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SHORT COMMUNICATIONS

Identification of Carbonyl Ylides in Reactions of Isothiazole 1,1-Dioxides with Rh(II)-Carbenoids

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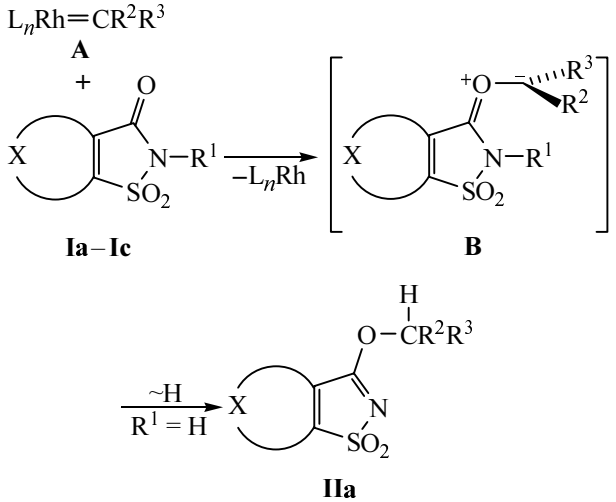
It was established in the study of catalytic reactions between diazo carbonyl compounds and oxoisothiazole 1,1-dioxides and their acyclic analogs that the reaction resulted exclusively in the O-alkylation of the carbonyl group in the sulfonimide fragment of the molecule (SO_2NHCO) with formation of O-alkyl imidates which formally were products of a carbene insertion into the O–H bond of the enol form of imides under consideration [1].

The conversion of sulfonamides **I** into O-alkyl imidates **II** involved apparently the primary attack on the oxygen of C=O group of electrophilic ketocarbenoid **A** giving an intermediate carbonyl ylide **B** [2], which was further stabilized into O-alkyl derivatives of imide **II** as a result of an intramolecular [1,4]-sigmatropic shift of the proton from the NH group to the anionic center of intermediate **B** [3].



X = $(CH)_4$, R^1 = H, R^2,R^3 = CO_2Et (**a**); X = $(CH)_4$, R^1 = Me, R^2,R^3 = CO_2Me (**b**); X = $(CH_2)_4$, R^1 = Ph, R^2,R^3 = COMe (**c**).

In order to identify the presumed intermediate carbonyl ylide **B** in the course of reaction by chemical methods we carried out a series of experiments using dimethyl acetylenedicarboxylate as the most efficient trap for reactive 1,3-dipoles [2].

It was established that in the course of catalytic decomposition of diethyl diazomalonate in the presence of saccharin (**Ia**) containing a free N–H bond and of dimethyl acetylenedicarboxylate (**III**) formed the same O-alkyl imidate **IIa** as in the absence of dipolarophile, and not a cycloadduct of compound **III** to carbonyl ylide **B**.

This fact apparently testifies to the faster occurrence of the stabilization of the intermediate carbonyl ylide **B** via intramolecular 1,4-migration of a proton than its intermolecular reaction with dimethyl acetylenedicarboxylate. Therefore we expected to obtain cycloadducts of carbonyl ylide **B** with dipolarophile **III** at the use under the same conditions of N-substituted sulfonamides lacking a hydrogen on the imide group able to migrate.

It proved however that the analogous catalytic reaction of dimethyl diazomalonate and diazoacetylacetone with N-methyl and N-phenylsubstituted isothiazole 1,1-dioxides (**Ib** and **Ic**) in the presence of reagent **III** also did not afford the cycloadducts with the dipolarophile. In both cases after the workup of the reaction mixture we recovered initial N-methyl and N-phenylsaccharins (**Ib** and **Ic**), and according to ^{1}H NMR spectra was also revealed the formation of a "dimer" bis(methoxycarbonyl)carbene.

To clear the reason of the failure to achive the carbonyl ylide addition to dipolarophile **III** in the course of intermolecular generation of ylides from N-substituted

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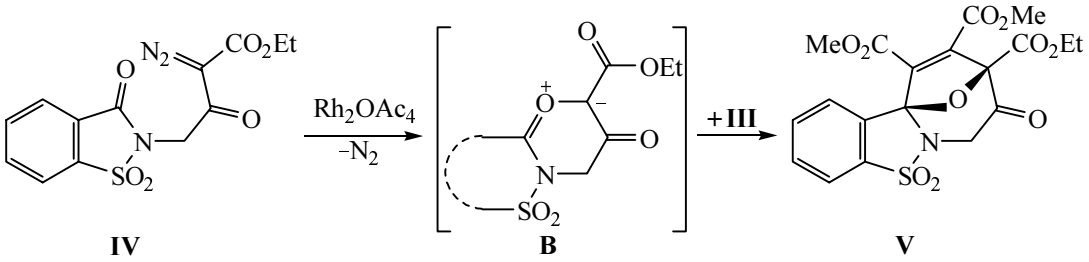

IV **B** **V**

saccharins (**Ib** and **Ic**) we studied under the same conditions the reactivity of an "intramolecular" carbonyl ylide **C**. To this end we synthesized by the three-stage synthesis from saccharin (**Ia**) similarly to the known procedure [4] N-alkyl-substituted diazooxoisothiazole 1,1-dioxide (**IV**) lacking a proton at the imide nitrogen and possessing a diazodicarbonyl fragment included directly in the structure of the initial substrate. It turned out that the catalytic decomposition of this diazoketoester **IV** in the presence of excess dimethyl acetylenedicarboxylate gave rise to the corresponding cycloadduct **V** of the intermediate carbonyl ylide **C** with dipolarophile **III** in a good yield (over 60%).

The essential difference in the reactivity of the "intermolecular" **B** and "intramolecular" C carbonyl ylides may be understood as follows. In the molecule of the carbonyl ylides **B** generated from *N*-methyl and *N*-phenylsaccharins (**Ia** and **Ib**) the two bulky substituents (CO_2Alk, COMe) of the carbenoid fragment of this intermediate are located orthogonal to the plane C^+–O–C^- of the dipole and create a significant steric hindrance to the dipolarophile access to the reacting orbitals of the carbonyl ylide.

At the same time in the dipolar structure of carbonyl ylide **C** all the four substituents at the carbon atoms of dipole should on the contrary *a priori* be actually located in the plane of the 1,3-dipole itself. Therewith the sterical hindrances to the access of dipolarophile **III** molecule to the reactive centers of intramolecular ylide **C** are obviously eliminated, and the cycloaddition can occur more efficiently.

The experimental data obtained are a good illustration to the dependence of multicenter concerted cycloadditions on the stereochemical features of the partners involved into the reaction [5].

Decomposition of diethyl diazomalonate in the presence of saccharin (Ia) and dipolarophile III. To a disperaion of 0.73 g (4 mmol) of saccharin (**Ia**) in 3 ml of anhydrous CH_2Cl_2 was added 0.8 g (4 mmol) of diethyl diazomalonate, 0.56 g (4 mmol) of dipolarophile **III**, in one portion was added 11 mg (24 μmol) of dirhodium tetraacetate, and the mixture was stirred for 3.5 h, and then applied to a small column packed with neutral silica gel (elution with pentane–ether mixture in a gradient mode). The main fraction (0.86 g) after removing the volatile substances in a vacuum was recrystallized from ether.

3-(Diethoxycarbonyl)methoxybenzo[*d*]isothiazole 1,1-dioxide (IIa). Yield 60%, colorless crystals, mp 81–82°C (from ether). ^{1}H NMR spectrum ($CHCl_3$), δ, ppm: 5.78 s (1H, OCH), 1.32 t (6H, $2CH_3$, *J* 7.14 Hz), 4.35 q (2H, CH_2, *J* 7.14 Hz), 4.33 q (2H, CH_2, *J* 7.14 Hz), 7.7–7.9 m ($4H_{arom}$). Found, %: C 49.3; H 4.69; N 4.16; S 9.49. $C_{14}H_{15}NO_7S$. Calculated, %: C 49.26; H 4.39; N 4.1; S 9.38.

Catalytic decomposition of dimethyl diazomalonate and diazoacetylacetone in the presence of N-substituted saccharin Ib and Ic and dipolarophile III. To a solution or dispersion of 5 mmol of saccharin **Ib** or **Ic**, 5 mmol diazo compound, and 5 or 25 (in the case of compound **Ib**) mmol of dipolarophile **III** in 20 ml of CH_2Cl_2 at 18–20°C was added in one portion 12–13 mg of dirhodium tetraacetate, and the mixture was stirred till complete decomposition of the diazo compound (9–10 h, TLC monitoring), the solvents and compound **III** were totally distilled off in a vacuum (1–2 mm Hg) at 25–35°C, and after workup described in the preceding experiment initial N-substituted isothiazole 1,1-dioxides **Ib** or **Ic** were isolated in 90–93% yields.

Catalytic decomposition of diazosaccharin (IV). To a solution of 1 g (2.9 mmol) of diazo compound **IV** and 3.26 g (23 mmol) of dipolarophile **III** in 5 ml of CH_2Cl_2 was added at stirring 13 mg (29.4 μmol) of dirhodium tetraacetate, the mixture was stirred for 12 h, and the arising reaction product gradually crystallized from the reaction mixture as white powder. On completion of the reaction (TLC monitoring) the separated precipitate was filtered off, thoroughly washed with cold dichloromethane, and dried in air.

Cycloadduct (V). Yield 0.8 g (61%), colorless crystals, mp 198–199°C (CH_2Cl_2). ^{1}H NMR spectrum

($CDCl_3$), δ, ppm: 1.31 t (3H, $OCH_2\underline{CH}_3$, *J* 7.2 Hz), 3.65 s (3H, OCH_3), 3.94 s (3H, OCH_3), 4.3 d.q (1H, $OC\underline{H}HCH_3$, *J* 10.8, 7.11 Hz), 4.4 d.q (1H, $OCH\underline{H}CH_3$, *J* 10.8, 7.12 Hz), 4.41 q (2H, *J* 18.8 Hz, δ_A 4.61, δ_B 4.22, NCH_2CO), 7.65–7.92 m (4H, CH_{arom}). Found, %: C 50.59; H 3.83; N 3.13. $C_{19}H_{17}NO_{10}S$. Calculated, %: C 50.55; H 3.79; N 3.10.

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