SYNTHESIS OF 2,2-DIALKYL(PHENYL)-4-(2-HYDROXYETHYL)THIADIAZINONES

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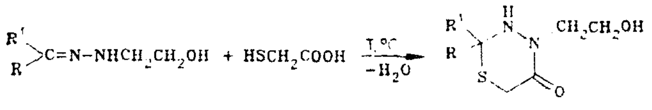
2,2-Dialkyl(phenyl)-4-(2-hydroxyethyl)thiadiazin-5-ones are formed as a result of the reaction of thioglycolic acid with 2-hydroxyethylhydrazones. The structures of the reaction products were proved by PMR and ^{13}C NMR spectrometry and the mass spectra.

It has been previously shown [1-3] that five- and six-membered phosphorus-, nitrogen-, and oxygen-containing compounds are formed in the reaction of N-β-hydroxyethylhydrazones with hexaalkyltriaminophosphines, aldehydes, and isocyanates. At the same time, acetone thiosemicarbazones exist in the open form in solution [4].

The aim of the present research was to study the reaction of thioglycolic acid with aldehyde and ketone N-β-hydroxyethylhydrazones and to establish the structures of the products.

Benzaldehyde and ketones react relatively readily with thioglycolic acid to give crystalline products I-IX (see Table 1). The structures of the products were proved by PMR and ^{13}C NMR spectroscopic data and mass spectrometry. The reaction between the N-β-hydroxyethylhydrazones and thioglycolic acid a priori may proceed with the formation of two cyclic and three linear compounds because of the presence of several reaction centers in the molecules, and this makes proving the structures of the reaction products an urgent matter.

An analysis of the spectral data makes it possible to conclude that 2,2-dialkyl(phenyl)-4-(2-hydroxyethyl)thiadiazin-5-ones I-IX are formed as a result of the reaction between thioglycolic acid and aldehyde and ketone N-β-hydroxyethylhydrazones.



I-IX

Thus triplet and quartet signals at 1.06 and 2.18 ppm, respectively, which are related to an ethyl group, are observed in the PMR spectrum of 2-methyl-2-ethyl-4-(β-hydroxyethyl)thiadiazin-5-one (III). The protons of the methyl group resonate at 1.77 ppm in the form of a singlet. The multiplet at 1.92 ppm characterizes ring methylene protons; anisochronicity of the S—CH_2 protons ($\Delta\delta$ = 0.16 ppm) is observed, and this confirms the asymmetric character of the $C_{(2)}$ atom. As expected, the protons of the >N—CH_2CH_2O— group resonate in the form of two triplets (δ_{CH_2N} 3.18 ppm and δ_{CH_2O} 3.67 ppm, an A_2X_2 spin system). The broad signal at 4.3-4.9 ppm should be ascribed to protons of NH (OH) groups existing in a state of rapid tautomeric exchange. The ratio of the integral intensities of the signals also confirms the proposed structure. One cannot exclude the possibility of the formation of an intramolecular hydrogen bond between the C=O, N—H, and O—H groups, as may be evidenced by the appearance in the PMR spectrum of a broad signal of a hydroxy group at 7.3 ppm.

Signals of eight carbon atoms — $C_{(8)}$ (8.4), $C_{(9)}$ (27.1), $C_{(7)}$ (30.0), $C_{(6)}$ (35.2), $C_{(10)}$ (52.4), $C_{(11)}$ (59.5), $C_{(2)}$ (72.7), and $C_{(5)}$ (171.5) — are observed in the ^{13}C NMR spectrum of III. The positions of all of the signals are in agreement with the thiadiazin-5-one structure.

The mass spectrum of III is characterized by the following principal peaks [m/z (I, %)]: M^+ 204 (44); $[M - CH_3]^+$ 189 (12); $[M - C_2H_5]^+$ 175 (97); $[M - C_2H_4O]^+$ 160 (99); $[M - C_4H_9O]^+$ 131 (59), 99 (100), 88 (30), 60 (96). The presence of an intense signal of an ion with a mass of 160 in the mass spectrum and the absence of peaks of ions caused by the detachment of an $NHCH_2CH_2OH$ particle in the case of linear structures make it possible to assume the formation of a six-membered thiadiazine ring.

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TABLE 1. Characteristics of 2,2-Dialkyl(phenyl)-4-(2-hydroxyethyl)thiadiazines I-IX

Compound	R	R'	mp, °C	Yield, %	Compound	R	R'	mp, °C	Yield, %
I	C_6H_5	H	136...138	59	V	$-C_2H_4-CH(OH)C_2H_4$		138...140	78
II	CH_3	CH_3	120...122	79	VI	CH_3	n-C_4H_9	107...109	79
III	CH_3	C_2H_5	124...126	51	VII	$-(CH_2)_4-$		128...130	82
IV	CH_3	C_6H_{13}	116...118	30	IX	n-C_3H_7	n-C_3H_7	104...106	77
					VIII	CH_3	C_6H_5	120...122	69

To verify this assumption we obtained the mass spectra of 2,2-dimethyl(β-hydroxyethyl)thiadiazin-5-one (II) and its trimethylsilyl derivative X. The mass-spectral fragmentation of these compounds is analogous to the mass-spectral fragmentation of III. The principal fragmentation pathway in these case is the detachment of C_2H_4O or $CH_2{=}CH{-}O{-}Si(CH_3)_3$ particles to give an ion with m/z 146 (100%).

EXPERIMENTAL

The PMR spectra of solutions of the synthesized compounds in $CDCl_3$ were recorded with a Bruker—Physik WH-270 spectrometer (270 MHz), while the ^{13}C NMR spectra of solutions in C_5D_5N were recorded with the same apparatus under conditions of total ^{13}C—{^1H} heteronuclear spin decoupling. The mass spectra were obtained with a Varian MAT-311A spectrometer under standard recording conditions: The accelerating voltage was 3 kV, the cathode emission current was 30 μA, the ionizing voltage was 70 eV, the samples were introduced directly into the ion source of the mass spectrometer, and the vaporization temperature was 80°C.

The results of elementary analysis of the synthesized compounds for C, H, N, and S were in agreement with the calculated values.

2-Phenyl-4-(β-hydroxyethyl)thiadiazin-5-one (I). A solution of 16.4 g (0.1 mole) of benzaldehyde 2-hydroxyethylhydrazone in 50 ml of benzene was placed in a reaction flask, and 9.2 g (0.1 mole) of thioglycolic acid was added dropwise with stirring at room temperature. The reaction mixture was then heated with stirring to 65-70°C and maintained at this temperature for 4 h. The solvent was removed by distillation until crystals formed, after which methanol was added. After a few hours, the I crystals were removed by filtration, washed with diethyl ether, and recrystallized from benzene—methanol (1:1).

Compounds II-IX were similarly obtained.

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