

SHORT  
COMMUNICATIONS

## Uncommon Reaction of Pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-trione with $\alpha$ -Enaminoester

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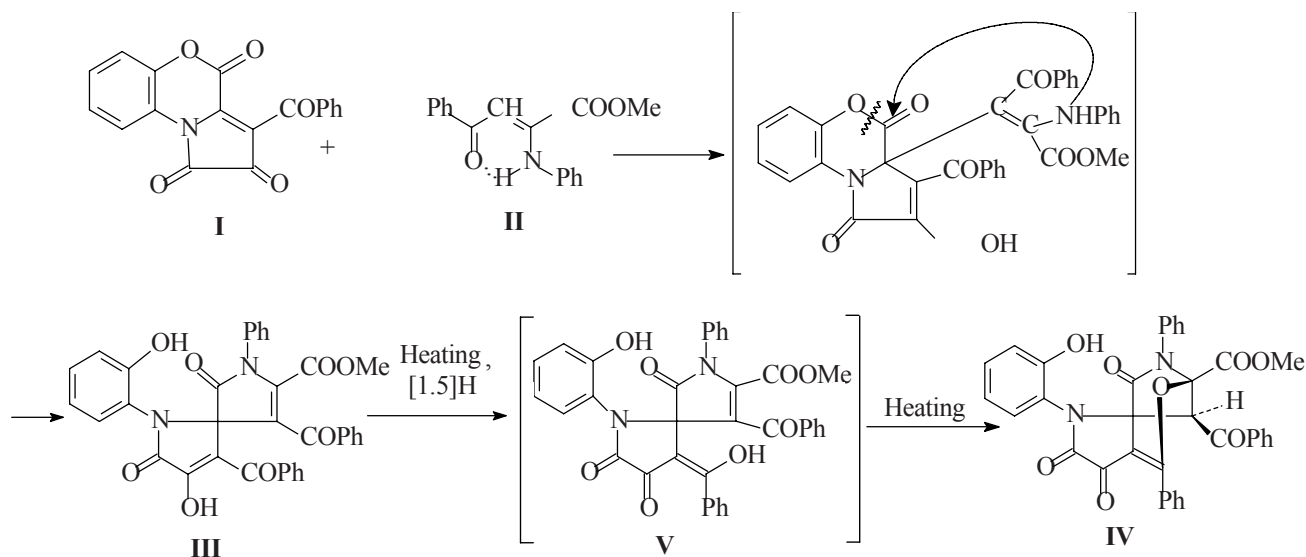
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Reactions with  $\alpha$ -enaminoesters of 1*H*-pyrrole-2,3-diones, in particular, those fused with azaheterocycles by the [*a*] side, were not formerly described.

In reaction of 3-benzoyl-1*H*-pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-trione (**I**) with a potential 1,3-CH<sub>2</sub>NH-binucleophile,  $\alpha$ -enaminoester methyl (2*E*)-2-anilino-4-oxo-4-phenyl-2-butenoate (**II**), at boiling in 1:1 ratio in anhydrous benzene we obtained in 20–25 min (till decoloration) in a virtually quantitative yield methyl 4,9-dibenzoyl-3-hydroxy-1-(2-hydroxyphenyl)-2,6-dioxo-7-phenyl-1,7-diazaspiro[4.4]nona-3,8-diene-8-carboxylate (**III**). Compound **III** during recrystallization from ethyl acetate underwent cyclization into methyl 11-benzoyl-2-(2-hydroxyphenyl)-3,4,10-trioxo-6,9-diphenyl-7-oxa-

2,9-diazatricyclo[6.2.1.0<sup>1,5</sup>]undec-5-ene-8-carboxylate (**IV**) whose structure was proved by XRD analysis.

Evidently in the first stage of the reaction the activated  $\beta$ -CH group of the enamino fragment of  $\alpha$ -enaminoester **II** added to the carbon atom in the position 3*a* of pyrrolobenzoxazinetrione **I** followed by (*Z*) $\leftrightarrow$ (*E*) isomerization and a closure of a pyrrole ring through an intramolecular attack of the free amino group of the side chain of  $\alpha$ -enaminoester **II** on the lactone carbonyl of the benzoxazine ring of compound **I** with its opening of C<sup>4</sup>–O<sup>5</sup> bond and the formation of intermediate substituted pyrrole-2-spiro-3'-pyrrole **III**. Formed spiro compound **III** at attempted recrystallization suffered an intramolecular cyclization by addition of an enol OH group of the tautomer



hydroxymethylene form **V** to the carbon atom in the position 5' in the neighbor pyrrole ring resulting in a compound with a bridging bond **IV**.

This reaction is the first example of an intramolecular cyclization of pyrrole-2-spiro-3'-pyrroles with a regioselective building of difficultly available functionalized heterocyclic system of 7-oxa-2,9-diaza-tricyclo-[6.2.1.0<sup>1,5</sup>]undecane.

**Methyl 4,9-dibenzoyl-3-hydroxy-1-(2-hydroxyphenyl)2,6-dioxo-7-phenyl-1,7-diazaspiro[4.4]-nona-3,8-diene-8-carboxylate (III)**. A solution of 1 mmol of compound **I** and 1 mmol of compound **II** in 10 ml of anhydrous benzene was boiled for 25 min (till decoloration), the reaction mixture was cooled, the separated precipitate was filtered off. Yield 87%, mp 200–202°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3152 br (OH), 1770 (COOMe), 1737 ( $\text{C}'=\text{O}$ ), 1724 ( $\text{C}^5=\text{O}$ ), 1672, 1620 ( $\text{C}^3-\text{C}=\text{O}$ ,  $\text{C}'-\text{C}=\text{O}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 3.20 s (3H, OMe), 7.10–7.98 group of signals (19H,  $\text{C}_6\text{H}_4 + 3\text{Ph}$ ), 9.80 s (1H,  $\text{OH}_{\text{phenol}}$ ), 12.60 br.s (1H,  $\text{OH}_{\text{enol}}$ ). Found, %: C 70.10; H 4.00; N 4.55.  $\text{C}_{35}\text{H}_{24}\text{N}_2\text{O}_8$ . Calculated, %: C 70.00; H 4.03; N 4.66.

**Methyl 11-benzoyl-2-(2-hydroxyphenyl)-3,4,10-trioxo-6,9-diphenyl-7-oxa-2,9-diazatricyclo-[6.2.1.0<sup>1,5</sup>]undec-5-ene-8-carboxylate (IV)**. A solution of 0.5 mmol of compound **III** was recrystallized from 10 ml of ethyl acetate, cooled, the separated precipitate was filtered off. Yield 92%, mp 201–203°C (from ethyl acetate). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3227 br ( $\text{OH}_{\text{phenol}}$ ), 1776 (COOMe), 1751 ( $\text{C}^2=\text{O}$ ), 1721 ( $\text{C}^5=\text{O}$ ), 1707 (COPh).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 3.22 s (3H, OMe), 5.29 s (1H,  $\text{C}''\text{H}$ ), 6.94–7.98 group of signals (19H, 3Ph +  $\text{C}_6\text{H}_4$ ), 10.01 s (1H,  $\text{OH}_{\text{phenol}}$ ). Found, %: C 69.89; H 4.07; N 4.70.  $\text{C}_{35}\text{H}_{24}\text{N}_2\text{O}_8$ . Calculated, %: C 70.00; H 4.03; N 4.66.

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

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