

SHORT
COMMUNICATIONSSpiro Heterocyclization of 1*H*-Pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-triones with Furazan-3,4-diamine

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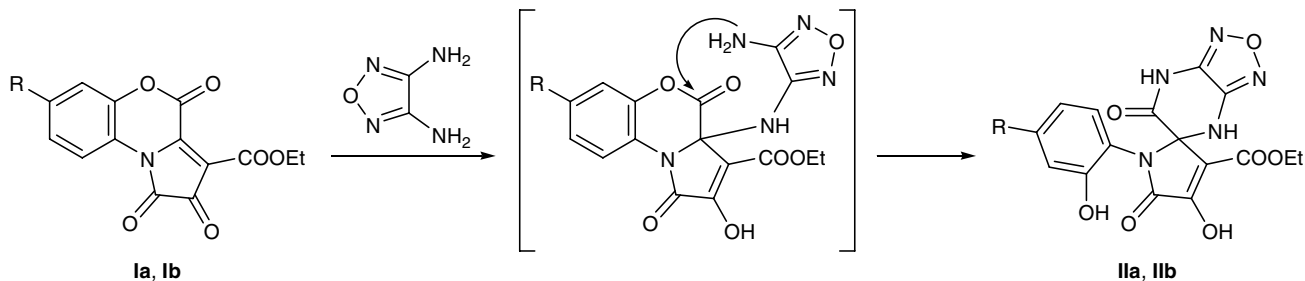
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We previously found [1] that 3-aryl-1*H*-pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-triones react with *o*-phenylenediamine via successive attack by the amino groups of the binucleophile at the C^{3a} and C⁴ carbon atoms of the substrate; the process is accompanied by cleavage of the oxazine ring at the C⁴–O⁵ and C^{3a}–N¹⁰ bonds and leads to the formation of 4-aryl-*N*-(2-hydroxyphenyl)-2,4-dioxo-3-[(*Z*)-3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene]butanamides. In the present communication we report on the reaction of ethyl 1,2,4-trioxo-2,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]benzoxazine-3-carboxylates **Ia** and **Ib** with 1,2,5-oxadiazole-3,4-diamine (3,4-diaminofurazan). The reaction was carried out by heating the reactants in boiling anhydrous benzene for 30–50 min, and the products were ethyl 4'-hydroxy-1'-(2-hydroxyphenyl)-5',6-dioxo-2',4,5,5',6,7-hexahydro-1'*H*-spiro[[1,2,5]oxadiazolo[3,4-*b*]pyrazine-5,2'-pyrrole]-3-carboxylates **IIa** and **IIb**. The spectral parameters of spiro heterocyclic systems **IIa** and **IIb** were fairly similar to those of model spiro[indole-3,2'-pyrroles] whose structure was proved by X-ray analysis [2, 3].

Presumably, the reaction of pyrrolobenzoxazines **Ia** and **Ib** with diaminofurazan includes successive attack

and C⁴ carbon atoms of the substrate with cleavage of the 1,4-oxazine ring at the C⁴–O⁵ bond. No expected cleavage of the oxazine ring at the C^{3a}–N¹⁰ bond occurs. Factors determining unusual stability of the resulting spiro heterocyclic system are under discussion. The described reaction is the first example of regioselective synthesis of previously inaccessible spiro[[1,2,5]oxadiazolo[3,4-*b*]pyrazine-5,2'-pyrrole] system having functional substituents in several positions of both spiro-fused fragments.

Ethyl 4'-hydroxy-1'-(2-hydroxyphenyl)-5',6-dioxo-2',4,5,5',6,7-hexahydro-1'*H*-spiro[[1,2,5]oxadiazolo[3,4-*b*]pyrazine-5,2'-pyrrole]-3-carboxylate (IIa**).** A solution of 0.0025 mol of compound **Ia** and 0.0037 mol of diaminofurazan in 15 ml of anhydrous benzene was heated for 30 min under reflux (until the mixture turned colorless). The mixture was cooled, and the precipitate was filtered off. Yield 64%, mp 193–194°C (from ethanol). IR spectrum, ν , cm^{–1}: 3320 br (OH, NH); 1720, 1690 (C=O). ¹H NMR spectrum, δ , ppm: 1.10 t (3H, Me, *J* = 7.0 Hz), 4.10 q (2H, CH₂O, *J* = 7.0 Hz), 6.74–7.20 m (4H, C₆H₄), 7.37 s (1H, 4-H), 8.63 s (1H, 7-H), 9.90 s (1H, 2''-OH), 12.50 s (1H, 4'-OH). ¹³C NMR spectrum (DMSO-*d*₆), δ _C, ppm: 13.89 (Me), 60.03 (OCH₂), 76.89 (C_{spiro}), 110.95–130.38



R = H (a), Me (b).

(C_{arom}), 143.21 (C^{3a}), 145.41 (C^{7a}), 154.83 (C^{2''}), 155.17 (C^{4'}), 161.44 (C^{5'}), 162.71 (COO), 163.68 (C⁶). Found, %: C 49.52; H 3.42; N 18.08. C₁₆H₁₃N₅O₇. Calculated, %: C 49.62; H 3.38; N 18.08.

Ethyl 4'-hydroxy-1'-(2-hydroxy-4-methylphenyl)-5',6-dioxo-2',4,5,5',6,7-hexahydro-1'H-spiro[[1,2,5]oxadiazolo[3,4-b]pyrazine-5,2'-pyrrole]-3-carboxylate (IIb) was synthesized in a similar way. Yield 90%, mp 179–182°C (from benzene). IR spectrum, ν , cm⁻¹: 3350 br (OH, NH); 1710, 1700, 1680 (C=O). ¹H NMR spectrum, δ , ppm: 1.09 t (3H, Me, J = 7.0 Hz), 2.19 s (3H, Me), 4.07 q (2H, CH₂O, J = 7.0 Hz), 6.56–6.82 m (3H, C₆H₃), 7.24 s (1H, 4-H), 8.51 s (1H, 7-H), 9.63 s (1H, 2''-OH), 12.42 s (1H, 4'-OH). Found, %: C 50.80; H 3.79; N 17.43. C₁₇H₁₅N₅O₇. Calculated, %: C 50.88; H 3.77; N 17.45.

The IR spectra were recorded in mineral oil on a UR-20 spectrometer. The ¹H and ¹³C NMR spectra

were measured on a Bruker WP-400 instrument from solutions in DMSO-*d*₆ using TMS as internal reference. The purity of the products was checked by TLC on Silufol plates using ethyl acetate as eluent (development with iodine vapor).

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