Experimental

The mass spectrum was measured on a Varian MAT AEI-MS-30 spectrometer with the use of the fast-atom bombardment technique. The ^{1}H NMR spectrum was recorded on a Bruker AMX-400 instrument (400 MHz). The chemical shifts were measured relative to internal standard (Me_4Si).

The initial compounds were prepared according to procedures reported in the literature: $Rh_3Cp_3(\mu\text{-}CO)_3 \cdot 0.5CH_2Cl_2$[5] and $RhCp(C_2H_4)_2$.[6]

A mixture of $Rh_3Cp_3(\mu\text{-}CO)_3 \cdot 0.5CH_2Cl_2$ (0.63 g, 1 mmol) and $RhCp(C_2H_4)_2$ (0.224 g, 1 mmol) was refluxed in *m*-xylene (50 mL) under an atmosphere of argon for 30 h. The solvent was evaporated, and the residue was extracted with CH_2Cl_2 until the extract was colorless. Chromatography of the extract gave $Rh_4Cp_4(\mu_3\text{-}CO)_2$ in a yield of 0.331 g (45%). Then the residue was washed with water until the extracts were colorless. When an aqueous solution of NH_4PF_6 was added to the resulting solution, a dark-blue finely crystalline precipitate of salt **1** was obtained. The yield was 0.027 g (~3% with respect to Rh). Found (%): C, 29.05; H, 2.54; P, 4.48. $C_{31}H_{30}F_{12}P_2Rh_6$. Calculated (%): C, 28.41; H, 2.31; P, 4.73.

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Methyl *N*-(benzylsulfonyl)oxamate as a probable intermediate in the synthesis of 4-hydroxy-5-phenyl-3(2*H*)-isothiazolone 1,1-dioxide from phenylmethanesulfamide and dimethyl oxalate in the presence of bases

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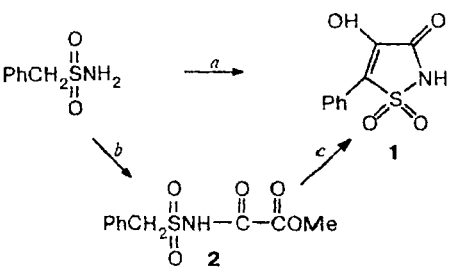
The formation of 4-hydroxy-5-phenyl-3(2*H*)-isothiazolone 1,1-dioxide from phenylmethanesulfamide and dimethyl oxalate under the action of bases is apparently a two-stage process involving the formation of linear methyl *N*-(benzylsulfonyl)oxamate followed by its cyclization. A stable complex of the heterocycle with dimethylformamide was synthesized.

Key words: phenylmethanesulfamide, dimethyl oxalate, 3(2*H*)-isothiazolone 1,1-dioxides.

Previously, it has been reported that 4-hydroxy-5-phenyl-3(2*H*)-isothiazolone 1,1-dioxide[1] (**1**), which possesses biological activity,[2] was synthesized from phenylmethanesulfamide and diethyl oxalate under the action of Bu^tOK in DMF. Compound **1** was also prepared, while in lower yield, by cyclization of methyl *N*-(benzylsulfonyl)oxamate (**2**), which has been synthesized by an independent procedure, under analogous conditions.[1]

We demonstrated that compound **2** was formed in the first step of condensation of phenylmethanesulfamide with dimethyl oxalate in the presence of a base. Apparently, compound **2** is an immediate precursor of heterocycle **1** in the above-mentioned reaction.



Reagents: *a*. 1) MeO_2CCO_2Me, Bu^tONa/Bu^tOH; 2) HCl/H_2O; *b*. 1) MeO_2CCO_2Me, $MeONa/MeOH$; 2) HCl/H_2O; *c*. 1) Bu^tONa/Bu^tOH; 2) HCl/H_2O.

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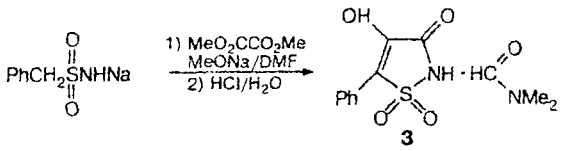
When the reaction was carried out in MeOH under the action of MeONa at 20 °C, it could be stopped in the stage of formation of compound **2**. Under these conditions, oxamate **2** was obtained in 57% yield. It appeared that in more basic media sulfimide **2** formed heterocycle **1** in 55% yield. As expected, under the action of the Bu^{t}ONa—Bu^{t}OH or MeONa—DMF system, as under the action of the Bu^{t}OK—DMF system, a mixture of phenylmethanesulfamide and dimethyl oxalate was converted immediately into isothiazolone 1,1-dioxide **1**,[1] which is apparently due to the fact that compound **2** that formed *in situ* underwent cyclization to heterocycle **1** under the above-mentioned conditions.

It should be noted that compound **1** gave a stable 1 : 1 complex with DMF (**3**), which was isolated when the reactions were carried out in this solvent.



3

The structure of complex **3** was confirmed by the data of elemental analysis and ^{1}H NMR spectroscopy.

Experimental

^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13 MHz) in DMSO-d_6. The chemical shifts were measured relative to DMSO (δ 2.50).

Methyl *N*-(benzylsulfonyl)oxamate (2). Dimethyl oxalate (0.37 g, 3.1 mmol) and phenylmethanesulfamide (0.53 g, 3.1 mmol) were successively added with stirring to a solution of MeONa in MeOH, which was prepared from Na (0.14 g, 6.2 mg-at.) in anhydrous MeOH (4 mL). The reaction mixture was stirred at 20 °C for 6 h and then poured into 6 *M* HCl (7 mL). The precipitate that formed was filtered off and washed with Et_2O (2 mL). Oxamate **2** was obtained in a yield of 0.45 g (57%), m.p. 120—122 °C (*cf.* Ref. 1: m.p. 117—122 °C). ^{1}H NMR (DMSO-d_6), δ: 3.80 (s, 3 H, CH_3); 4.73 (s, 2 H, CH_2); 7.33—7.43 (m, 5 H, Ph).

4-Hydroxy-5-phenyl-3(2*H*)-isothiazolone 1,1-dioxide (1). Method *A*. Dimethyl oxalate (0.28 g, 2.3 mmol) and phenylmethanesulfamide (0.4 g, 2.3 mmol) were successively added to a solution of Bu^{t}ONa in Bu^{t}OH, which was prepared by dissolving Na (0.11 g, 4.8 mg-at.) in anhydrous Bu^{t}OH (6 mL) on heating. The reaction mixture was stirred at 40 °C for 2 h. After cooling, the mixture was mixed with 6 *M* HCl (7 mL). The precipitate that formed was filtered off and washed with hexane (2 mL). Compound **1** was obtained in a yield of 0.29 g (55%), m.p. 260—262 °C (*cf.* Ref. 1: m.p. 262—264 °C). ^{1}H NMR (DMSO-d_6), δ: 6.65 (br.s, 1 H, OH); 7.38—7.55 (m, 4 H, H_m, H_p, OH); 7.79—7.85 (m, 2 H, H_o). ^{13}C NMR (DMSO-d_6), δ: 118.2 (^{4}C); 125.8 (*ipso*-C); 126.7 (C_o or C_m); 128.8 (C_o or C_m); 130.7 (C_p); 145.9 (^{3}C); 160.5 (^{5}C).

Method *B*. Oxamate **2** (0.5 g, 1.9 mmol) was added with stirring to a solution of Bu^{t}ONa in Bu^{t}OH, which was prepared by dissolving Na (0.1 g, 4.3 mg-at.) in anhydrous Bu^{t}OH (6 mL) on heating. The reaction mixture was stirred at 40—45 °C for 2.5 h, kept at 20 °C for 12 h, and diluted with 6 *M* HCl (8 mL). The precipitate that formed was filtered off. Compound **1** was obtained in a yield of 0.23 g (55%), m.p. 260—262 °C.

Complex of 4-hydroxy-5-phenyl-3(2*H*)-isothiazolone 1,1-dioxide with DMF (3). Dimethyl oxalate (0.34 g, 2.8 mmol) was added to a suspension of MeONa (prepared by dissolving Na (0.07 g, 2.8 mg-at.) in MeOH (4 mL) followed by removal of the solvent *in vacuo*) in anhydrous DMF (4 mL) at 20 °C. Then the sodium salt of phenylmethanesulfamide (0.55 g, 2.8 mmol) was added in five portions over 15 min. The reaction mixture was stirred at 20 °C for 24 h, diluted with 6 *M* HCl (5 mL), and filtered. The 1 : 1 complex of isothiazolone dioxide **1** with DMF was precipitated from the mother liquor on storage for 24 h. The precipitate was filtered off and dried on the filter in air. Complex **3** was obtained in a yield of 0.29 g (35%), m.p. 264—267 °C. Found (%): C, 48.55; H, 4.59; S, 10.69. $C_{12}H_{14}N_2O_5S$. Calculated (%): C, 48.32; H, 4.70; S, 10.74. ^{1}H NMR (DMSO-d_6), δ: 2.73 (s, 3 H, CH_3); 2.89 (s, 3 H, CH_3); 7.37—7.55 (m, 3 H, H_m, H_p); 7.8 (d, 2 H, H_o); 7.96 (s, 1 H, CH).

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