TAUTOMERISM OF 5-THIOACYLHYDRAZINOISOXALINE-2 AND 5-(2-HYDROXYIMINOPROPYL)-1,3,4-THIADIAZOLINE-2

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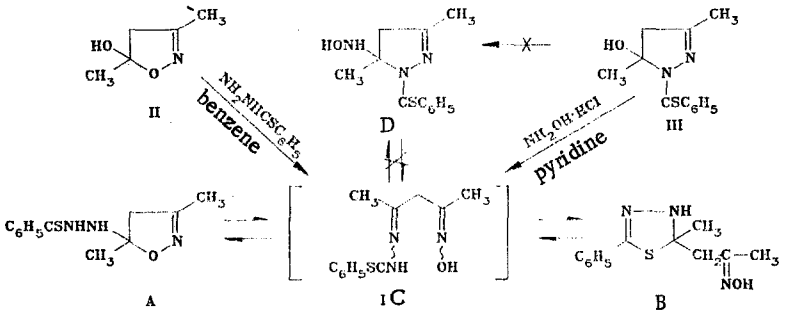
We have found that in the crystalline state and in nonpolar solvents the compound obtained from thiobenzhydrazide and 5-hydroxy-3,5-dimethylisoxazoline-2 [1] exists as 5-thiobenzoylhydrazino-3,5-dimethylisoxazoline-2 (IA). After short refluxing of the reactants in benzene the compound was obtained with a yield of 50%; mp 120-122° (from hexane). IR spectrum in $CHCl_3$: 1620 (C=N), 3180 (NH); in liquid petrolatum: 1625 (C=N), 3140 cm^{-1} (NH). PMR spectrum ($CDCl_3$, −50°): 1.63 (s, CH_3); 1.88 (t, J = 0.8 Hz, CH_3); 2.83, 3.02 (AB system, J_{AB} = 18.0 Hz, CH_2); 6.73 (d, J = 8.0 Hz, NH); 7.2-7.7 (m, C_6H_5); 10.95 ppm (d, J = 8.0 Hz, NH-CS). ^{13}C NMR spectrum ($CDCl_3$): 12.9 (CH_3, J_{CH} = 129 Hz), 22.7 (CH_3, J_{CH} = 129, J_{CCCH} = 4 Hz), 46.5 (CH_2, J_{CH} = 133, J_{CCCH} = 4.0 Hz), 98.0 ($C_{(s)}$), J_{CCH} = 4.5 Hz), 157.0 (C=N, J_{CCH} = 6.5 Hz), 193.1 ppm (C=S). See [2, 3] for comparison.

In polar media (CD_3OD, DMFA-D_7, DMSO-D_6, pyridine-D_5) another cyclic form appears suddenly, based on the PMR spectra, which, according to the data in [3], must be considered as 2-phenyl-5-(2-hydroxyiminopropyl)-1,3,4-thiadiazoline-2 (IB). PMR spectrum (DMFA-D_7, −50°): 1.57 (s, CH_3), 1.87 (s, CH_3), 2.88 (s, CH_2), 7.2-7.6 (m, C_6H_5), 8.29 (s, NH), 10.25 ppm (s, OH). ^{13}C NMR spectrum (DMSO-D_6): 15.2 (qu, CH_3), 26.9 (qu, CH_3), 46.9 (t, CH_3), 83.0 ($C_{(s)}$), 143.5 (C=N), 152.4 ppm (C=NOH). In the NMR spectra of the mixture the signals of the tautomer A are not shown since they practically coincide with the signals of the spectra in $CDCl_3$. Besides the bands of the form A shown above, the IR spectrum in DMSO shows absorption of the OH group (3450) and of further two C=N bonds at 1630 and 1640 cm^{-1}. The content of tautomer B depends on the nature of the solvent (27% in CD_3OD, 24% in DMFA-D_7, 30% in DMSO-D_6, and 34% in pyridine-D_5).

Compound I is obtained by the reaction of 5-hydroxypyrazoline III with hydroxylamine hydrochloride in pyridine; however, the yield is less than 10%; the main products are the dioxane of acetylacetone and the isoxazoline II which were identified by comparison with known samples. It is interesting that another possible form D did not occur; this was established by carrying out the syntheses directly in the ampul of the NMR spectrometer.



The A ⇄ B tautomerism represents a new example of a ring-ring equilibrium between the derivatives of two different heterocycles, the only case of which has been described in [3].

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