F-NMR (188 MHz, (D_6)acetone): −83.18. FAB-MS: 498/500 ([*M* + H]$^+$). Anal. calc. for $C_{17}H_{15}BrF_3NO_6S$ (498.27): C 40.98, H 3.03, N 2.81; found: C 40.81, H 3.11, N 2.79.

5,5,5-Trifluoro-4,4-dihydroxy-3-[(5-methyl-1,1-dioxido-4-phenylisothiazol-3-yl)oxy]pentan-2-one (**4e**). Yield: 61%. White solid. M.p. 144–146°. UV (EtOH): 219 (3.53), 285 (3.03). IR: 1667*s* (C=O), 1573*s* (C=N), 1321*s* (SO_2), 1169*s* (SO_2). ^{1}H-NMR (200 MHz, (D_6)acetone): 2.41 (*s*, Me); 2.44 (*s*, Me); 5.65 (*s*, CH); 7.19 (*s*, OH); 7.26 (*s*, OH); 7.49–7.63 (*m*, 5 arom. H). ^{13}C-NMR (50 MHz, (D_6)acetone): 9.4 (2 Me); 85.0 (CH); 92.7 (*q*, ^2J(C,F) = 32.8, $C(OH)_2$); 122.7 (*q*, ^1J(C,F) = 288.8, CF_3); 126.8 (arom. C)); 128.8 (2 arom. CH); 130.0 (2 arom. CH); 130.2 (arom. C); 130.4 (C(3a)); 152.6 (C(7a)); 170.8 (C(3)); 197.7 (C=O). ^{19}F-NMR (188 MHz, (D_6)acetone): −82.64. ESI-MS: 394 ([*M* + H]$^+$). Anal. calc. for $C_{15}H_{14}F_3NO_6S$ (393.33): C 45.80, H 3.59, N 3.56; found: C 45.82, H 3.93, N 3.55.

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