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Cyclic and acyclic sulfonimides in reactions with Rh(II)-ketocarbenoids: a new access to chemoselective *O*-functionalization of the imidic carbonyl groups†‡

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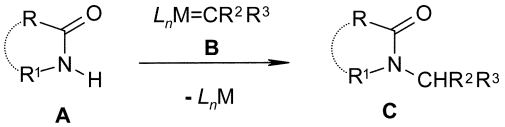
Catalytic decomposition of diazoacetylacetone, diazoacetoacetic, diazomalonic, and diazoacetic esters using dirhodium tetraacetate in the presence of isothiazol-3(2*H*)-one 1,1-dioxides and a number of *N*-(arenesulfonyl)carboxamides in solutions of methylene chloride or dichloroethane gives rise to *O*-alkylation of the imidic carbonyl groups by Rh(II)-carbenoids and the formation of *O*-alkylimidates as the final products. The reaction proceeds with high chemoselectivity *via* carbonyl ylides and offers a powerful method for the synthesis in good yields of the imidates with polyfunctional *O*-alkyl groups. On the basis of X-ray analysis and ^{1}H- and ^{13}C-NMR studies it was shown that the resulting acyclic *O*-alkylimidates have the *E*-configuration in the solid state and in solution. Unlike acyclic analogues, the cyclic carbonyl ylide derived from substituted diazosaccharin by intramolecular cyclization of the appropriate diketocarbenoid is capable of reacting with DMAD in a 1,3-cycloaddition process.

Introduction

Insertion reactions of metal-stabilized carbenes (carbenoids) into X–H bonds of different compounds (X = C, N, O, S, *etc.*) has become a recent standard procedure in organic synthesis.[1,2] A special area in this field occupies the insertion of carbenoids **B** into N–H bonds of amides, lactams and similar structures **A** (Scheme 1), which took on great popularity after the elaboration of a general approach for the synthesis of bicyclic β-lactams on the basis of this transformation.[3] Since then, the high efficiency of carbenoid N–H insertion was repeatedly demonstrated in the synthesis of a wide variety of N-containing structures **C**.[4,5]



Scheme 1 Ordinary direction of Rh(II)-ketocarbenoid reactions with amides, lactams and associated systems containing the CO–NH-moiety in the molecule.

In the context of our research in the chemistry of isothiazol-3(2*H*)-one 1,1-dioxides and their reactions with diazo compounds[6] we undertook an attempt to realize the insertion reaction of ketocarbenoids into the N–H bond of these 5-membered cyclic imides as well as of their acyclic analogues, *N*-(arenesulfonyl)carboxamides. The primary goal of the presented study was to develop a new strategy for the synthesis of the potentially biologically active *N*-alkyl-functionalized sulfonimides.[7,8]

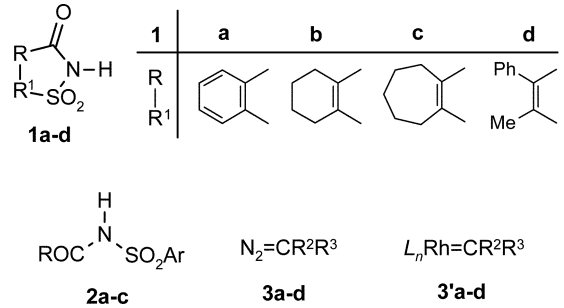
Sulfonimides possess a few nucleophilic groups that can serve as potential centres for interaction with metal-stabilized carbenes, exhibiting a pronounced electrophilic reactivity.[1,2] Nevertheless, one might expect that an electrophilic carbenoid will primarily react with the nitrogen atom of an imidic system, giving rise to *N*-alkylated sulfonimides as usually occur in reactions of electrophiles with saccharins.[7] Basically, a similar tendency is observed in the previously described reactions of amides and lactams with a variety of carbenoids,[3–5,9] although in catalytic reactions of diazoacetic esters a few examples of *O*-alkylation of the amide carbonyl group also exist.[10]

According to our previous results[11] we now report the Rh(II)-catalyzed decomposition of diazocarbonyl compounds in the presence of isothiazol-3(2*H*)-one 1,1-dioxides **1** and *N*-(arenesulfonyl)carboxamides **2**.

Results and discussion

Chemical product studies of Rh(II)-catalyzed reactions

Four cyclic sulfonimides were used in this research: 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide (saccharin) **1a**; two hydrogenated analogues 4,5,6,7-tetrahydro-1,2-benzisothiazol-3(2*H*)-one and 5,6,7,8-tetrahydro-4*H*-cyclohepta[d]isothiazol-3(2*H*)-one 1,1-dioxides **1b**,**c** respectively; and the monocyclic 5-methyl-4-phenyl-isothiazol-3(2*H*)-one 1,1-dioxide **1d** (Scheme 2).



2: R, Ar = Me, Tol (**a**); Me, *p*-ClC$_6$H$_4$ (**b**); Ph, Tol (**c**)
3, 3' : R^2, R^3 = CO$_2$Alk (**a**); COMe, CO$_2$Et (**b**); COMe (**c**); H, CO$_2$Et (**d**)

Scheme 2 Isothiazole 1,1-dioxides **1**, acyclic sulfonimides **2** and diazocarbonyl compounds **3** for Rh(II)-catalyzed reactions.

† Electronic supplementary information (ESI) available: X-ray crystal structures of compounds **4c** and **5b**. See http://dx.doi.org/10.1039/b508317f

‡ Dedicated to Professor Manfred Regitz on the occasion of his 70th birthday.

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Among the acyclic imidic substrates for our investigation were selected *N*-(arenesulfonyl)carboxamides **2a**–**c**, with different natures of the acyl substituents (COMe, COPh) on the imidic N atom and *para*-substituents (Me, Cl) on the aryl ring.

Diketocarbenoids were generated from three different types of diazocompounds: diazomalonic **3a** and diazoacetoacetic **3b** esters; diazoacetylacetone **3c**; and, for comparison, also from diazoacetic ester **3d**, which is stabilized with only one carbonyl group (Scheme 2). Catalytic decomposition of diazocompounds was performed by the addition of 1–2 mol% of dirhodium tetraacetate at 15–20, 45 or 80–83 °C in dry dichloromethane or dichloroethane. Upon completion of the reaction as indicated by TLC, the reaction mixture was separated on the column with neutral silica gel.

As could be expected, as a consequence of the catalytic decomposition of diazocompounds **3a**–**d** by $Rh_2(OAc)_4$ in the presence of sulfonimides **1a**–**c** and **2a**,**b** the adducts of the imidic substrates and the corresponding ketocarbenes in the ratio of 1 : 1 were isolated. Spectroscopic investigations, however, revealed that the compounds obtained did not have the structure of the assumed *N*-alkylated products. It turned out that they comprised *O*-alkylimidates **4** and **5**, that is, the formal insertion products of the corresponding ketocarbenes into the O–H bond of the enol form of imides **1** and **2** (Table 1). Reaction generally proceeded with a good preparative yield (up to 90–95%) and by the data of ^{1}H NMR spectroscopy of the 'crude' reaction mixture the occurrence of isomeric N-alkyl derivatives **6** of imides under these conditions was not observed.

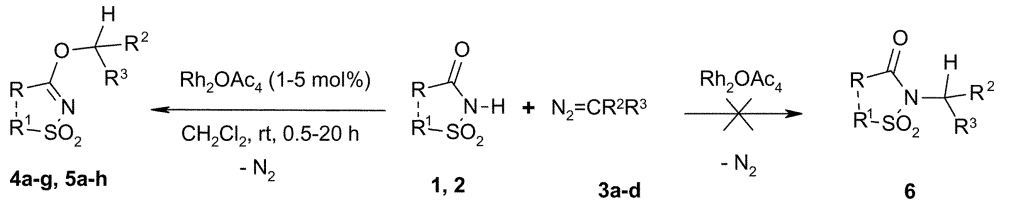
At the same time during the catalytic decomposition of diazocompounds **3a**,**c**,**d** in the presence of sulfonimide **2c** bearing the *N*-aroyl substituent, after work-up of the reaction mixture only the initial sulfonimide **2c** (80–87%) was isolated, although from the ^{1}H NMR data immediately upon completion of the catalytic process significant amounts (>35–40%) of the corresponding imidates **5i**,**j** were detected in the reaction mixture (Table 1). Variation of the reaction and experimental conditions (using reduced temperature, separation of reaction mixture without silica gel, *etc.*) did not give a positive result, evidently due to the easy hydrolysis of *O*-alkylimidates **5i**,**j** during the work-up procedure, and we did not manage to isolate them in pure form.

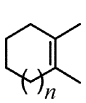
To summarize, it can be concluded that the above transformation of cyclic and acyclic sulfonimides **1** and **2** offers a new *O*-alkylation reaction of imidic carbonyl groups by metal-carbenes and enables a one-stage synthesis of *O*-alkylimidates with a polyfunctional framework in the molecule.

Spectroscopic investigations and structure of *O*-alkylimidates 4, 5

Owing to the lack of literature data regarding the spectroscopic properties of the *O*-alkylation products of imides by ketocarbenoids, a detailed study of imidates **4** and **5** using ^{1}H- and ^{13}C-NMR spectroscopy was undertaken . The aim of this part of our research was to elucidate the characteristic parameters of *O*-alkylimidates **4** and **5** and the possibility of their subsequent

Table 1 *O*-Alkylation of isothiazol-3(2*H*)-one 1,1-dioxides **1** and acyclic sulfonamides **2** *via* Rh(II)-ketocarbenoids **3**′ from diazocarbonyl compounds **3**[a]



Imidate	R–R^1	R^2, R^3	Yield (%)[b]	Imidate	R	R^1	R^2, R^3	Yield (%)[b]
4a		CO_2Me, CO_2Me	90	**5a**	Me	Tol	CO_2Me, CO_2Me	90
4b		COMe, CO_2Et	76	**5b**	Me	*p*-ClC_6H_4	CO_2Me, CO_2Me	87
4c		COMe, COMe	86[11]	**5c**	Me	Tol	COMe, CO_2Et	78
4d		H, CO_2Et	80	**5d**	Me	*p*-ClC_6H_4	COMe, CO_2Et	68
4e		CO_2Et, CO_2Et[c]	95[11]	**5e**	Me	Tol	COMe, COMe	77
4f		COMe, COMe[c]	86[11]	**5f**	Me	*p*-ClC_6H_4	COMe, COMe	47
4g		CO_2Et, CO_2Et	81[11]	**5g**	Me	Tol	H, CO_2Et	41
				5h	Me	*p*-ClC_6H_4	H, CO_2Et	28
				5i	Ph	Tol	CO_2Me, CO_2Me	>40[d]
				5j	Ph	Tol	COMe, COMe	>35[d]

[a] For detailed reaction conditions see the Experimental section. [b] Isolated yield after flash chromatography. [c] Compound **4e**, $n = 1$; **4f**, $n = 2$. [d] From the data of ^{1}H NMR spectra.

Table 2 ^{13}C NMR spectra of imidates **4a**–**g**, **5a**,**b**,**g**,**h** and *N*-alkyl derivatives **6a**–**c** in 0.2–0.3 mol solutions of $CDCl_3$

	Compounds **4**, **5**, **6**		Signals of carbon atoms, δ/ppm[a]			
Entry	No.	R^2, R^3	O–*C*H or N–*C*H	N=*C*–O or N–*C*=O	AlkO–*C*=O or Me–*C*=O	Other C atoms
1	**4a**	CO_2Me, CO_2Me	76.0	168.2	163.1	53.9 (OCH_3), 122.2, 124.0, 125.5, 133.8, 134.7, 143.7 (C-arom.)
2	**4e**[b]	CO_2Et, CO_2Et	76.3	170.6	162.9	14.1 (CH_3), 20.4, 20.79, 20.84, 21.0 (CH_2), 63.3 (OCH_2), 131.9 (4-C), 155.2 (5-C)
3	**4g**[b]	CO_2Et, CO_2Et	77.1	170.8	162.9	14.3 (CH_3), 63.6 (OCH_2), 126.5, 129.1, 129.2, 130.0 (C-arom.), 130.6 (4-C), 152.8 (5-C)
4	**5a**	CO_2Me, CO_2Me	74.6	168.3	164.3	20.0 (CH_3Ar), 21.9 (CH_3C=N), 53.7 (OCH_3), 127.2, 129.8, 138.3, 144.2 (C-arom.)
5	**5b**	CO_2Me, CO_2Me	74.7	172.3	164.1	20.2 (CH_3C=N), 53.7 (OCH_3), 128.6, 129.5, 139.7, 139.8 (C-arom.)
6	**4b**	COMe, CO_2Et	82.3	168. 2	194.9, 162.7	14.1(CH_3CH_2), 27.5 (CH_3CO), 63.3(CH_3CH_2), 122.2, 123.9, 125.7, 133.8, 134.8, 143.7 (C-arom.)
7	**4c**[b]	COMe, COMe	89.8	168.3	197.0	27.8 (CH_3CO), 122.7, 123.9, 126.0, 134.2, 135.2, 144.1 (C-arom.)
8	**4f**[b]	COMe, COMe	90.0	170.9	196.8	25.0, 25.5, 26.6, 26.8, 29.5 (CH_2), 27.6 (CH_3CO), 132.8 (4-C), 157.3 (5-C)
9	**4d**	H, CO_2Et	66.1	168.9	165.6	13.8 (CH_3CH_2O), 61.9 (CH_3CH_2O), 121.7, 123.5, 125.7, 133.6, 134.4, 143.2 (C-arom.)
10	**5g**	H, CO_2Et	63.8	172.6	166.5	13.8 (CH_3CH_2), 19.6 (CH_3C=N), 21.4 (CH_3Ar), 61.3 (CH_3CH_2), 126.6, 129.3, 138.3, 143.4 (C-arom.)
11	**5h**	H, CO_2Et	63.1	172.2	165.4	12.9 (CH_3CH_2), 19.0 (CH_3C=N), 60.5 (CH_3CH_2), 127.2, 128.0, 138.1, 138.7 (C-arom.)
12	**6a**	CO_2Me, CO_2Me	54.7	168.2	158.6	54.2 (OCH_3), 121.7, 126.1, 127.0, 135.1, 135.8, 137.9 (C arom.)
13	**6b**	H, CO_2Et	39.1	165.9	158.7	14.0 (CH_3CH_2), 62.2 (CH_3CH_2), 121.2, 125.4, 126.9, 134.5, 135.2, 137.6 (C-arom.)
14	**6c**	H, $COCH_2CO_2Et$	46.6	166.1	158.8	14.0 (CH_3CH_2), 46.54 ($COCH_2CO$), 61.8 (OCH_2), 121.2, 125.3, 126.8, 134.6, 135.2, 137.6 (C-arom.), 193.6 (NCH_2CO)

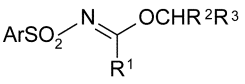
[a] For the sake of convenience the data for O–*C*H, N=*C*–O, N–*C*=O, N–*C*H, AlkO–*C*=O and Me–*C*=O groups are placed in the three first carbon signal columns of the table. [b] Data from the preliminary publication.[11]

use for the identification of similar compounds by spectroscopic methods. Some of these results are considered below (Table 2); other data are given in the Experimental section.

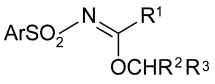
In the ^1H NMR spectra sharp singlet signals of methine ($OCHR^2R^3$; 5.4–5.9 ppm) or methylene group (OCH_2CO_2Et; 4.5–5.0 ppm) were observed. In the carbon spectra strong signals of the same fragments ($OCHR^2R^3$ and OCH_2CO_2Et) appear at 75–90 and 63–66 ppm, respectively. The signal shift of the methine carbon atom strongly depends upon the substituents R^2. With two acyl substituents the corresponding atom was found around 90 ppm (**4c**,**f**). Replacement of one of them with an alkoxycarbonyl group causes a high-field shift to 82 ppm (**4b**). Incorporation of one more alkoxycarbonyl group (**4a**,**e**,**g**) results in further shifting of the O*C*H signal to stronger field and was hence found at 76–77 ppm.

The signals of the proton and carbon atoms of the O–*CH* fragment in the NMR spectra of acyclic *O*-alkylimidates **5a**,**b** are typically observed in the same regions (5.4–5.5 and 74.6–74.7 ppm) which were found for their analogues **4a**,**e**,**g** in the series of saccharins (5.7–5.9 and 76.0–77.1 ppm; Table 2).

Acyclic imidates **5** can exist as *Z*- and *E*-stereoisomers *E*-**5** and *Z*-**5**. According to the literature data,[12] *O*-alkylimidates with small substituents (Me, Et, *etc.*) at the C=N bond normally have the *E*-configuration, but with bulky substituents (*t*-Bu, Ph and others) on the carbon and nitrogen atoms of this bond, the *Z*-stereoisomer also appears in equilibrium.[13] In specific cases, the *E*- and *Z*-isomers of the imidates can be separated using flash chromatography or recrystallization of the stereoisomeric mixture.[12,14]



E-**5**



Z-**5**

In the proton spectra of imidates **5a**–**h**, bearing a methyl group on the C atom of the C=N bond, only one signal for the protons of the O–*CH* group at 5.4–5.5 ppm or of the O–*CH*$_2$ group at 4.5–4.6 ppm were observed. Therefore, one can conclude that the *O*-alkylimidates **5** in solution at ordinary temperatures most likely persist as a single stereoisomer. In the ^1H NMR spectrum of the 'crude' reaction mixture of imidate **5i** from sulfonimide **2c** with the more bulky phenyl group at the C atom of the C=N bond two separate signals were found (at 5.61 and 5.73 ppm). It seems likely that in solution two stereoisomers of imidate **5i** are present, but we were not able to isolate them as pure products.

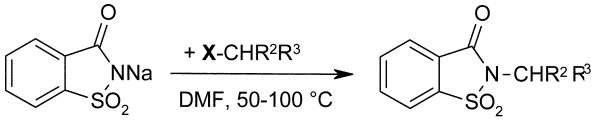
It also should be noted that compounds **4b**,**c**,**f** and **5c**–**f** with an acetyl group in 1,3-dicarbonyl fragment of the molecule are not enolized in solution and in the solid state, according to NMR and IR spectroscopy. This is contrary to similar *N*-alkyl derivatives from amides and lactams which exist solely in the enol form.[9a,15] This finding greatly simplifies the spectroscopic identification of *O*-alkylated sulfonimides.

The structures of **4** and **5** were also confirmed by X-ray structure determination with adducts **4c** and **5b**, derivatives of the cyclic **1** and acyclic **2** imides correspondingly, whose geometry is presented in Fig. S1 and S2 (see ESI†). These data unambiguously ascertained the structure of the resultant compounds **4** and **5** as *O*-alkyl derivatives of the sulfonimides. On this basis it is also evident that *O*-alkylimidates **5** of acyclic sulfonimides have the *E*-configuration, and both *O*-alkylimidates **4** and **5** have the *s-cis* conformation with regard to the C(7)–O(3)CHR^2R^3 bond.

N-Alkylation of sulfonimides 1 and 2 using alkyl halides

To produce isomeric *N*-alkyl derivatives **6** and by this means to obtain indirect corroboration of the structure of *O*-alkylimidates **4** and 5 by chemical methods, a few reactions of sulfonimides **1** and **2** with electrophilic alkyl halides, namely – with bromomalonic, bromoacetoacetic and chloroacetic esters were also studied. Reactions were carried out with sodium and potassium salts of the imides **1a** and **2a** in solutions of dry DMF or THF.[16]

Reaction of the sodium salt of saccharin **1a** with the above-mentioned alkyl halides in DMF solution produced the relevant *N*-alkyl-substituted saccharins **6a–c** (Scheme 3). For advantageous preparation of *N*-bis(alkoxycarbonyl)methylene derivatives **6a** from the sodium salt of saccharin **1a**-Na and the corresponding bromomalonates it was necessary to carry out the reactions at a temperature of about 70 °C. Increasing the temperature to 100–120 °C in the reaction with ethyl bromomalonate resulted in the sole formation of *N*-substituted saccharin **6b**, probably due to the easy hydrolysis followed by decarboxylation of one of the ester groups of the initially-formed derivative of malonic acid **6a** ($R^3 = CO_2Et$) at temperatures above 100 °C.[16b]



6a: $R^2, R^3 = CO_2Me$ (Et); **b:** $R^2 = H$, $R^3 = CO_2Et$;
c: $R^2 = H$, $R^3 = COCH_2CO_2Et$

Scheme 3 *N*-Alkylation of isothiazole 1,1-dioxide **1a** using alkyl halides.

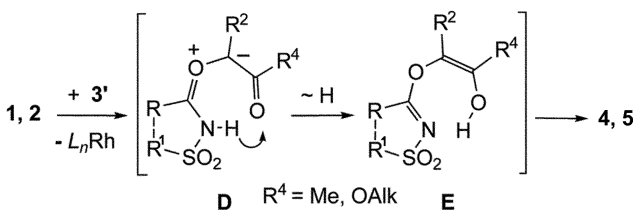
Positive results were not achieved in the experiments with the acyclic sulfonimides **2a**,**b** or their potassium and sodium salts under the same conditions; also, substitution of DMF for tetrahydrofuran[16c] in alkylation reactions of the sodium salt **1a**-Na with alkyl halides also failed.

As evident from spectral data of the *N*-substituted imides **6a–c**, the major difference in the proton and carbon spectra of isomeric *O*- and *N*-alkyl derivatives **4** and **6** is exhibited in the location of the signals for H and C atoms of the methine and methylene groups (O–*CH*, N–*CH* and O–CH_2, N–CH_2) (see Table 2 and the Experimental section). The proton signals of these groups shift to stronger field by 0.6–0.7 ppm upon moving from *O*-alkylimidates **4a**,**d** to the corresponding *N*-alkylation products **6a** and **6b**, while the signals of the C atoms of the same groups move to stronger field by 21–24 ppm. Pronounced distinctions (4.5–6.5 ppm) are also found in the location of the imidate and carbonyl carbon atoms (N=*C*–O and N–*C*=O) of the sulfonimidic derivatives **4** and **6**.

These correlations clearly demonstrate the essential differences in the proton and carbon NMR spectra of *N*- and *O*-alkyl-substituted sulfonimides **4** and **6**, and allow us to make conclusive structural assignments based on these data.

Trapping of intermediate carbonyl ylide and likely pathway of the reaction

The mechanism of formation of the *O*-alkyl imidates **4** and **5** apparently involves intermediate generation of the carbonyl ylide **D** due to initial attack of the electrophilic ketocarbenoid **3′** on the carbonyl oxygen atom (Scheme 4).[2a,b,10,17,18] The succeeding stabilization of ylide **D** into *O*-alkyl imidates **4** and **5** may occur by intramolecular NH group hydrogen transfer either *via* a [1,4]-sigmatropic hydrogen shift[10c,d] or by H-migration to the anionic centre of the carbonyl ylide through intermediate **E**.



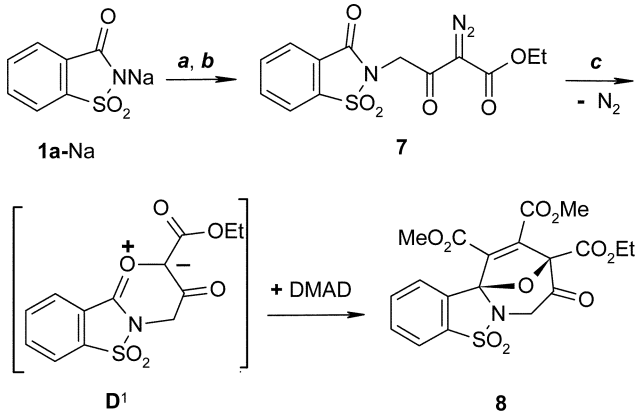
Scheme 4 Carbonyl ylide pathway for *O*-alkylation of sulfonimides **1**, **2** *via* ketocarbenoids **3′**.

Formation of the O–H insertion products **4**, **5**, by the 'oxonium' pathway involving the enol form of sulfonimides **1**, **2** and then oxonium ylides, seems unlikely.[11]

Attempts to obtain experimental support in favour of the intermediate occurrence of carbonyl ylides **D** with the help of their cycloaddition to dimethyl acetylenedicarboxylate (DMAD)[2b,17,18] using sulfonimides **1**, **2** with an unsubstituted N–H group have been unsuccessful. Catalytic decomposition of diazomalonic ester **3a** in the presence of imides **1a** or **2a** with an excess of DMAD results in the formation of *O*-alkylimidates **4a** or **5a**.

These data clearly indicate that the stabilization of carbonyl ylide **D** *via* an intramolecular [1,4]-H-shift occurs more rapidly than its intermolecular reaction with DMAD. Therefore, cycloadducts of the carbonyl ylide and DMAD should be expected using *N*-substituted sulfonimides with no possibility for H-migration. However, similar catalytic reaction of diazomalonic ester **3a** with *N*-methyl- or *N*-phenyl-substituted saccharins **1e**,**f** in the presence of DMAD also failed to produce cycloadducts. In both cases only the initial N–Me- and N–Ph-isothiazoles **1e**,**f** were found in the reaction mixture, together with significant quantities of the bis(methoxycarbonyl)carbene 'dimer' (identified by NMR spectra).

In order to explain the reasons behind the unsuccessful attempts of adding 'intermolecular' C=O-ylides **D** from *N*-substituted saccharins **1e**,**f** to DMAD, the reactivity of their assumed 'intramolecular' analogue – carbonyl ylide **D¹** – was examined under the same conditions. For this purpose, *N*-alkyl-substituted oxoisothiazole 1,1-dioxide **7** was prepared with the diazocarbonyl moiety directly in the structure of the starting substrate and without the 'free' hydrogen at the imidic nitrogen atom (Scheme 5).

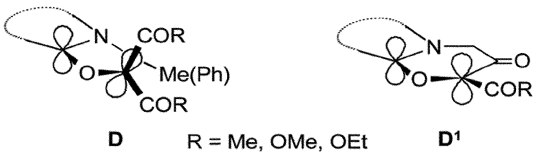


Scheme 5 Synthesis and catalytic decomposition of diazosaccharin **7** in the presence of DMAD. *Reagents and conditions*: ***a***) $BrCH_2COCH_2CO_2Et$, DMF, 90 °C, 46%; ***b***) *p*-acetamidobenzenesulfonyl azide (ABSA), Et_3N, CH_2Cl_2, 20 °C, 84%; ***c***) $Rh_2(OAc)_4$, DMAD, CH_2Cl_2, 12 h, 61%.

The catalytic decomposition of this diazosaccharin **7** in the presence of an 8-fold excess of DMAD resulted in the formation of the relevant cycloadduct **8** of the intermediate 'intermolecular' carbonyl ylide **D¹** with dipolarophile (DMAD) in good yield (*ca.* 60%).

The essential discrepancy in reactivity of the 'intermolecular' **D** and 'intramolecular' **D¹** carbonyl ylides could be explained in the following manner. Owing to the presence of the substituent (Me or Ph) at the imidic N atom in the molecule of carbonyl ylide **D**, two bulky groups (CO_2Alk, COMe) of the carbene fragment are apparently positioned orthogonally to the plane of the dipole C^+–O–C^- and thereby cause severe steric hindrance

for the approach of the dipolarophile to the reacting orbitals of this 'intermolecular' C=O ylide (Scheme 6).



Scheme 6 Different stereochemistries of 'inter-' and 'intra-molecular' carbonyl ylides **D** and **D¹**.

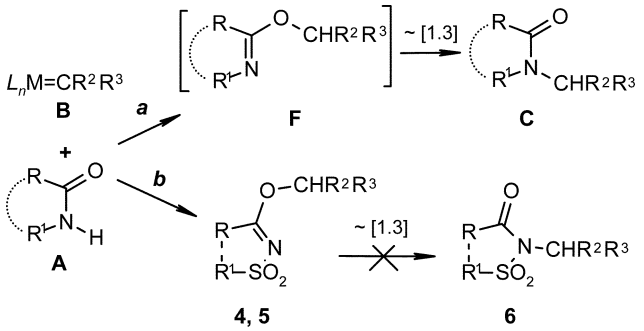
By contrast, all four substituents at the dipole's C atoms are actually located in the plane of the 1,3-dipole itself in the dipolar structure of the 'intramolecular' carbonyl ylide **D¹**. As a consequence of these changes, the steric problems for the approach of DMAD to the reactive centers of ylide **D¹** are clearly removed and cycloaddition between these moieties can proceed more effectively.

Thus, the main line of interaction of Rh(II)-ketocarbenoids with cyclic and acyclic sulfonimides is the initial attack on the oxygen atom of the carbonyl group, with intermediate formation of the carbonyl ylide that ultimately leads to *O*-alkylation of these imidic substrates. As has already been mentioned above, essentially only *N*-alkylation products of the starting compounds were isolated in similar reactions of amides, lactams and related structures with a variety of ketocarbenoids.[3–5,9,15] The reason for such a drastic difference in the ketocarbenoid's reactivity with amides, lactams and sulfonimides **1** and **2** (as investigated by us) is still not understood.

The amidic moiety (O=C–NH) of isothiazol-3(2*H*)-one 1,1-dioxides **1** and acyclic sulfonimides **2** is a typical ambident system,[7a,19] capable of interacting with electrophilic reagents at the nitrogen or/and oxygen atoms of this group. In view of the amide character of their structure the *N*-substituted sulfonimides should be thermodynamically more stable than the isomeric *O*-substituted derivatives related to the imidate structure.[7a,20] This conclusion is corroborated by numerous examples of irreversible thermal isomerisation of *O*-alkyl(aryl)imidates into their associated *N*-derivatives,[7a,16c,21–23] known as the *Lander–Chapman* rearrangement.[12,21] The trend toward oxygen-to-nitrogen rearrangement increases substantially with multiple bonds and electron accepting groups in the migrating fragment of the imidate.[7a] And in the presence of a specific catalyst this rearrangement can take place even at moderate temperatures,[23] *i.e.* catalytic reaction can proceed bypassing the stage of isolable *O*-alkyl derivatives.

Based on the aforesaid it may be suggested that initially in the course of amide and lactam reactions with ketocarbenoids, *O*-alkylation products **F** are generated (Scheme 7, route '***a***') as in the case of sulfonimides **1**, **2** which then experience oxygen-to-nitrogen rearrangement of the diketocarbene fragment under the reaction conditions; also, as the final products of this process, *N*-derivatives **C** are produced.

For *O*-alkylimidates **4**, **5** (route '***b***'), a similar rearrangement can be presumably hindered in view of the bulky and strongly electronegative SO_2 group adjacent to the end point of migration. This group can strongly reduce the electrophilicity of the α-N-atom and in addition prevent migration of the bulky O-substituent to the nitrogen atom because of steric reasons. It is apparently this reason that gives the opportunity for isolation of the initial *O*-alkylation derivatives of sulfonimides from reaction mixture.



Scheme 7 Assumed ways of carbenoid reaction with amides, lactams (***a***) and sulfonimides (***a***).

Conclusion

We have shown that: (a) rhodium-catalysed decomposition of diazocarbonyl compounds in the presence of saccharins and *N*-(arenesulfonyl)acetamides is a powerful tool for the *O*-functionalization of their carbonyl groups by reaction with the transient ketocarbenoids; and (b) the discovered reaction is a highly chemoselective process, which provides a new and effective approach for the structure of *O*-alkylimidates from oxoisothiazole 1,1-dioxides and *N*-(arenesulfonyl)acetamides. The reasons for the dissimilar chemical behaviour of amides, lactams and sulfonimides in reactions with metal-stabilized carbenes are as yet unclear, and this is a subject of current investigation in our laboratories.

Experimental

General notes

^{1}H and ^{13}C NMR spectra were measured on VARIAN 'Gemini 200', 'Gemini 300' and BRUKER DRX-600 'AVANCE' spectrometers, at working frequencies of 200, 300, and 600 MHz for ^{1}H NMR and 50.3, 75.45 and 150.92 MHz for ^{13}C NMR spectra; solutions were in $CDCl_3$ or DMSO-d_6, internal standard Me_4Si (δ, ppm), J values are given in Hz. Infrared spectra were obtained using an ATI Mattson 'Genesis Series FTIR' or with a Specord IR-75 instrument. Mass spectra were determined by electron impact at 70 eV on a Quadrupol-MS VG 12–250 (VG Instruments GmbH, Manchester Analytical). Microanalysis was performed on an Heraeus CHNS Rapid Analyser. Melting points were determined on a Boetius micro melting point apparatus and were uncorrected.

All reactions were carried out in carefully dried and distilled solvents. Rhodium(II) acetate and saccharin **1a** were commercially available (Fluka). Other 3-oxoisothiazoles **1** and sulfonimides **2** were prepared according to the previous publications[24,25] and for extra purification they were sublimated *in vacuo* at 30–50 °C/0.05 mm Hg. Diazodicarbonyl compounds **3a–c** were prepared from the corresponding 1,3-dicarbonyl compounds and arenesulfonyl azides using a diazotransfer reaction[1,26] followed by distillation *in vacuo*. Commercially available diazoacetic ester **3d** (Fluka) was distilled just before carrying out the catalytic reaction, bp 58–60 °C/1 mm Hg.

Reactions were monitored by thin-layer chromatography (TLC) on Silufol UV/VIS plates using 254 nm UV light and J_2 as the visualizing agents. Neutral silica gel (MERCK 70–230 mesh or CHEMAPOL L 40/100) was used for column chromatography.

General procedure for catalytic decomposition of diazomalonates 3a, diazoacetoacetic esters 3b and diazoacetylacetone 3c in the presence of sulfonimides 1, 2 to produce *O*-alkylimidates 4a,b and 5a–f

To a solution or suspension of sulfonimides **1**, **2** (2.0 mmol) and diazocompound **3a–c** (2.3 mmol) in 5–15 mL in methylene chloride or dichloroethane at 18–20 °C was added in one portion 5–10 mg (11–23 μmol) of dirhodium tetraacetate and

the mixture was stirred to completion of the decomposition of the diazocompound (3–24 h in the case of diazomalonates **3a**, and 20–40 min for the decomposition of the diazocompounds **3b**,**c**; control using TLC). The solvent was removed *in vacuo* to a volume of 2–3 mL and the residue was filtered through a small layer of neutral silica gel (eluent mixture of CH_2Cl_2–Et_2O = 1 : 1 to 1 : 2). The isolated compounds were analyzed by means of spectroscopic methods and, if need be for additional purification, they were crystallized from the appropriate solvents.

After complete decomposition of the diazoacetoacetic ester **3b** and diazoacetylacetone **3c** in the presence of *N*-(4-Cl-benzenesulfonyl)acetamide **2b** and concentration of the resultant mixture to a volume of 3–4 mL, the unreacted imide **2b** was separated by filtration and the mother liquid was treated analogously to general procedure.

3-(Dimethoxycarbonyl)methoxy-1,2-benzisothiazole 1,1-dioxide 4a. Yield 0.56g (90%), colorless crystals, R_f = 0.18 (hexane–Et_2O 1 : 1), mp 116–117 °C (from CH_2Cl_2–hexane) (Found: C, 46.2; H, 3.7; N, 4.3. Calc. for $C_{12}H_{11}NO_7S$: C, 46.0; H, 3.5; N, 4.5%); ν_{max}(KBr)/cm^{-1} 2997s, 2308vs, 1757m, 1337m, 1160m; δ_H (300 MHz, $CDCl_3$, Me_4Si) 3.92 (6H, s, 2OCH_3), 5.96 (1H, s, OCH), 7.73–7.93 (4H, m, H-arom.); *m*/*z* (EI) 313 (M$^+$, 7.5%), 282 (15.3), 269 (7.5), 249 (27.8), 212 (27.5), 198 (50.4), 166 (35.6), 150 (10.9), 117 (50.8), 102 (100.0).

3-(Acetylethoxycarbonyl)methoxy-1,2-benzisothiazole 1,1-dioxide 4b. Yield 0.31g (50%), colorless crystals, R_f = 0.18 (hexane–Et_2O 1 : 1), mp 74 °C (from Et_2O) (Found: C, 50.2; H, 4.2; N, 4.5; S, 10.3. Calc. for $C_{13}H_{13}NO_6S$: C, 50.2; H, 4.2; N, 4.5; S, 10.3%); ν_{max}(KBr)/cm^{-1} 3436, 1739, 1617, 1558, 1396, 1340, 1249, 1172, 592, 536; δ_H(300 MHz, $CDCl_3$, Me_4Si) 1.32 (3H, t, *J* 7.0, CH_3), 2.46 (3H, s, CH_3), 4.37 (2H, q, *J* 7.0, CH_2), 5.9 s (1H, OCH), 7.2–8.3 (4H, m, H-arom.); *m*/*z* (EI) 311 (M$^+$, 2.3%), 43 (100).

(Dimethoxycarbonyl)methyl ester of *N*-(4-methylbenzenesulfonyl)imidoylacetic acid 5a. Yield 0.61g (90%), colourless crystals, R_f = 0.33 (hexane–Et_2O 1 : 1), mp 122–123 °C (from CH_2Cl_2–petroleum) (Found: C, 49.0; H, 5.0; N, 4.1; S, 9.3. Calc. for $C_{14}H_{17}NO_7S$: C, 49.0; H, 5.0; N, 4.1; S, 9.3%); ν_{max}($CHCl_3$)/cm^{-1} 3020vs, 2940vs, 1750m, 1625m, 1154w; δ_H(300 MHz, $CDCl_3$, Me_4Si) 2.43 (3H, s, N=CCH_3), 2.62 (3H, s, CH_3Ar), 3.7 (6H, s, 2 OCH_3), 5.47 (1H, s, OCH), 7.31 (2H, d, *J* 8.7, H-arom.), 7.75 (2H, d, *J* 8.7, H-arom.); *m*/*z* (EI) 343 (M$^+$, 4.0%), 312 (2.2), 155 (76.1), 147 (47.4), 139 (6.7), 132 (3.8), 91 (100.0), 65 (21.5), 59 (9.3), 47 (10.1), 43 (7.7).

(Dimethoxycarbonyl)methyl ester of *N*-(4-chlorobenzenesulfonyl)imidoylacetic acid 5b. Yield 0.63 g (87%), colourless crystals, R_f = 0.3 (hexane–Et_2O 1 : 1), mp 104 °C (from CH_2Cl_2–petroleum) (Found: C, 43.1; H, 3.9; N, 3.8; S, 8.85. Calc. for $C_{13}H_{14}ClNO_7S$: C, 42.9; H, 3.9; N, 3.8; S, 8.8%); ν_{max}($CHCl_3$)/cm^{-1} 3024s, 2932vs, 1747m, 1619m, 1322m, 1156m, 1082m, 650m; δ_H(300 MHz, $CDCl_3$, Me_4Si) 2.64 (3H, s, N=CCH_3), 3.72 (6H, s, 2 OCH_3), 5.45 (1H, s, OCH), 7.49 (2H, d, *J* 7.8, H-arom.), 7.81 (2H, d, *J* 7.8, H-arom.); *m*/*z* (EI) 363 (M$^+$, 5.0%), 332 (7.2), 175 (77.4), 167 (37.1), 159 (10.9), 152 (6.3), 111 (95.4), 65 (24.6), 59 (8.0), 47 (9.6), 43 (8.4).

(Acetylethoxycarbonyl)methyl ester of *N*-(4-methylbenzenesulfonyl)imidoylacetic acid 5c. Yield 0.53 g (78%), oily compound, R_f = 0.24 (hexane–Et_2O 2 : 1); δ_H(300 MHz, $CDCl_3$, Me_4Si) 1.13 (3H, t, *J* 7.0, CH_2CH_3), 2.19 (3H, s, CH_3C=O), 2.37 (3H, s, CH_3Ar), 2.56 (3H, s, N=CCH_3), 4.08 (2H, q, *J* 7.0, CH_2CH$_3$), 5.41 (1H, s, OCH), 7.25 (2H, d, *J* 8.1, H-arom.), 7.68 (2H, d, *J* 8.1, H-arom.); *m*/*z* (EI) 341 (M$^+$, 1.2%), 326 (1.4), 300 (3.3), 274 (1.9), 258 (12.8), 254 (4.8), 211 (4.8), 198 (4.7), 171 (7.7), 155 (84.0), 108 (53.8), 91 (100.0), 65 (35.9), 49 (28.2).

(Acetylethoxycarbonyl)methyl ester of *N*-(4-chlorobenzenesulfonyl)imidoylacetic acid 5d. Yield 0.49 g (68%), oily compound, R_f = 0.27 (hexane–Et_2O 1 : 1); δ_H(300 MHz, $CDCl_3$, Me_4Si) 1.17 (3H, t, *J* 7.4, CH_2CH_3), 2.21 (3H, s, CH_3C=O), 2.61 (3H, s, N=CCH_3), 4.11 (2H, q, *J* 7.4, CH_2CH$_3$), 5.38 (1H, s, OCH), 7.46 (2H, d, *J* 9.0, H-arom.), 7.76 (2H, d, *J* 9.0, H-arom.); *m*/*z* (EI) 361 (M$^+$ 3.5%), 345 (7.1), 319 (16.4), 296 (7.8), 278 (40.3), 274 (20.2), 211 (77.0), 183 (61.1), 175 (19.7), 171 (22.2), 156 (19.4), 129 (36.1), 111 (25.0), 103 (16.6), 83 (99.3), 67 (66.6), 55 (42.7), 43 (100.0).

(Diacetyl)methyl ester of *N*-(4-methylbenzenesulfonyl)-imidoylacetic acid 5e. Yield 0.48g (77%), oily compound, R_f = 0.23 (hexane–Et_2O 2 : 1); δ_H(300 MHz, $CDCl_3$, Me_4Si) 2.14 (6H, s, 2 COCH_3), 2.38 (3H, s, CH_3Ar), 2.59 (3H, s, N=CCH_3), 5.40 (1H, s, OCH), 7.28 (2H, d, *J* 8.0, H-arom.), 7.67 (2H, d, *J* 8.0, H-arom.); *m*/*z* (EI) 311 (M$^+$, 1.0%), 279 (1.2), 285 (1.2), 270 (16.0), 243 (7.2), 227 (15.2), 214 (15.3), 197 (6.24), 187 (8.3), 173 (12.6), 155 (20.0), 114 (19.5), 108 (13.0), 91 (69.5), 72 (32.0), 65 (26.5), 43 (100.0).

(Diacetyl)methyl ester of *N*-(4-chlorobenzenesulfonyl)-imidoylacetic acid 5f. Yield 0.31 g (47%), oily compound, R_f = 0.25 (hexane–Et_2O 1 : 1); δ_H(300 MHz, $CDCl_3$, Me_4Si) 2.16 (6H, s, 2CH_3CO), 2.64 (3H, s, N =CCH_3), 5.40 (1H, s, OCH), 7.48 (2H, d, *J* 9.0, H-arom.), 7.75 (2H, d, *J* 9.0, H-arom.); *m*/*z* (EI) 331 (M$^+$, 4.1%), 290 (1.3), 272 (1.1), 253 (3.2), 248 (8.5), 214 (3.2), 175 (47.2), 159 (8.1), 153 (8.5), 141 (7.5), 128 (8.3), 111 (41.6), 75 (13.8), 43 (100).

Decomposition of diazoacetic ester 3d in the presence of imides 1a, 2a,b to produce *O*-alkylimidates 4d, 5g,h

(a) To a suspension of 0.5 g (2.7 mmol) saccharin **1a** in 8 mL of dichloromethane was added 7 mg (15.8 μmol) of dirhodium tetraacetate, then under stirring was added dropwise over 30 min a solution of 0.66 g (5.4 mmol) diazoacetic ester **3d** in 4 mL CH_2Cl_2 and reaction mixture was stirred for 20 min at room temperature. The solvent was evaporated to a volume of *ca.* 3 mL and residue was filtered through a small layer of silica gel (eluent pentane–diethyl ether = 1 : 1), the main fraction was dried with $MgSO_4$, and after removal of the solvents the imidate **4d** was recrystallized from a mixture of CH_2Cl_2–petroleum = 2 : 1.

(b) To a solution of 2.55 g (12 mmol) imide **2a** and 30 mg (68 μmol) $Rh_2(OAc)_4$ in 15 mL CH_2Cl_2 was added dropwise over 5 h a solution of 1.7 g (15 mmol) diazoacetic ester **3d** in 30 mL dichloromethane. On completion of the reaction (control *via* TLC) the catalyst was removed by filtration of the reaction mixture through a layer of silica gel (7 g), to obtain an analytically pure sample of imidate **5g**. The isolated compound was additionally subjected to chromatography on silica gel (40 g, eluent petroleum–CH_2Cl_2 = 1 : 1).

(c) To a suspension of the imide **2b** (0.5 g; 2.1 mmol) and 10 mg (22 μmol) of $Rh_2(OAc)_4$ in 15 mL CH_2Cl_2 was added dropwise with stirring over 1 h a solution of 0.48 g (4.2 mmol) diazoacetic ester **3d** in 20 mL CH_2Cl_2, and after work-up of the reaction mixture in a similar way to the preceding experiment was obtained the imidate **5h**.

3-(Ethoxycarbonyl)methoxy-1,2-benzisothiazole 1,1-dioxide 4d. Yield 0.58 g (80%), colourless crystals, R_f = 0.2 (hexane–Et_2O 1 : 1), mp 76–77 °C (from CH_2Cl_2–petroleum) (Found: C, 49.1; H, 4.1; N, 5.25. Calc. for $C_{11}H_{11}NO_5S$: C, 49.1; H, 4.1; N, 5.2%); ν_{max}(KBr)/cm^{-1} 3438s, 2983vs, 1756m, 1558m, 1398m, 1332m; δ_H(300 MHz, $CDCl_3$, Me_4Si) 1.31 (3H, t, *J* 7.2, OCH$_2$CH_3), 4.3 (2H, q, *J* 7.2, OCH_2CH$_3$), 5.1 (2H, s, CH_2CO$_2$Et), 7.73–7.9 (4H, m, H-arom.). HRMS, [M + H]$^+$: found 270.04304, calc. 270.04307.

(Ethoxycarbonyl)methyl ester of *N*-(4-methylbenzenesulfonyl)-imidoylacetic acid 5g. Yield 1.47 g (41%), colourless liquid, $R_f = 0.23$ (hexane–CH_2Cl_2 3 : 1), n_D^{20} 1.5158 (Found: C, 52.2; H, 5.8; N, 4.6; S, 10.8. Calc. for $C_{13}H_{17}NO_5S$: C, 52.2; H, 5.7; N, 4.7; S, 10.7%); ν_{max}(KBr)/cm^{-1} 2983vs, 1754m, 1621m, 1303m, 1159m, 682m; δ_H(300 MHz, $CDCl_3$, Me_4Si) 1.17 (3H, t, *J* 7.2, CH_2CH_3), 2.42 (3H, s, CH_3Ar), 2.56 (3H, s, N=CCH_3), 4.08 (2H, q, *J* 7.2, CH_2CH_3), 4.62 (2H, s, CH_2CO_2Et), 7.31 (2H, d, *J* 8.4, H-arom.), 7.79 (2H, d, *J* 8.4, H-arom.). HRMS, [M + H]$^+$: found 300.09032, calc. 300.09002.

(Ethoxycarbonyl)methyl ester of *N*-(4-chlorobenzenesulfonyl)-imidoylacetic acid 5h. Yield 0.19 g (28%), colourless liquid, $R_f = 0.26$ (hexane–CH_2Cl_2 3 : 1) (Found: C, 45.1; H, 4.45; N, 4.3; S, 10.1. Calc. for $C_{12}H_{14}NO_5SCl$: C, 45.1; H, 4.4; N, 4.4; S, 10.0%); ν_{max}(KBr)/cm^{-1} 2889vs, 1693m, 1561m, 1347m, 1130m, 636m; δ_H(300 MHz, $CDCl_3$, Me_4Si) 1.09 (3H, t, *J* 7.3, CH_2CH_3), 2.53 (3H, s, N=CCH_3), 4.01 (2H, q, *J* 7.3, CH_2CH_3), 4.54 (2H, s, CH_2CO_2Et), 7.40 (2H, d, *J* 8.5, H-arom.), 7.75 (2H, d, *J* 8.5, H-arom.); *m*/*z* (EI) 319 (M$^+$, 3.8%), 274 (3.3), 216 (10), 175 (95), 152 (6.1), 128 (7.2), 111 (100.0), 103 (87.5), 75 (72.5), 59 (10.0), 50 (13.8), 42 (50).

N-Alkylation of the imide 1a using alkyl halides

(a) A solution of dimethyl bromomalonate (1 g, 4.7 mmol) in 1 mL DMF was added to 1 g (4.9 mmol) of sodium salt **1a**-Na in 2 mL DMF. The resultant mixture was heated for 3 h at 70 °C, cooled, poured out into 15 mL of water, and the precipitated *N*-alkylimide **6a** was filtered off and crystallized from a mixture of CH_2Cl_2–hexane = 1 : 1. In a similar reaction with diethyl bromomalonate, after heating for 5 h at 120 °C, *N*-(ethoxycarbonyl)methyl saccharin **6b** was isolated in 95% yield.

(b) A solution of 2.19 g (0.018 mol) ethyl chloroacetate in 4 mL DMF was added to 3.69 g (0.018 mol) of saccharin **1a** sodium salt in 4 mL DMF. The resulting mixture was heated at 100 °C for 8 h, cooled, poured into 20 mL of water, and precipitated crystals of *N*-alkylimide **6b** were filtered off and recrystallized from a mixture of CH_2Cl_2–petroleum = 1 : 1.

***N*-(Dimethoxycarbonyl)methyl-1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide 6a.** Yield 0.9 g (61%), colourless crystals, $R_f = 0.14$ (hexane–Et_2O 2 : 1), mp 156–157 °C (from CH_2Cl_2–hexane) (Found: C, 46.0; H, 3.6; N, 4.3. Calc. for $C_{12}H_{11}NO_7S$: C, 46.0; H, 3.5; N, 4.5%); ν_{max}($CHCl_3$)/cm^{-1} 3000s, 2937vs, 2298vs, 1745m, 1340s, 1177m; δ_H(300 MHz, $CDCl_3$, Me_4Si) 3.87 (6H, s, 2OCH_3), 5.26 (1H, s, NC*H*), 7.84–8.07 (4H, m, H-arom.); *m*/*z* (EI) 313 (M$^+$, 2.9%), 282 (3.9), 269 (18.4), 254 (84.2), 226 (36.8), 190 (26.3), 183 (68.4), 166 (18.4), 162 (13.1), 152 (15.7), 146 (28.9), 130 (13.1), 118 (10.5), 104 (76.3), 76 (100.0), 59 (42.1), 50 (55.2).

***N*-(Ethoxycarbonyl)methyl-1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide 6b (R^3 = CO_2Et).** Yield 4.3g (89%), colourless crystals, $R_f = 0.4$ (hexane–CH_2Cl_2 1 : 1), mp 105–106 °C (from CH_2Cl_2) (lit.,[16a] 107 °C;[16b] 94–95 °C) (Found: C, 49.2; H, 4.15; N, 5.2. Calc. for $C_{11}H_{11}NO_5S$: C, 49.1; H, 4.1; N, 5.2%); ν_{max}(KBr)/cm^{-1} 3446 (73), 2992 (75), 1749 (49), 1459 (64), 1267 (64); δ_H(200 MHz, $CDCl_3$, Me_4Si) 1.25 (3H, t, *J* 7.2, OCH_2CH_3), 4.23 (2H, q, *J* 7.2, OCH_2CH_3), 4.42 (2H, s, CH_2CO_2Et), 7.86–8.05 (4H, m, H-arom.).

Synthesis and catalytic decomposition of diazo saccharin 11

(a) To a solution of the Na-salt of saccharin **1a** (9.8 g, 0.048 mol) in 12 mL DMF was added 10.1 g (0.048 mol) of γ-bromoacetoacetic ester under heating to 50 °C. The mixture was stirred at 90 °C for 3 h, cooled, poured into 100 mL of cold water, and the precipitated crystals were filtered off, washed with water and dried. To prepare an analytically pure sample the resultant substance **6c** was recrystallized from a mixture of petroleum–CH_2Cl_2 = 1 : 1.

***N*-(3′-Ethoxycarbonyl-2′-oxopropyl)-1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide 6c.** Yield 6.8 g (46%), colourless crystals, R_f = 0.35 (hexane–Et_2O 1 : 1), mp 100–101 °C (from CH_2Cl_2–petroleum) (Found: C, 50.2; H, 4.2; N, 4.5. Calc. for $C_{13}H_{13}NO_6S$: C, 50.2; H, 4.2; N, 4.5%); ν_{max}(KBr)/cm^{-1} 3469s, 2981vs, 1731m, 1330m, 1184m; δ_H(200 MHz, $CDCl_3$, Me_4Si) 1.27 (3H, t, *J* 7.0, OCH_2CH_3), 3.6 (2H, s, $COCH_2CO$), 4.21 (2H, q, *J* 7.0, OCH_2CH_3), 4.67 (2H, s, NCH_2), 7.83–8.03 (4H, m, H-arom.); *m*/*z* (EI) 311 (M$^+$, 3.2%), 265 (13.5), 266 (16.2), 196 (100.0), 169 (8.1), 132 (59.3), 115 (40.1), 104 (35.4), 87 (13.5), 76 (29.7), 50 (16.0), 43 (51.4).

(b) A solution of Et_3N (0.71 g, 7 mmol) in 5 mL CH_2Cl_2 was added under cooling to a mixture of *N*-alkyl saccharin **6c** (2 g, 6.4 mmol) and *p*-*N*-(acetyl)benzenesulfonyl azide (1.52 g, 6.7 mmol) in 10 mL CH_2Cl_2. The obtained mixture was stirred at 18–20 °C until completion of the diazotransfer process (*ca.* 2 h, control *via* TLC). The precipitated sulfonamide was separated by filtration, and the residue from the mother liquid after evaporation of the solvent and Et_3N was chromatographed on silica gel (20 g, eluent: petroleum–diethyl ether = 1 : 4). The resulting diazocompound **11** was recrystallized from diethyl ether.

***N*-(3′-Diazo-3′-ethoxycarbonyl-2′-oxopropyl)-1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide 7.** Yield 1.8 g (84%), pale-yellow crystals, R_f = 0.25 (hexane–Et_2O 1 : 1), mp 147–148 °C (from Et_2O) (Found: C, 46.3; H, 3.3; N, 12.4. Calc. for $C_{13}H_{11}N_3O_6S$: C, 46.3; H, 3.3; N, 12.5%); ν_{max}(KBr)/cm^{-1} 3525vs, 2154s, 1739m, 1708m, 1673s, 1338m, 1309w; δ_H(300 MHz, $CDCl_3$, Me_4Si) 1.36 (3H, t, *J* 7.2, OCH_2CH_3), 4.21 (2H, q, *J* 7.2, OCH_2CH_3), 4.99 (2H, s, NCH_2CO), 7.83–8.09 (4H, m, H-arom.); δ_C(75.5 MHz, $CDCl_3$, Me_4Si) 14.2 (CH_3CH_2O), 45.2 (NCH_2), 61.9 (OCH_2), 75.7 (C=N_2), 121.0, 125.1, 126.9, 134.4, 135.0, 137.6 (C-arom.), 159.0 (NC=O), 159.0 (CO_2Et), 182.5 (CH_2C=O); *m*/*z* (EI) 337 (M$^+$, 1.1%), 309 (8.3), 292 (3.7), 282 (2.3), 212 (7.9), 196 (100.0), 169 (8.3), 145 (15.3), 132 (11.1), 104 (27.9), 77 (27.8), 76 (28.0), 69 (6.9), 50 (11.6).

(c) To a solution of diazosaccharin **7** (1.0 g, 2.9 mmol) and 3.26 g (23 mmol) DMAD in 5 mL CH_2Cl_2 with stirring was added 13 mg (29.4 μmol) of dirhodium tetraacetate. The evolution of N_2 started 10 min after the addition of the catalyst and proceeded for 12 h (control using TLC), therewith the reaction product crystallized gradually from the reaction mixture as a white powder. After complete decomposition of the diazo compound **7** the precipitate of adduct **8** was filtered off and carefully washed with dichloromethane.

2,3-Dimethoxycarbonyl-4-ethoxycarbonyl-5-oxo-8,8-dioxo-9,10-benzo-11-oxa-8-thia-7-aza-tricyclo[5,3,1^{1,4}0^{1,7}]undec-2,9-dien 8. Yield 0.8 g (61%), colourless crystals, R_f = 0.09 (hexane–CH_2Cl_2 1 : 3), mp 198–199 °C (from CH_2Cl_2) (Found: C, 50.6; H, 3.8; N, 3.1. Calc. for $C_{19}H_{17}NO_{10}S$: C, 50.55; H, 3.8; N, 3.1%); ν_{max}(KBr)/cm^{-1} 3627m, 2956m, 1758vs, 1733vs, 1648s, 1313vs; δ_H(600 MHz, $CDCl_3$, Me_4Si) 1.31 (3H, t, *J* 7.2, CH_3), 3.65 (3H, s, CH_3), 3.94 (3H, s, CH_3), 4.33, 4.40 (2H, dq, *J* 10.8, 7.12, OCH_2CH_3), 4.32 (1H, d, *J* 18.8, NCH_2CO), 4.72 (1H, d, *J* 18.8, NCH_2CO), 7.69–7.93 (4H, m, H-arom.); δ_C(150 MHz, $CDCl_3$, Me_4Si) 14.1 (OCH_2CH_3), 48.2 (6-C), 53.3 (OCH_3), 53.6 (OCH_3), 63.7 (OCH_2CH_3), 92.5 (4-C), 97.6 (1-C), 121.8, 126.2, 131.2 (10-C), 132.7, 134.1, 135.5 (9-C) (C-arom.), 134.6 (2-C), 143.9 (3-C), 159.3, 161.2, 161.9 (all C=O, ester), 184.8 (5-C); *m*/*z* (EI) 451 (M$^+$, 1.1%), 423 (28.5), 350 (7.1), 331 (38.5), 286 (100.0), 258 (27.1), 227 (7.8), 169 (6.4), 141 (11.4), 59 (5.7).

Crystal structure determination of imidates 4c and 5b

Single crystals of the compounds **4c** and **5b** suitable for X-ray diffraction were selected directly from the analytical samples.

Table 3 Crystallographic data for imidates **4c** and **5b**

Parameter	**4c**	**5b**
Formula	$C_{12}H_{10}NO_5S$	$C_{13}H_{14}NO_7ClS$
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	7.6162(5)	8.051(1)
b/Å	9.1924(5)	8.774(2)
c/Å	10.6592(6)	11.745(2)
α/°	107.647(1)	91.894(3)
β/°	97.265(1)	105.771(3)
γ/°	110.172(1)	90.555(3)
V/Å^3	644.88(7)	797.9(2)
Z	2	2
D_c/g cm^{-3}	1.443	1.514
μ(Mo Kα)/mm^{-1}	0.266	0.405
$2\theta_{max}$/°	28.6	27.0
Measured/unique reflections	4173/2907	4891/3383
R_{int}	0.0138	0.0159
Parameters refined	217	264
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0379, 0.1069	0.0425, 0.1046
$R1$, $wR2$ (all data)	0.0417, 0.1104	0.0639, 0.1219

Crystallographic measurements were made using an AXS BRUKER 1 K CCD-detector (graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), empirical absorption correction using SADABS.[27a] The essential experimental conditions and crystal data are given in Table 3. The structures were solved by direct methods and refined in the anisotropic approximation for the non-hydrogen atoms using SHELXS-86 and SHELXL-97.[27b,c] All H atoms were located by difference Fourier map and refined isotropically.

CCDC reference numbers 270185 (**4c**) and 270186 (**5b**). See http://dx.doi.org/10.1039/b508317f for crystallographic data in CIF or other electronic format.

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