

SHORT  
COMMUNICATIONS

## Spiro Recyclization of Pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-triones by the Action of Acyclic Enamines

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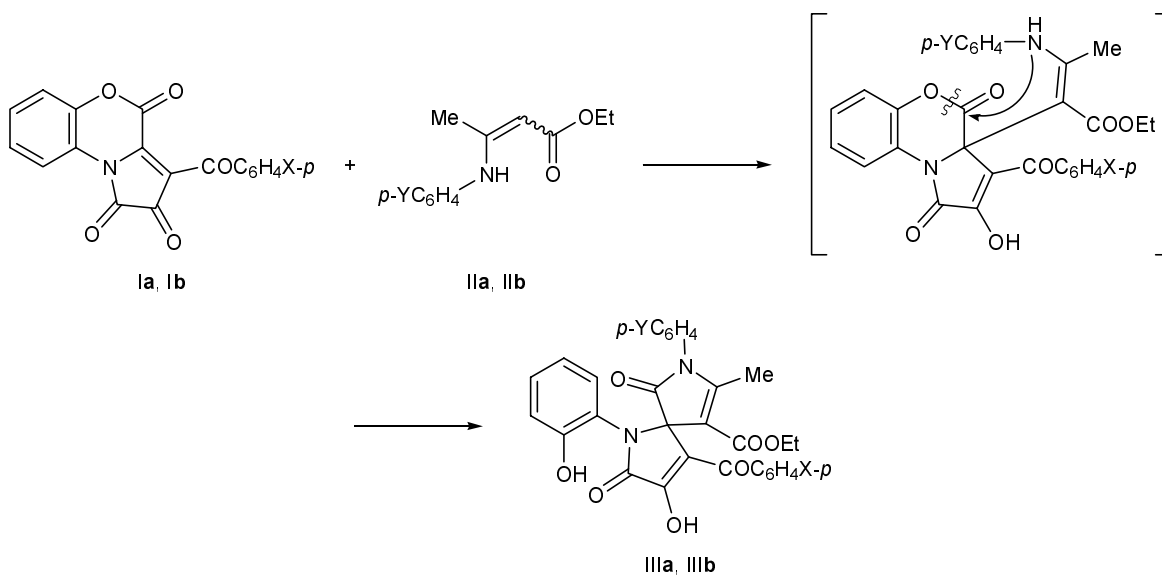
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Reactions of substituted pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-triones with acyclic enamines were not described previously. We performed reactions of 3-aryl-2,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-triones **Ia** and **Ib** [1] with ethyl 3-arylaminobut-2-enoates **IIa** and **IIb** at a ratio of 1:1 in anhydrous benzene by heating the reaction mixture for a short time (4–5 min) at the boiling point and obtained the corresponding ethyl 4-aryl-7-aryl-3-hydroxy-1-*o*-hydroxyphenyl-8-methyl-2,6-dioxo-1,7-diazaspiro[4.4]nona-3,8-diene-9-carboxylates **IIIa** and **IIIb** in almost quantitative yield. The spectral parameters of spiro compounds **IIIa** and **IIIb** were analogous to the corresponding parameters of model hexahydroindole-3-spiro-2'-dihydropyrroles whose structure was proved by X-ray analysis [2].

Presumably, the first reaction step involves addition of the activated  $\beta$ -CH group of the enamino fragment in ester **IIa** or **IIb** to the carbon atom in position 3*a* of pyrrolobenzoxazinetrione **Ia** or **Ib**, as was reported for reactions of the latter with mononucleophiles. Next follows closure of pyrrole ring via intramolecular attack by the side-chain amino group on the lactone carbonyl carbon atom in the benzoxazine ring, which is accompanied by cleavage of the oxazine ring at the C<sup>4</sup>–O<sup>5</sup> bond. It should be emphasized that the revealed reaction is a fairly rare example of regioselective synthesis of difficultly accessible spirobipyrrole system with purposefully variable functional substituents in several positions of both pyrrole rings.

**Ethyl 3-hydroxy-1-*o*-hydroxyphenyl-4-*p*-methoxybenzoyl-8-methyl-2,6-dioxo-7-*p*-tolyl-1,7-diaza-**



**I**, X = MeO (**a**), Br (**b**); **II**, Y = Me (**a**), Cl (**b**); **III**, X = MeO, Y = Me (**a**); X = Br, Y = Cl (**b**).

**spiro[4.4]nona-3,8-diene-9-carboxylate (IIIa).** A solution of 1 mmol of compound **Ia** and 1 mmol of enamine **IIa** in 10 ml of anhydrous benzene was heated for 4 min under reflux. The mixture was cooled, and the precipitate was filtered off. Yield 96%, mp 198–199°C (from ethyl acetate). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3200 br (OH); 1756 (COOEt); 1701, 1698 ( $\text{C}^2=\text{O}$ ,  $\text{C}^6=\text{O}$ ); 1653 (COAr).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.20 t (3H,  $\text{CH}_3\text{CH}_2$ ,  $J = 7.1$  Hz), 2.01 s (3H, Me), 2.37 s (3H,  $\text{C}_6\text{H}_4\text{Me-}p$ ), 3.86 s (3H, OMe), 4.04 q (2H,  $\text{CH}_3\text{CH}_2$ ,  $J = 7.1$  Hz), 6.80–7.84 m (12H,  $\text{C}_6\text{H}_4$ ), 9.78 s (1H, OH), 12.13 br.s (1H, 3-OH). Found, %: C 67.63; H 5.00; N 4.95.  $\text{C}_{32}\text{H}_{28}\text{N}_2\text{O}_8$ . Calculated, %: C 67.60; H 4.96; N 4.93.

**Ethyl 7-*p*-bromophenyl-4-*p*-chlorobenzoyl-3-hydroxy-1-*o*-hydroxyphenyl-8-methyl-2,6-dioxo-1,7-diazaspiro[4.4]nona-3,8-diene-9-carboxylate (IIIb)** was synthesized in a similar way from compounds **Ib** and **IIb**. Yield 95%, mp 262–264°C (from ethyl acetate). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3360 br, 3100 br (OH); 1758 (COOEt); 1722 ( $\text{C}^2=\text{O}$ ,  $\text{C}^6=\text{O}$ ); 1654 (COAr).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.21 t (3H,

$\text{CH}_3\text{CH}_2$ ,  $J = 7.1$  Hz), 1.99 s (3H, Me), 4.04 q (2H,  $\text{CH}_3\text{CH}_2$ ,  $J = 7.1$  Hz), 6.80–8.00 m (12H,  $\text{C}_6\text{H}_4$ ), 9.93 s (1H, OH), 12.82 br.s (1H, 3-OH). Found, %: C 56.50; H 3.44; N 4.38.  $\text{C}_{30}\text{H}_{22}\text{BrClN}_2\text{O}_7$ . Calculated, %: C 56.49; H 3.48; N 4.39.

The IR spectra were recorded on a UR-20 spectrophotometer from samples dispersed in mineral oil. The  $^1\text{H}$  NMR spectra were recorded on a Bruker WP-400 instrument from solutions in  $\text{DMSO-}d_6$  using tetramethylsilane 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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#### REFERENCES

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