

Spiro-bis-heterocyclization of 5-Methoxycarbonyl-2,3-dihydro-2,3-pyrrolediones Effected by Acyclic Enamines

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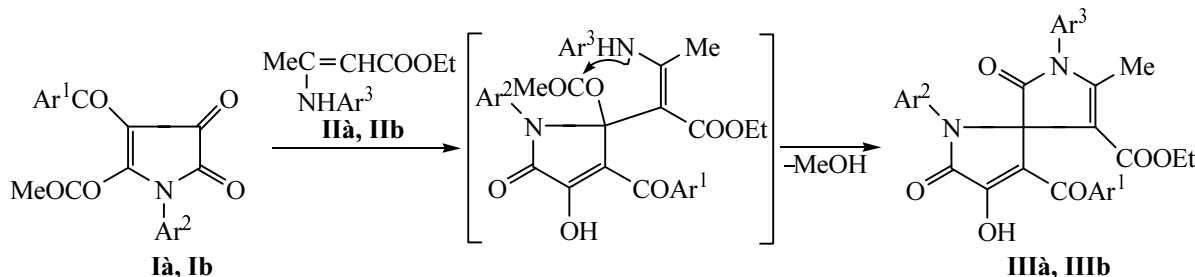
Reactions of monocyclic 2,3-dihydro-2,3-pyrrolediones with acyclic enamines were not described before. By reaction of 1-aryl-4-aryl-5-methoxycarbonyl-2,3-dihydro-2,3-pyrrolediones **Ia** and **Ib** [1] with ethyl C-arylamino-2-butenates (ethyl esters of 3-arylamino-2-butenic acids) **IIa** and **IIb** taken in a ratio 1:1 carried out by short (0.5–1 min) boiling in the anhydrous benzene we obtained in good yield 1-aryl-3-aryl-4-hydroxy-5-oxo-2,5-dihydropyrrole-2-spiro-3'-(1-aryl-5-methyl-2-oxo-4-ethoxycarbonyl-2,3-dihydropyrroles) (**IIIa** and **IIIb**). The spectral characteristics of spiro compounds **IIIa** and **IIIb** are very similar to those of the model hexahydroindole-3-spiro-2'-dihydropyrroles whose structure was proved by the X-ray diffraction analysis [2, 3].

Apparently in the first stage of the process the activated β -CH group of the enamine fragment from compounds **IIa** and **IIb** added to the carbon in the 5 position of pyrrolediones **Ia** and **Ib** followed by intramolecular closure of a pyrrole ring due to an intramolecular nucleophilic attack of the amino group from enamines **IIa** and **IIb** on the ester carbonyl (in the substituent at the position 5 in pyrrolediones **Ia** and **Ib**) with methanol elimination.

It should be noted that the reaction under consideration is a very rare example of a regioselective building up of a difficultly accessible spiro-bis-heterocyclic system of pyrrole-spiro-pyrrole with desirably varied substituents in several positions of both heterocycles.

3-Benzoyl-4-hydroxy-5-oxo-1-phenyl-2,5-dihydropyrrole-2-spiro-3'-(5-methyl-2-oxo-1-*p*-tolyl-4-ethoxycarbonyl-2,3-dihydropyrrole) (**IIIa**). A solution of 1 mmol of compound **Ia** and 1 mmol of enamine **IIa** in 10 ml of anhydrous benzene was boiled for 1 min, then cooled, the separated precipitate was filtered off. Yield 86%, mp 237–238°C (). IR spectrum, cm^{-1} : 3450 br, 3180 br (OH), 1754 (COOEt), 1698, 1682 ($\text{C}^2=\text{O}$, $\text{C}^5=\text{O}$), 1633 (COPh). ^1H NMR spectrum, δ , ppm: 1.22 t (3H, CH_3CH_2 , J 7.1 Hz), 2.07 s (3H, Me), 2.39 s (CH, $\text{C}_6\text{H}_4\text{Me-4}$), 4.11 q (2H, CH_3CH_2 , J 7.1 Hz), 7.14–7.76 group of signals (14H, 2Ph + C_6H_4), 12.60 br.s (1H, OH). Found, %: C 71.26; H 5.03; N 5.32. $\text{C}_{31}\text{H}_{26}\text{N}_2\text{O}_6$. Calculated, %: C 71.25; H 5.02; N 5.36.

4-Hydroxy-5-oxo-1-*p*-tolyl-3-*p*-ethoxy-benzoyl-2,5-dihydropyrrole-2-spiro-3'-(5-methyl-2-oxo-1-*p*-chlorophenyl-4-ethoxycarbonyl-2,3-dihydropyrrole)



I, Ar¹ = Ar² = Ph (**a**); Ar¹ = $\text{C}_6\text{H}_4\text{OEt}$, Ar² = $\text{C}_6\text{H}_4\text{Me-4}$ (**b**); **II**, Ar³ = $\text{C}_6\text{H}_4\text{Me-4}$ (**a**), $\text{C}_6\text{H}_4\text{Cl-4}$ (**b**); **III**, Ar¹ = Ar² = Ph, Ar³ = $\text{C}_6\text{H}_4\text{Me-4}$ (**a**); Ar¹ = $\text{C}_6\text{H}_4\text{OEt}$, Ar² = $\text{C}_6\text{H}_4\text{Me-4}$, Ar³ = $\text{C}_6\text{H}_4\text{Cl-4}$ (**b**).

(IIIb). Yield 85%, mp 255-257°C (decomp., from ethyl acetate). IR spectrum, cm^{-1} : 3410 br, 3300 br (OH), 1758 (COOEt), 1722 ($\text{C}=\text{O}$, $\text{C}^5=\text{O}$), 1678 (COAr). ^1H , δ , ppm: 1.21 t (3H, CH_3CH_2 , J 7.1 Hz), 1.36 t (3H, CH_3CH_2 , J 6.9 Hz), 2.11 s (3H, Me), 2.34 s (3H, $\text{C}_6\text{H}_4\text{Me-4}$), 4.08 q (2H, CH_3CH_2 , J 7.1 Hz), 4.14 q (2H, CH_3CH_2 , J 6.9 Hz), 7.00–7.76 group of signals (12H, $3\text{C}_6\text{H}_4$) 12.45 br.s (1H, OH). Found, %: C 65.96; H 4.85; N 4.68. $\text{C}_{33}\text{H}_{29}\text{ClN}_2\text{O}_7$. Calculated, %: C 65.94; H 4.86; N 4.66.

IR spectra of compounds obtained were recorded on a spectrophotometer UR-20 from mulls in mineral oil. ^1H NMR spectra were registered on a spectrometer Bruker WP-400 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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