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SYNTHESIS AND TRANSFORMATIONS OF CHLORO DERIVATIVES OF 4,7-DIOXOBENZO-2,1,3-THIADIAZOLE

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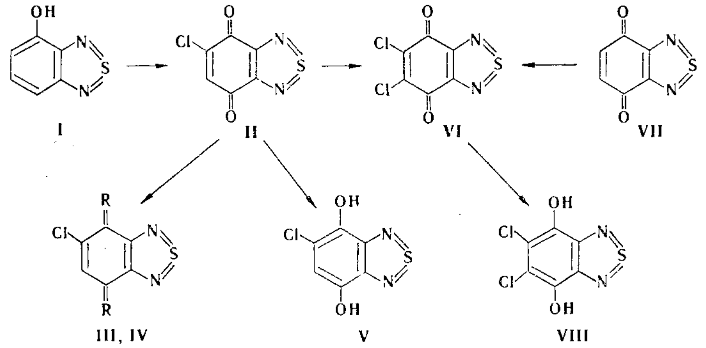
5-Chloro-4,7-dioxo- and 5,6-dichloro-4,7-dioxobenzo-2,1,3-thiadiazoles were synthesized, and their reduction to the corresponding dihydroxy derivatives was studied. The bis(semicarbazone) and bis(thiosemicarbazone) of the 5-chloro derivative were obtained, and their antivirus activities were determined.

We have previously [1, 2] reported the synthesis and chemical transformations of 4,7-dioxo- and 5-methyl-4,7-dioxobenzo-2,1,3-thiadiazoles. The present paper is a continuation of these studies and is devoted to the synthesis and proof of the structures of chloro derivatives of 4,7-dioxobenzo-2,1,3-thiadiazole.

The reaction of 4-hydroxybenzo-2,1,3-thiadiazole (I) with a 30% solution of hydrogen peroxide in the presence of an acid gives 5-chloro-4,7-dioxobenzo-2,1,3-thiadiazole (II), which reacts with 2 moles of semicarbazide or thiosemicarbazide to give, respectively, bis(semicarbazone) III and bis(thiosemicarbazone) IV.

Thiadiazole II is readily reduced by sulfur dioxide or sodium hydrosulfite to 5-chloro-4,7-dihydroxybenzo-2,1,3-thiadiazole (V).



III $R=N-NH-CO-NH_2$; IV $R=N-NH-CS-NH_2$

A C=O absorption band at 1707 cm^{-1} is present in the IR spectrum of II; this band is absent in the spectrum of V, but an absorption band of OH stretching vibrations appears at 3540 cm^{-1}.

The chlorination of II with gaseous chlorine in acetic acid gives 5,6-dichloro derivative VI in high yield; this product is identical to the quinone formed in the chlorination of 4,7-dioxobenzo-2,1,3-thiadiazole (VII) with a known structure [2].

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Quinone VI is converted to dihydroxythiadiazole VIII by the action of sulfur dioxide or sodium hydrosulfite.

A C=O absorption band is present in the IR spectrum of VI at 1705 cm^{-1}. this band is absent in the spectrum of VIII, but an absorption band of OH stretching vibrations appears at 3520 cm^{-1}:

Compounds III and IV were tested for their antivirus activity.* It was shown that IV *in ovo* has moderate antivirus activity with respect to the virus of the Leningrad A_2 group (the index of protection was 50%).

EXPERIMENTAL

The course of the reactions and the individuality of the substances were monitored by means of thin-layer chromatography (TLC) on Silufol UV-254 in an acetone–chloroform–hexane system (2:1:2) (system A) or in a chloroform–toluene system (1:1) (system B) with development of the spots with ammonia vapors. The melting points of the substances were determined with a Boetius apparatus. The IR spectra of solutions of the compounds in carbon tetrachloride or chloroform were recorded with a Perkin–Elmer 577 spectrometer.

5-Chloro-4,7-dioxobenzo-2,1,3-thiadiazole (II). A 50-ml sample of concentrated hydrochloric acid was added to a solution of 4.8 g (31.6 mmole) of I in 150 ml of acetonitrile, and the mixture was heated to 50°C. A 100-ml sample of a 30% solution of hydrogen peroxide was added dropwise at 50°C, and the mixture was heated up to the boiling point and refluxed for 1.5 h. It was then cooled to 20°C, and 200 ml of water was added. The resulting precipitate was removed by filtration, washed with water, and dried to give 2.3 g of thiadiazole II with R_f 0.88 (system A). The filtrate was extracted three times with chloroform, the chloroform extracts were filtered, and the solvent was removed to give a residue containing 0.3 g of II with R_f 0.88 (system A). The overall yield of II, with mp 148-149°C (from dichloroethane), was 2.6 g (41.5%). Found: Cl 17.9; S 16.2%. $C_6HClN_2O_2S$. Calculated: Cl 17.7; S 16.0%.

5-Chlorobenzo-2,1,3-thiadiazole 4,7-Bis(semicarbazone) (III). A 0.556-g (5 mmole) of semicarbazide hydrochloride and 0.5 g (2.5 mmole) of II were added to a solution of 0.28 g (5 mmole) of potassium hydroxide in 30 ml of ethanol, and the mixture was refluxed for 45 min. It was then cooled and poured into water, and the precipitate was removed by filtration, washed with water, and dried to give 0.6 g (77%) of III, which swelled and darkened without melting at 260-263°C and had R_f 0.675 (system A). Found: N 35.1%. $C_8H_7ClN_8O_2S$. Calculated: N 35.6%.

5-Chlorobenzo-2,1,3-thiadiazole 4,7-Bis(thiosemicarbazone) (IV). A 0.454-g (5 mmole) sample of thiosemicarbazide was added to a solution of 0.5 g (2.5 mmole) of II in 15 ml of ethanol, and the mixture was refluxed for 10 min. It was then cooled, and the precipitate was removed by filtration to give 0.76 g (88%) of IV with mp 153-155°C and R_f 0.23 (system B). Found: Cl 9.6; S 26.9%. $C_8H_7ClN_8S_3$. Calculated: Cl 10.2; S 27.7%.

5-Chloro-4,7-dihydroxybenzo-2,1.3-thiadiazole (V). A) A mixture of 1.3 g (6.48 mmole) of thiadiazole II, 10 ml of methanol, and 3 ml of water was refluxed for 2 h with simultaneous bubbling of sulfur dioxide through the mixture. The mixture was then cooled, 15 ml of water was added, and the resulting precipitate was removed by filtration, washed with water, and dried to give 0.75 g (57%) of V with mp 145-147°C and R_f 0.72 (system A). Found: Cl 17.0; S 15.7%. $C_6H_3ClN_2O_2S$. Calculated: Cl 17.5; S 15.8%.

B) A solution of 2 g (10 mmole) of sodium hydrosulfite in 20 ml of water was added to a hot solution of 0.43 g (2 mmole) of thiadiazole II in 15 ml of dichloroethane and 3.5 ml of ethyl acetate, and the mixture was shaken for 5 min. The organic layer was separated and filtered, and the solvent was removed. The residue contained 0.25 g (58%) of V with mp 145-147°C. The R_f value of 0.72 (system A) was in agreement with the R_f value of V obtained by method A.

5,6-Dichloro-4,7-dioxobenzo-2,1,3-thiadiazole (VI). A) A 0.23-g (1.8 mmole) sample of iodine was added to a solution of0.6 g (2.6 mmole) of thiadiazole II in 5 ml of glacial acetic acid heated to 60-65°C, and saturation of the reaction mixture wwith gaseous chlorine was begun immediately. Chlorine was bubbled into the refluxing mixture for 2 h, after which it

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*The tests were conducted by O. G. Yasinskaya and V. V. Ivanova.

was cooled, and the precipitate was removed by filtration, washed with water, and dried to give 0.6 g (85%) of VI, which was crystallized from dichloroethane and sublimed at 188-190°C to give a product with R_f 0.8 (system A). Found: Cl 30.2; N 10.6%. $C_6Cl_2N_2O_2S$. Calculated: Cl 30.2; N 10.9%.

B) A 0.2-g (1.6 mmole) sample of iodine was added to a solution of 0.25 g (1.1 mmole) of VII in 5 ml of glacial acetic acid heated to 90°C, and bubbling of chlorine into the mixture was begun immediately. Bubbling of chlorine through the refluxing mixture was continued for 1 h, after which the mixture was cooled, and the precipitate was removed by filtration, washed with water, and dried to give 0.23 g (65%) of VI, which was crystallized from dichloroethane and sublimed at 189-190°C. The R_f value of 0.8 (system A) was in agreement with the R_f value of VI obtained by method A.

5,6-Dichloro-4,7-dihydroxybenzo-2,1,3-thiadiazole (VIII). A) Sulfur dioxide was bubbled into a mixture of 0.71 g (3 mmole) of thiadiazole VI in 7 ml of methanol and 1.5 ml of water heated to the boiling point for 30 min, after which the mixture was cooled and treated with 10 ml of water. The resulting precipitate was removed by filtration, washed with water, and dried to give 0.6 g (84%) of VIII with mp 245-247°C and R_f 0.48 (system A). Found: N 11.3; S 13.1%. $C_6H_2Cl_2N_2O_2S$. Calculated: N 11.8; S 13.5%.

B) A solution of 1.7 g (10 mmole) of sodium hydrosulfite in 17 ml of water was added to a hot solution of 0.41 g (1.7 mmole) of thiadiazole VI in 12 ml of ethylene glycol and 3 ml of ethyl acetate, and the mixture was stirred for 3 min. It was then cooled and extracted with chloroform. The chloroform extracts were filtered, and the solvent was removed to give 0.22 g (53%) of VIII with mp 245-247°C. The R_f value of 0.48 (system A) was in agreement with the R_f value of VIII obtained by method A.

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INVESTIGATION OF THE STRUCTURE OF SUBSTITUTED 3H,6H-6-SILA-3-AZAACEANTHRYLENES BY PMR SPECTROSCOPY

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The structure of substituted 3H,6H-6-sila-3-azaaceanthrylenes was confirmed as a result of an analysis of the PMR spectra and by the spectra at 360 MHz. Computer analysis of the ABCD spectrum of the phenylene protons demonstrated the characteristic nature of the spin–spin coupling constants (SSCC) in the indicated series.

The preparation of compounds that belong to the previously unknown heterocyclic system of one of the isomeric dihydrosilaazaaceanthrylenes, the molecules of which contain a 1H-pyridine (pseudoazulene) fragment, was described in [1, 2]. In the present paper we present a detailed analysis of the PMR spectra in order to confirm the structure of the following compounds of this series: 3H,6H-6,6-dimethyl-3-benzyl-1,2-dicarbomethoxy-, 3H,6H-6,6-dimethyl-3-benzyl-2-cyano-, 3H,6H-3,6,6-trimethyl-2-cyano-, and -1,2-dicarbomethoxy-6-sila-3-azaaceanthrylenes (I-IV):

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