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To the dear memory of Professor I.K.Korobitsyna

Chemistry of Diazocarbonyl Compounds: XX.* Chemoselective O-Alkylation of 3(2*H*)-Oxoisothiazole-1,1-dioxides with the Use of Rh(II)-Carbenoids

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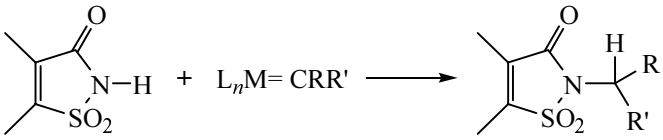
Abstract—Catalytic decomposition of diazoacetylacetone, ethyl diazoacetate, and diethyl diazomalonate effected by dirhodium tetraacetate in the presence of 3(2H)-oxoisothiazole-1,1-dioxides resulted in O-alkylation of amide carbonyl of the heterocycle affording the corresponding enol ethers in preparative yield. The reaction occurred chemoselectively. The 1,3-dicarbonyl derivatives of 3-hydroxyisothiazole-1,1-dioxides obtained in contrast to analogous N-alkylated products are not enolized in solutions and in crystals.

Within last 10–15 years the synthetic potential of saccharine chemistry was considerably extended with new procedures for functionalization and transfunctionaliation of this heterocyclic system, for expansion and opening of the ring, fusion of heterocycles, for preparation of chiral derivatives of isothiazole-1,1-dioxides, etc. [2–4]. Besides the compounds of this class attract attention for they possess versatile biological activity [2–4], and saccharin although its harmlessness for human organism is dubious [5] still is widely used as substitute for sugar. Therefore the study of reactivity underlying development of new methods of oxoisothiazole-1,1,-dioxides functionalization remains an urgent task of organic chemistry.

We investigate of reactions of saccharine and its analogs with metallocarbenes and other intermediates originating from diazo compounds [6]. A molecule of 3(*2H*)-oxoisothiazole-1,1-dioxide **A** possesses several nucleophilic groups, potential reaction sites for attack of carbenoids **B** that have pronounced electrophilic character [7, 8]. It was however presumable that intermediate **B** would react first of all with the nitrogen of the heterocycle, for the electrophilic reagents were known to react with saccharins with a free N–H groups to give N-substituted derivatives [2, 3]. A similar trend was observed in the formerly described reactions of amides and lactams with diketocarbenoids and other structurally related substances [9].**

In this connection we expected that the reaction of carbenoids **B** with oxaisothiazole-1,1-dioxides **A** would afford N-alkylated products **C** and thus we would be able



A **B** **C**

I, R, R' = $(CH)_4$ (**a**), $(CH_2)_4$ (**b**), $(CH_2)_5$ (**c**); R = Ph, R' = Me (**d**); R, R' = Me (**a**); R = Me, R' = O-*i*-Pr (**b**); R, R' = OFt (**c**); R, R' = $CH_2C(Me_2)CH_2$ (**d**); R, R' = $OC(Me_2)O$ (**e**); $L_n = (OAc)_n$. R^1, $R^2 = (CH)_4$, $R^3 = R^4$ = Me (**a**); R^1, $R^2 = (CH_2)_5$, $R^3 = R^4$ = Me (**b**); R^1 = Ph, $R^2 = R^3 = R^4$ = Me (**c**); R^1, $R^2 = (CH)_4$, R^3 = Me, R^4 = O-*i*-Pr (**d**); R^1, $R^2 = (CH_2)_4$, $R^3 = R^4$ = OEt (**e**); R^1 = Ph, R^2 = Me, $R^3 = R^4$ = OEt (**f**).

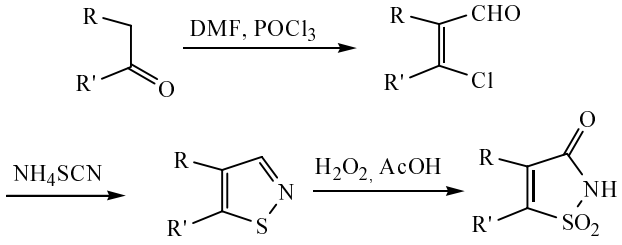
* For communication XIX see [1].

** The term "diketocarbenoids" is used here as a general notation of diacyl-, acyl(alkoxycarbonyl)-, and di(alkoxycarbonyl)carbenoids with two carbonyls in the α,α'-position with respect to carbenoid carbon.

to develop a new procedure for functionalization of the N–H bond of the substrate.

We report here on results of catalytic decomposition by rhodium tetraacetate of a series of diazodicarbonyl compounds in the presence of saccharine and its analogs. We selected as objects of investigation 3(*2H*)-oxo-1,2-benzisothiazole-1,1-dioxide (**Ia**) (saccharine), its hydrogenised analog 3(*2H*)-oxo-4,5,6,7-tetrahydro-1,2-benzisothiazole-1,1-dioxide (**Ib**), 3(*2H*)-oxocyclohepta-[*d*]isothiazole-1,1-dioxide (**Ic**), and also a monocyclic representative of the isothiazoles series under study, 5-methyl-4-phenyl-3(*2H*)-oxoisothiazole-1,1-dioxide (**Id**). Except for saccharine (**Ia**) all other compounds were prepared by a three-stage procedure from the corresponding ketones involving as the final stage isothiazoles oxidation with hydrogen peroxide in the glacial acetic acid [10, 11].

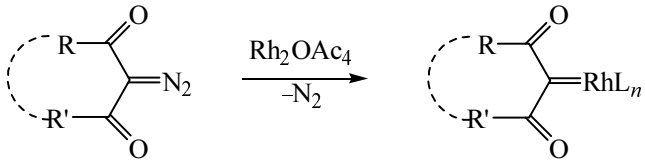
In order to elucidate the opportunities and limitations of the process under investigation we used for generating diketocarbenoids **III** various acyclic and cyclic 2-diazo-1,3-dicarbonyl compounds: diazoacetylacetone (**IIa**), ethyl diazoacetoacetate (**IIb**), diethyl diazomalonate (**IIc**), diazodimedone (**IId**), and its heterocyclic analog, 5-diazo-4,6-dioxo-2,2-dimethyl-1,3-dioxane (**IIe**).



Ia–d

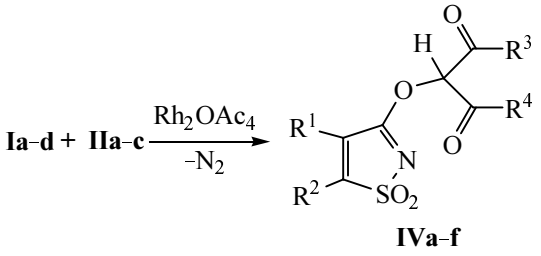
I, R, R' = $(CH)_4$ (**a**), $(CH_2)_4$ (**b**), $(CH_2)_5$ (**c**); R = Ph, R' = Me (**d**).

The catalytic decomposition of diazo compounds **IIa–e** in the presence of $Rh_2(OAc)_4$ was carried out in anhydrous dichloromethane or 1,2-dichloroethane at 15–20°C or at elevated temperature; on reaction completion (TLC monitoring) the reaction mixture was separated on a column packed with silica gel, and the isolated substances were recrystallized.



IIa–e **IIIa–e**

The catalytic reaction of oxoisothiazole-1,1-dioxides **Ia–d** with acyclic diazodicarbonyl compounds **IIa–c**



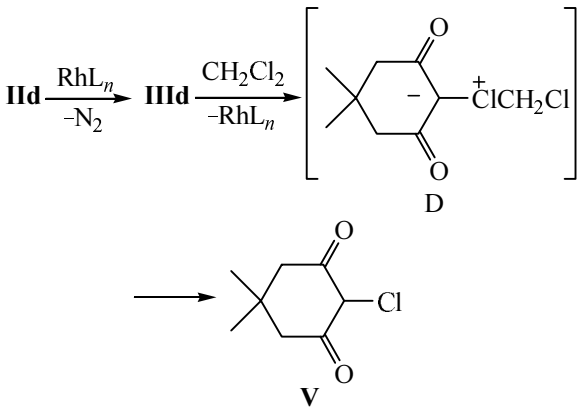
IVa–f

R^1, R^2 = $(CH)_4$, R^3 = R^4 = Me (**a**); R^1, R^2 = $(CH_2)_5$, R^3 = R^4 = Me (**b**); R^1 = Ph, R^2 = R^3 = R^4 = Me (**c**); R^1, R^2 = $(CH)_4$, R^3 = Me, R^4 = O-*i*-Pr (**d**); R^1, R^2 = $(CH_2)_4$, R^3 = R^4 = OEt (**e**); R^1 = Ph, R^2 = Me, R^3 = R^4 = OEt (**f**).

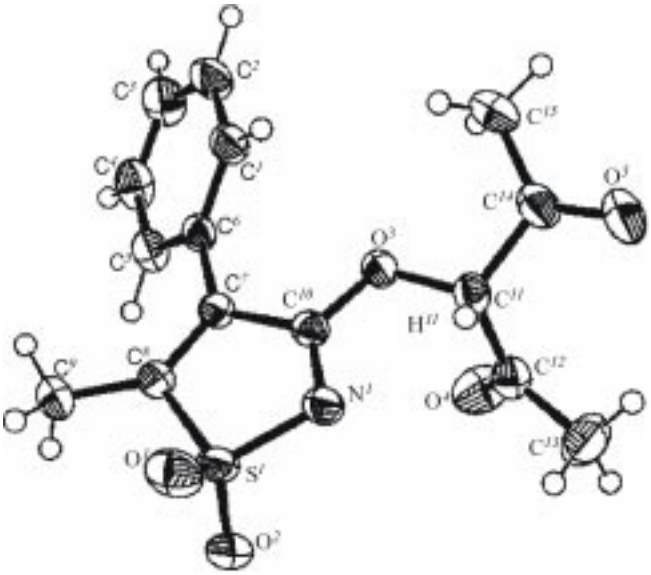
yielded adducts of substrates **I** and carbenoid intermediates **IIIa–c** at a molar ratio 1:1. The thorough spectral investigations (see further) showed that the compounds obtained had a structure of enol ethers of oxoisothiazoles **IVa–f** and not of expected N-alkylamides, i.e. formally they are products of diketocarbenoids **III** insertion into O–H bond of the enol form of 3(2*H*)-oxoisothiazoles **I**.

Under conditions we developed for reactions of diazo compounds **IIa–c** and subsequent separation of reaction products ethers **IV** were obtained in preparative yields (73–95%), and according ^{1}H NMR spectra registered just after completion of the reaction side products in significant amounts were not detected.

Reaction with cyclic diazodicarbonyl compounds **IId, e** under similar conditions obviously proceeded in different way. At catalytic decomposition of diazodimedone **IId** 5,5-dimethyl-2-chloro-1,3-cyclohexanedione (**V**) was isolated in over 60% yield. It is presumable that in this case the corresponding diacylcarbenoid **IIId** reacts mainly with the solvent (CH_2Cl_2) giving rise to an intermediate halogenonium ylide D that through a series of further transformations affords finally 5,5-dimethyl-2-chloro-1,3-cyclohexanedione (**V**).



The catalytic decomposition of heterocyclic analog of diazodimedone (**IId**), 5-diazo-4,6-dioxo-2,2-dimethyl-1,3-



Molecular strusture of 3-(diacetylmethoxy)-5-methyl-4-phenyl-1,2-isothiazole-1,1-dioxide molecule **(IVc)** according to X-ray data

dioxane (**IIe**), in the presence of $Rh_2(OAc)_4$ under the same conditions proceeded very slow. As shown by TLC even after several days the reaction mixture contained considerable amounts of initial reagents **Ia** and **IIe**. The attempts to intensify the process by adding new portions of the catalyst or by heating to 83°C (boiling in 1,2-dichloroethane) resulted in multicomponent mixtures of products. We failed to isolate individual compounds from the mixture.

Inasmuch as published data on spectral characteristics of O-alkylation products generated by treating imides and amides with diketocarbenoids were lacking we thoroughly studied ethers **IVa–f** by means of mass spectrometry, IR, ^1H and ^{13}C NMR spectroscopy. This part of investigation was aimed at determination of characteristic spectral parameters of enol O-ethers **IV** for making it possible to use these characteristics for identification of analogous compounds by spectral methods. Besides an X-ray diffraction study was performed with adduct **IVc** containing two acetyl substituents in the 1,3-dicarbonyl fragment of the molecule. The main results of the analytical part of the study are considered below.

In the electron-impact mass spectra of all prepared compounds **IVa–f** were observed molecular ion peaks $[M]^{+\cdot}$ (*m/z*: 281, 299, 321, 325, 345, 381 respectively), therewith for ethers **IVe, f** containing two ethoxycarbonyl groups in the carbenoid fragment of the molecule these peaks were among the most abundant in the spectra (70 and 45% from the maximum). In the spectra of enol ethers **IVa–d** containing two or at least one acetyl group in the molecular structure the molecular ion peaks were of a very low intensity (1–5%), apparently due to their low stability against electron impact and easy ejection of acetyl cation $(CH_3C{=}O)^+$ or ketene molecule $(CH_2{=}C{=}O)$ from these molecular ions. This is evidenced by appearance in the mass spectra of compounds **IVa–d** of ions having *m/z* 43 and maximal abundance (100%).

In general the first stages of molecular ions fragmentaion for ethers **IVa–f** involve successive degradation of the side chain, namely, of the carbenoid fragment of the molecule of these heterocyclic compounds with elimination of molecules C_2H_4, C_3H_7, CO, $CH_2C{=}O$, H_2O, CH_3CO_2H etc. that is common for carboxylic acids esters and 1,3-dicarbonyl compounds [12].

Another characteristic feature of fragmentation of molecular and fragment ions of ethers **IVa–f** is intermediate formation under conditions of mass spectrum recording of ions corresponding to initial sulfonamides **Ia–d** that have taken up one hydrogen atom and possessing even molecular masses of 184, 188, 202, and 224 respectively. The successive fragmentation paths of these ions are very similar to that of molecular ions of oxoisothiazole-1,1-dioxides **Ia–d** and their simplest 3-alkoxy derivatives occurring under similar conditions[12, 13].

In the IR spectrum of each obtained compound **IVa–f** usually in the region 1000–2000 cm^{-1} a number of strong absorption bands is observed of stretching vibrations of carbonyl [1718–1746 (C=O oxo) and 1762–1771 cm^{-1} (C=O ester)], C=N group (1574–1650 cm^{-1}), and SO_2 group (1361–1399 and 1164–1176 cm^{-1}). These absorption bands are consistent with the assumed structure of compounds **IV** [2, 3, 11]. However the IR spectra of these compounds do not contain unambiguous indications of the existence of enol tautomers.

^1H and ^{13}C NMR spectra of adducts obtained contain complete sets of proton and carbon signals corresponding to the structures of enol ethers **IVa–f**. The signals from the oxothiadiazole and diketocarbenoid fragments of the molecule show that the adducts are formed in 1:1 ratio. The position of signals is in general close to the corresponding parameters in the NMR spectra of initial **Ia–d** and **IIa–c**. The main change in the spectra of compounds **IV** compared to those of the initial reagents consisted in appearance of a clear one-proton singlet from a methine group $[OCH(COR^3)COR^4]$ in the region 5.6–6.0 ppm of the ^1H NMR spectra and a strong signal from the carbon atom of the same group in the region 76–91 ppm of the ^{13}C NMR spectra.

The position of the methine carbon is strongly affected by the character of substituents R^3 and R^4, same as is observed for the position of the carbon from the CN_2 groups in initial diazodicarbonyl compounds **IIa–c**. The most downfield position (90–91 ppm) hold signals of carbon atoms from OCH group of adducts **IVa–c** with two acyl substituents. On replacing one of these by an alkoxycarbonyl group in compound **IVd** this signal shifted to stronger field by 7.3–7.9 ppm (the signal was observed at 82–83 ppm). Introducing one more alkoxycarbonyl group into the molecules of adducts **IVe, f** resulted in still further upfield shift of the OCH group signal by 6.5–7.5 ppm (to 76–77 ppm).

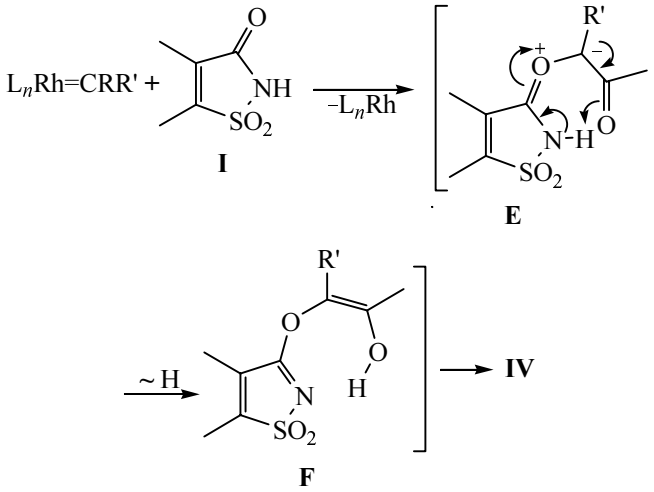
It should be pointed out that compounds **IVa–d** with acyl groups in the 1,3-dicarbonyl fragment of the molecule are practically nonenolized in chloroform solution (according to ^1H and ^{13}C NMR data) and in the crystalline state (according to X-ray analysis). This fact distinguished these compounds from analogous N-alkyl derivatives prepared from amides and lactames that exist exclusively in enol form [8, 14]. This feature significantly simplifies the identification in the reaction mixtures of the O-alkylated products under consideration by spectral methods.

Hence it can be concluded that the carbon signals from the methine group (O<u>C</u>H) in the ^{13}C NMR spectra of enol ethers **IV** are located in a narrow region of spectrum characteristic of each definite type of substituents R^3 and R^4. Therefore these signals can be a reliable source of identification in reaction mixtures of products of O-alkylation at the amide carbonyl group. It should be also noted that the methine signals under discussion in the ^1H and ^{13}C NMR spectra of compounds of **IV** type are located in "free", not overloaded with other resonances spectral regions thus facilitating their efficient application to a diagnostic task.

The molecular structure of one among the adducts, 3-(diacetylmethoxy)-5-methyl-4-phenyl-1,2-isothiazole-1,1-dioxide (**IVc**), established by X-ray diffraction analysis is presented on figure, the main geometric parameters of molecule **IVc** are given in table. These data unambiguously testify in favor of the O-(alkyl)isothiazole structure of compounds obtained, and also confirm the lack of enolization (in crystal) in arising from this reaction derivatives **IV** of 1,3-dicarbonyl compounds.

Main structural parameters of 3-(diacetylmethoxy)-5-methyl-4-phenyl-1,2-isothiazole-1,1-dioxide molecule (**IVc**)

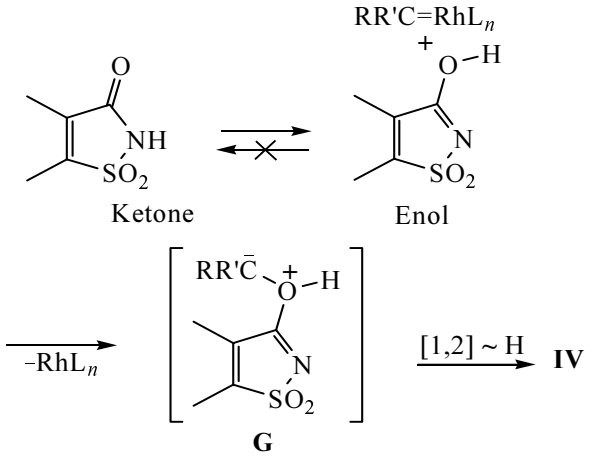
Bond	d, Å	Bond angles	ω, deg	Torsion angles	τ, deg
S^1–O^1	1.4248(13)	$O^1S^1O^2$	117.41(7)	$O^1S^1N^1C^{10}$	–115.72(12)
S^1–O^2	1.4312(13)	$O^1S^1N^1$	110.57(8)	$O^2S^1N^1C^{10}$	113.53(12)
S^1–N^1	1.6503(14)	$O^2S^1N^1$	109.35(8)	$C^8S^1N^1C^{10}$	–0.27(13)
S^1–C^8	1.7697(16)	$O^1S^1C^8$	110.79(8)	$C^1C^6C^7C^8$	139.03(18)
O^3–C^{10}	1.3230(18)	$O^2S^1C^8$	109.64(8)	$C^5C^6C^7C^8$	–39.6(2)
O^3–C^{11}	1.4414(19)	$N^1S^1C^8$	97.22(7)	$C^1C^6C^7C^{10}$	–43.4(2)
O^4–C^{12}	1.199(2)	$C^{10}O^3C^{11}$	114.32(12)	$C^5C^6C^7C^{10}$	137.89(16)
O^5–C^{14}	1.196(2)	$C^{10}N^1S^1$	106.81(11)	$C^6C^7C^8S^1$	177.12(13)
N^1–C^{10}	1.287(2)	$C^8C^7C^{10}$	108.82(13)	$C^{10}C^7C^8S^1$	–0.72(15)
C^1–C^2	1.383(3)	$C^7C^8C^9$	133.98(16)	$N^1S^1C^8C^7$	0.63(13)
C^1–C^6	1.395(2)	$C^7C^8S^1$	107.50(12)	$S^1N^1C^{10}O^3$	–178.19(12)
C^3–C^4	1.381(3)	$C^9C^8S^1$	118.51(13)	$S^1N^1C^{10}C^7$	–0.13(18)
C^4–C^5	1.384(3)	$N^1C^{10}O^3$	122.13(14)	$C^{11}O^3C^{10}N^1$	0.3(2)
C^5–C^6	1.400(2)	$N^1C^{10}C^7$	119.64(13)	$C^{11}O^3C^{10}C^7$	–177.80(13)
C^6–C^7	1.477(2)	$O^3C^{10}C^7$	118.21(13)	$C^8C^7C^{10}N^1$	0.6(2)
C^7–C^8	1.338(2)	$O^3C^{11}C^{14}$	109.06(14)	$C^8C^7C^{10}O^3$	178.75(14)
C^7–C^{10}	1.495(2)	$O^3C^{11}C^{12}$	109.51(13)	$C^6C^7C^{10}O^3$	0.8(2)
C^8–C^9	1.485(2)	$C^{14}C^{11}C^{12}$	111.34(14)	$C^{10}O^3C^{11}C^{14}$	–163.93(14)
C^{11}–C^{14}	1.533(2)	$O^3C^{11}H^{11A}$	108.6(11)	$C^{10}O^3C^{11}C^{12}$	74.01(16)
C^{11}–C^{12}	1.539(2)	$C^{14}C^{11}H^{11A}$	112.7(11)	$O^3C^{11}C^{12}O^4$	22.4(2)
C^{11}–H^{11A}	0.94(2)	$C^{12}C^{11}H^{11A}$	105.5(11)	$C^{14}C^{11}C^{12}O^4$	–98.3(2)
C^{12}–C^{13}	1.493(3)	$O^4C^{12}C^{13}$	124.73(18)	$O^3C^{11}C^{14}O^5$	–169.6(2)
C^{14}–C^{15}	1.494(3)	$O^4C^{12}C^{11}$	119.43(16)	$C^{12}C^{11}C^{14}O^5$	–48.7(3)
		$C^{13}C^{12}C^{11}$	115.81(17)	$O^3C^{11}C^{14}C^{15}$	12.3(3)
		$O^5C^{14}C^{15}$	123.14(18)	$C^{12}C^{11}C^{14}C^{15}$	133.3(2)
		$O^5C^{14}C^{11}$	118.25(18)		
		$C^{15}C^{14}C^{11}$	118.58(17)		



The formation mechanism of enol ethers **IV** that may be formally regarded as carbenoid insertion products into the O–H bond of the enol form of oxoisothiazole-1,1-dioxides **I** apparently primarily involves an attack of electrophilic diketocarbenoid **III** on the oxygen of a carbonyl group affording intermediate carbonyl ylide **E** [15, 16]. The subsequent stabilization of ylide **E** giving enol ether **IV** may occur either through a 1,4-sigmatropic shift of a proton [16] of NH group or by migration of this proton to the anionic site of the carbonylylide via enol intermediate **F**.

The products of insertion into the O–H bond **IVa–f** hardly can arise along "oxonium" pathway, i.e. involving enol forms of cyclic sulfonimides **I** and then oxonium ylides **G**.

Spectral investigations of 3-oxobenzo-1,2-isothiazoles, saccharin, and its analogs **I** show [2, 3, 11] that these carbonyl compounds exist in solutions and in crystalline state exclusively in the ketoamide form and contain no enol tautomer. At the same time the presence of the latter can be regarded as a necessary condition for proceeding of the process under consideration through oxonium ylide



G along the above scheme that is generally accepted for substrates containing O–H bond and for enolized carbonyl compounds [7, 8, 17].

The reaction of saccharin and its analogs that we have discovered is a new process of O-alkylation with metallocarbenes of amide carbonyl groups in oxoisothiazole-1,1-dioxides that provides a possibility in one stage to introduce polycarbonyl substituents into the position *3* of the heterocyclis system and that nobody has investigated before.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on spectrometer Brucker 500 at operating frequencies 500 (^{1}H) and 126 MHz (^{13}C) in $CDCl_3$, internal reference TMS. Mass spectra of compounds **IVa–f** were measured at direct admission of samples into the ionization chamber, ionizing electrons energy 70 eV. IR spectra were recorded an spectrophotometer Specord 75IR from KBr pellets.

X-ray diffraction study was carried out on a colorless single crystal of compound **IVc**, crystal habit 0.3 × 0.25 × 0.3 mm, obtained by crystallization from a mixture CH_2Cl_2–Et_2O, ~1:2. Crystals of O-ether **IVc** tetragonal, *a* 10.433(4), *b* 10.433(4), *c* 14.425(1) Å, $\alpha = \beta = \gamma = 90°$, *V* 1570.2(7) Å^3, C_{calc} 1.359 g/cm^3, space group *P4(3)*. The measurement was carried out at 293(2) K on a diffractometer Siemens SMART CCD, using radiation of wavelength 0.71073 Å. Extinction factors were evaluated by SADABS program, the processing of structural data was performed by SHELXS97 software [18].

Saccharin (**Ia**) was prepared from commercial saccharine sodium salt, tetrahydrosaccharin **Ib** and oxoisothiazoles **Ic, d** were synthesized by procedures [10, 11, 19]. Oxoisothiazoles **Ia–d** were additionally purified by sublimation in a vacuum at 40°C (0.05 mm Hg). Melting points of sublimed compounds are as follows: 228–229 (**Ia**), 135–136 (**Ib**), 116–117 (**Ic**), 183–184°C (**Id**).

Diazocarbonyl compounds IIa–e were synthesized by diazotransfer [20, 21] and purified by distillation or sublimation in a vacuum. Diazoacetylacetone (**IIa**), bp 29–30°C (0.1 mm Hg), n_D^{20} 1.5071. ^{13}C NMR spectrum (0.2 mol l^{-1}), δ, ppm: 191.5 (C=O), 82.5 (CN_2), 26.6 (CH_3). Ethyl diazoacetoacetate (**IIb**), bp 40–42°C (1.5 mm Hg), n_D^{20} 1.4725. ^{13}C NMR spectrum (0.3 mol l^{-1}), δ, ppm: 183.9 (C=O), 161.4 (C=O), 76.3 (CN_2), 61.4 (CH_2), 28.1 ($CO\underline{C}H_3$), 14.3 ($CH_2\underline{C}H_3$). Diethyl diazomalonate (**IIc**), bp 44–45°C (0.1 mm Hg), n_D^{20} 1.4830. ^{13}C NMR spectrum (0.2 mol l^{-1}), δ, ppm: 161.2 (C=O), 71.9 (CN_2), 61.7 (CH_2), 14.4 (CH_3). 2-Diazo-5,5-dimethyl-1,3-cyclohexanedione (**IId**), mp 107–108°C (subl.).

^{13}C NMR spectrum (0.2 mol l^{-1}), δ, ppm: 189.6 (C=O), 83.05 (CN_2), 50.5 (CH_2), 31.0 ($\underline{C}Me_2$), 28.3 (CH_3). 5-Diazo-2,2-dimethyl-1,3-dioxane-4,6-dione (**IIe**), mp 96–97°C (subl.). ^{13}C NMR spectrum (0.2 mol l^{-1}), δ, ppm: 158.5 (C=O), 107.0 (O–C–O), 65.4 (CN_2), 26.6 (CH_3).

The reaction progress was monitored by TLC on Silufol UV-254 plates, for column chromatography was used neutral silica gel Chemapol L 40/100 or Merck (70–230 mesh).

The procedure for catalytic decomposition of acyclic diazodicarbonyl compounds **IIa–c** was published in [6].

Catalytic decomposition of 2-diazo-5,5-dimethyl-1,3-cyclohexanedione (IId). To a solution of 0.42 g (2.5 mmol) of diazodimedone **IId** in 20 ml of dichloromethane was added 0.37 g (2 mmol) of saccharine (**Ia**), and at stirring and cooling to 0–5°C 10 mg of dirhodium tetraacetate was charged to the reaction mixture. In 10–15 min the cooling was removed, and the mixture was stirred till the completion of reaction (TLC monitoring). In the course of reaction saccharine (**Ia**) dissolved completely, the green color of the reaction mixture turned brown, and the nitrogen evolution ceased. The mixture was charged on to a small column packed with silica gel, the gradient elution was performed with ethyl ether–petroleum ether mixture. On removing solvents and recrystallization of the main product from a mixture Et_2O–CH_2Cl_2, ~ 2:1, we obtained 0.27 g (61%) 5,5-dimethyl-2-chloro-1,3-cyclohexanedione (**V**), mp 162–165°C (subl.). ^{1}H NMR spectrum (0.2 mol l^{-1}, δ, ppm: 1.11 s (6H, $2CH_2$), 2.47 s (4H, $2CH_2$), 5.70 br.s (~ 1H, CHCl).

Catalytic decomposition of 5-diazo-2,2-dimethyl-1,3-dioxane-4,6-dione (IIe) under similar conditions (2.5 mmol of saccharin, 2.5 mmol of diazo compound, 10 mg of Rh_2OAc_4, CH_2Cl_2) proceeded exceedingly slow. In two days at 18–20°C and after boiling in CH_2Cl_2 the reaction mixture contained mainly initial compounds (TLC data). At separation of the reaction mixture on silica gel we recovered 0.34 g (79.5%) of diazodioxodioxane **IIe** and 0.34 g (74%) of saccharin (**Ia**); we failed to isolate any individual compounds from other fractions.

The reaction carried out in 1,2-dichloroethane at 83°C for 1 h with reagents and catalyst taken in the same amounts afforded a multicomponent mixture (TLC data). However the separation of the mixture on silica gel afforded as in the first run only the initial diazodioxodioxane **IIe** and saccharin (**Ia**) in over 80% yield.

3-(Diacetylmethoxy)benzo[*d*]isothiazole-1,1-dioxide (IVa). Yield 86%, mp 166–168°C (from Et_2O–CH_2Cl_2) [6]. IR spectrum, cm^{-1}: 1720, 1614, 1554, 1401, 1361, 1329, 1212, 1171, 1056. ^{13}C NMR spectrum, δ, ppm: 27.8, 89.8 (OCH), 122.7, 123.9, 126.0, 134.2, 135.2, 144.1, 168.3, 197.0. Mass spectrum, *m/z* (I_{rel}, %): 281 (1.4) $[M]^{+\cdot}$, 264 (0.7), 239 (10.0), 222 (5.7), 217 (3.6), 184 (10.7), 175 (2.9), 166 (4.3), 146 (7.9), 133 (5.0), 103 (32.9), 76 (12.1), 51 (6.7), 43 (100). Found, %: C 51.43, 51.42; H 3.90, 3.91; N 4.93, 4.85; S 11.50, 11.23. $C_{12}H_{11}NO_5S$. Calculated, %: C 51.24; H 3.91; N 4.98; S 11.38.

3-(Diacetylmethoxy)-4,5-pentamethylenisothiazole-1,1-dioxide (IVb). Colorless substance, yield 86%, mp 159–160°C (from a mixture petroleum ether–CH_2Cl_2). IR spectrum, cm^{-1}: 1746, 1718, 1640, 1564, 1447, 1379, 1321, 1216, 1164, 1074, 1108, 996. ^{1}H NMR spectrum (0.3 mol l^{-1}) δ, ppm: 1.83–1.95 m (6H, 3 CH_2), 2.33 s (6H, 2 CH_3), 2.68–2.62 m (4H, 2 CH_2), 5.69 s (1H, OCH). ^{13}C NMR spectrum, δ, ppm: 25.0, 25.5, 26.6, 26.8, 29.5, 27.6, 90.0 (OCH), 132.8, 157.3, 170.9, 196.8. Mass spectrum, *m/z* (I_{rel}, %): 299 (5.0) $[M]^+$, 282 (1.4), 257 (14.3), 240 (3.6), 229 (2.5), 214 (2.1), 202 (5.7), 193 (6.4), 168 (5.0), 151 (7.1), 136 (6.4), 122 (7.9), 99 (7.9), 93 (15.0), 77 (11.4), 65 (10.0), 53 (7.1), 43 (100). Found, %: C 52.49, 52.30; H 5.78, 5.68; N 4.53, 4.52; S 10.30, 10.64. $C_{13}H_{17}NO_5S$. Calculated, %: C 52.17; H 5.68; N 4.68; S 10.70.

3-(Diacetylmethoxy)-5-methyl-4-phenylisothiazole-1,1-dioxide (IVc). Yield 73%, mp 154–155°C (from Et_2O–CH_2Cl_2) [6]. IR spectrum, cm^{-1}: 1724, 1629, 1566, 1420, 1376, 1326, 1209, 1174, 1135. ^{13}C NMR spectrum, δ, ppm: 10.7, 27.9, 90.6 (OCH), 126.9, 129.5, 129.7, 130.0, 130.9, 153.3, 170.6, 197.2. Mass spectrum, *m/z* (I_{rel}, %): 321 (4.6) $[M]^+$, 306 (1.4), 279 (22.1), 257 (7.9), 250 (5.0), 236 (14.3), 224 (7.3), 215 (7.1), 198 (7.1), 186 (8.6), 173 (7.1), 156 (7.1), 144 (6.4), 130 (7.1), 115 (35.7), 99 (9.3), 89 (3.6), 77 (5.0), 63 (2.9), 51 (4.3), 43 (100). Found, %: C 56.11, 56.21; H 4.76, 4.75; N 4.28, 4.36; S 9.79, 9.53. $C_{15}H_{15}NO_5S$. Calculated, %: C 56.07; H 4.67; N 4.36; S 9.96.

3-(Acetylisopropoxycarbonylmethoxy)-benzo[*d*]-isothiazole-1,1-dioxide (IVd). Colorless oily substance, yield 76%. IR spectrum (KBr), cm^{-1}: 1769, 1733, 1616, 1567, 1461, 1393, 1337, 1253, 1173, 1100, 1063. ^{1}H NMR spectrum (0.3 mol l^{-1}), δ, ppm: 1.32 d, 1.35 d (6H, $2CH_3$, *J* 6.2 Hz,), 2.48 s (3H, CH_3C=), 5.20 septet (1H, $OCHMe_2$, *J* 6.2 Hz,), 5.90 s [1H, OCHAc (CO_2-*i*-Pr)], 7.75–7.96 m (4H, arom). ^{13}C NMR spectrum, δ, ppm: 21.8, 21.6, 27.7, 71.9, 82.5(OCH), 122.3, 124.0, 133.8, 134.8, 125.8, 143.8, 162.3, 168.3, 194.9. Mass spectrum, *m/z* (I_{rel}, %): 325 (0.9) $[M]^+$, 283 (1.6), 261 (3.6), 241 (2.1), 219 (3.0), 202 (2.1), 184 (28.6), 175 (4.6), 166 (4.3),

144 (6.7), 118 (3.9), 103 (16.4), 102 (25.7), 84 (12.1), 76 (9.6), 55 (10.0), 43 (100).

3-(Diethoxycarbonylmethoxy)-4,5-tetramethylenisothiazole-1,1-dioxide (IVe). Yield 95%, mp 59–60°C (from a mixture petroleum ether–CH_2Cl_2) [6]. IR spectrum, cm^{-1}: 1768, 1650, 1574, 1399, 1331, 1247, 1166, 1117. ^{13}C NMR spectrum, δ, ppm: 14.1, 20.4, 20.79, 20.84, 21.0, 63.3, 76.3 (OCH), 131.9, 155.2, 162.9, 170.6. Mass spectrum, *m/z* (I_{rel}, %): 345 (70.1) $[M]^+$, 317 (7.1), 299 (41.4), 273 (20.0), 261 (10.0), 245 (16.4), 227 (47.1), 216 (30.7), 199 (9.3), 188 (82.1), 179 (15.0), 169 (40.0), 160 (32.1), 150 (10.7), 131 (25.7), 122 (33.6), 114 (17.1), 107 (60.0), 96 (15.0), 86 (18.6), 79 (100), 69 (21.4), 52 (28.6), 43 (30.0). Found, %: C 48.79; H 5.62; N 3.96; S 9.49. $C_{14}H_{19}NO_7S$. Calculated, %: C 48.69; H 5.50; N 4.05; S 9.27.

3-(Diethoxycarbonylmethoxy)-5-methyl-4-phenylisothiazole-1,1-dioxide (IVf). Colorless substance, yield 80%, mp 104–106°C (from Et_2O–CH_2Cl_2). IR spectrum, cm^{-1}: 1771, 1748, 1650, 1563, 1379, 1332, 1248, 1176, 1098, 1031. ^1H NMR spectrum (0.3 mol l^{-1}), δ, ppm: 1.28 t (6H, $2CH_3$, *J* 7.14 Hz) 2.34 s (3H, CH_3C=), 4.32 q (4H, $2CH_2O$, *J* 7.14 Hz), 5.80 s (1H, OCH), 7.47 br.s (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 10.5, 14.3, 63.6, 77.1 (OCH), 126.5, 129.1, 130.0, 130.6, 129.2, 152.8, 162.9, 170.8. Mass spectrum, *m/z* (I_{rel}, %): 381 (45.4) $[M]^+$, 353 (2.5), 336 (11.4), 308 (4.6), 280 (4.3), 263 (5.7), 252 (3.3), 236 (41.4), 224 (12.1), 202 (5.7), 171 (22.1), 156 (7.1), 144 (15.7), 130 (11.4), 115 (100), 105 (14.3), 89 (10.7), 77 (12.9), 65 (7.1), 51 (8.6), 43 (12.1). Found, %: C 53.2; H 4.9; N 3.45; S 8.09. $C_{17}H_{19}NO_7S$. Calculated, %: C 53.54; H 4.98; N 3.67; S 8.39.

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