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SHORT COMMUNICATIONS

Spiro-Heterocyclization of Pyrrolobenzoxazinetriones Effected by Thiourea

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Reaction of 3-aroyl-2,4-dihydro-1*H*-pyrrolo[2,1-*c*]-[1,4]benzoxazine-1,2,4-triones with thiourea at boiling in a mixture acetonitrile–DMF was found to give 3-[α-(5-oxo-2-thioxo-4-imidazolidinylidene)phenacyl]-2*H*-1,4-benzoxazin-2-ones [1].

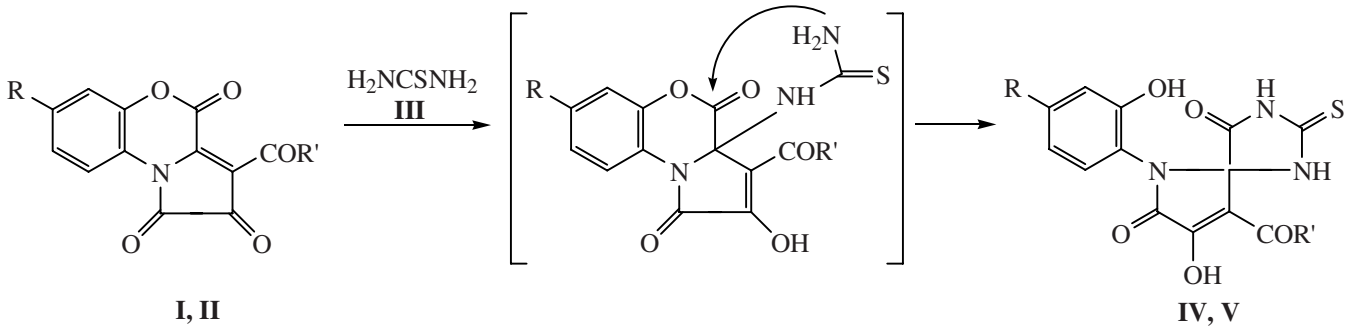
In reaction of 3-methoxycarbonyl- and 3-benzoyl-7-methyl-2,4-dihydro-1*H*-pyrrolo[2,1-*C*][1,4]benzoxazine-1,2,4-triones **I** and **II** with thiourea (III) in a ratio 1:1.5 at boiling in anhydrous benzene for 10–15 min we obtained in good yield spiro compounds **IV** and **V** respectively. The spectral characteristics of imidazole-4-spiro-2'-pyrroles **IV** and **V** and model indole-3-spiro-2'-pyrroles whose structure was confirmed by X-ray analysis are very similar (see Scheme).

Evidently in the reaction of pyrrolobenzoxazinetriones **I** and **II** with thiourea the amino groups of the binucleophile attack in succession the carbon atoms in positions *3a* and *4* of pyrrolobenzoxazinetriones, and the oxazine ring suffered cleavage at the C^4–O^5 bond, but the expected rupture of the ring at the C^{3a}–N^{10} bond did not occur under the conditions used.

The described reaction is an example of a regioselective building up of the previously inaccessible spiro-bis-heterocyclic system imidazole-4-spiro-2'-pyrrole with desired substituents variation in several positions of both heterocycles.

Methyl 8-hydroxy-6-(2-hydroxyphenyl)-4,7-dioxo-2-thioxo-1,3,6-triazaspiro[4,4]non-8-ene-9-carboxylate (IV). A solution of 3.6 mmol of compound **I** and 5.5 mmol of thiourea (**III**) in 15 ml of anhydrous benzene was boiled for 15 min (till discoloration), then it was cooled, and the separated precipitate was filtered off. Yield 74%, mp 179–181°C (from acetone). IR spectrum, cm^{-1}: 3330 (NH), 3180 br (OH), 1713 (C=O, COO). ^1H NMR spectrum, δ, ppm: 3.68 s (3H, MeO), 6.76–7.26 m (4H, C_6H_4), 9.00 s (1H, $OH_{phenol.}$), 9.23 s (1H,

Scheme.



I, II **IV, V**

I, IV, R = H, R' = OMe; **II, V**, R = Me, R' = Ph.

NH), 9.68 s (1H, NH), 12.30 br.s (1H, $OH_{enol.}$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 51.43 (CH_3O), 84.52 (C_{spiro}), 109.42–130.53 (C^{Ar}), 154.75 (C^{8}), 154.81 (C^{7}=O), 161.65 (COO), 164.12 (C^{4}=O), 183.28 (C=S). Found, %: C 48.10; H 3.25; N 12.01; S 9.22. $C_{14}H_{11}N_3O_6S$. Calculated, %: C 48.14; H 3.17; N 12.00; S 9.18.

9-Benzoyl-8-hydroxy-6-(2-hydroxy-4-methylphenyl)-2-thioxo-1,3,6-triazaspiro[4,4]non-8-ene-4,7-dione (V). A solution of 3.0 mmol of compound **II** and 4.5 mmol of thiourea (**III**) in 15 ml of anhydrous benzene was boiled for 10 min (till discoloration), then it was cooled, and the separated precipitate was filtered off. Yield 74 %, mp 208–210°C (from acetonitrile). IR spectrum, cm^{-1}: 3366 (NH), 3152 br (OH), 1709, 1690 br (C=O). ^1H NMR spectrum, δ, ppm: 2.25 s (3H, Me), 6.60–7.75 m (8H, Ph + C_6H_3), 8.85 s (1H, NH), 9.13 s (1H, OH_{phenol}), 9.43 s (1H, NH), 12.50 br.s (1H, OH_{enol}). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 20.89 (CH_3), 85.20 ($C_{spiro.}$), 116.85–140.22 (C^{Ar}), 153.05 (C^{8}), 154.45 (C^{7}=O), 164.96 (C^{4}=O), 183.73 (C=S), 188.00 (COPh). Found, %: C 58.65; H 3.76; N 10.23; S 7.89. $C_{20}H_{15}N_3O_5S$. Calculated, %: C 58.67; H 3.69; N 10.26; S 7.83.

IR spectra of compounds obtained were recorded on a spectrophotometer FMS-1201 from mulls in mineral oil. ^1H and ^{13}C NMR spectra were registered on a spectrometer Bruker WP-400 in DMSO-d_6, internal reference TMS. The homogeneity of compounds obtained was checked by TLC on Silufol plates, eluent ethyl acetate, development in iodine vapor.

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