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SHORT COMMUNICATIONS

Nucleophilic [3+3]-Addition of Heterocyclic Enamine to Monocyclic 1*H*-Pyrrole-2,3-diones

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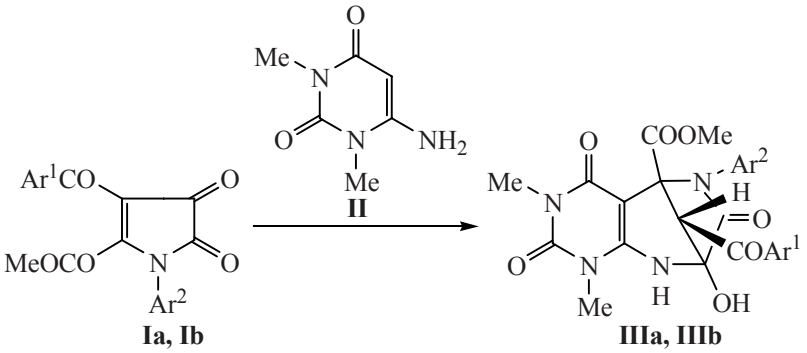
Reactions of monocyclic 1*H*-pyrrole-2,3-diones with heterylamines were not described before.

In reactions of substituted 1*H*-pyrrole-2,3-diones (methyl 1-aryl-3-aroyl-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylates) **Ia** and **Ib** with 6-amino-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (**II**) in 1:1 ratio at boiling in anhydrous 1,2-dichloroethane for 4–6 h (till the intense red color of initial compounds **Ia** and **Ib** disappeared) we unexpectedly obtained methyl 11-aryl-12-aroyl-9-hydroxy-4,6-dimethyl-3,5,10-trioxo-4,6,8,11-tetraazatricyclo[7.2.1.$0^{2,7}$]dodec-2(7)-ene-1-carboxylate **IIIa** and **IIIb**. The spectral characteristics of compounds **IIIa** and **IIIb** are close to those of a model substituted 3,10,13-triazapentacyclo[10.7.1.$0^{1,10}$.$0^{4,9}$.$0^{14,19}$]eicosa-4,6,8,14(19)-tetraene whose structure was proved by XRD [1].

Evidently the formation of bridged compounds **IIIa** and **IIIb** occurred due to the addition of groups β-CH and NH_2 of the enamino fragment from the heterylamine **II** to atoms C^2 and C^4 respectively in monocyclic pyrrolediones **Ia** and **Ib**.

The described reaction is the first example of the nucleophilic [3+3]-addition of an enamino fragment of a heterylamine to monocyclic 1*H*-pyrrole-2,3-diones, and also a new preparation method for difficultly available functionalized bridged heterocyclic system of 4,6,8,11-tetraazatricyclo[7.2.1.$0^{2,7}$]dodecene.

Methyl 12-benzoyl-9-hydroxy-4,6-dimethyl-3,5,10-trioxo-11-phenyl-4,6,8,11-tetraazatricyclo-[7.2.1.$0^{2,7}$]dodec-2(7)-ene-1-carboxylate (IIIa). A solution of 1 mmol of compound **Ia** and 1 mmol of enamine **II** in 10 ml of anhydrous 1,2-dichloroethane was boiled for 4 h, and on cooling the separated precipitate was filtered off. Yield 74%, mp 210–211°C (decomp., dichloroethane). IR spectrum, ν, cm^{-1}: 3330 (NH), 3160 br (OH), 1759 (C^5=O), 1738 (C^3=O), 1721 (COOMe), 1704 (C^{10}=O), 1643 (COPh). ^{1}H NMR spectrum, δ, ppm: 3.09 s (3H, Me), 3.16 s (3H, Me), 3.37 s



$Ar^1 = Ar^2 = Ph$ (**a**); $Ar^1 = C_6H_4Br$-4, $Ar^2 = C_6H_4Me$-4 (**b**).

(3H, COOMε), 4.83 s (1H, $C^{12}H$), 7.19–7.99 group of signals (10H, 2Ph), 7.84 s (1H, OH), 8.52 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 27.73, 30.14 (2Me), 51.37 (CH), 54.70 (C^{1}), 65.50 (MeOCO), 85.64 (C^{9}), 125.43, 127.97, 128.87, 133.86, 137.33, 150.80 (C^{5}), 157.85 (C^{2}), 166.08 (MεOCO), 167.05 (C^{10}), 196.15 (PhCO). Found, %: C 61.42; H 4.64; N 11.38. $C_{25}H_{22}N_4O_7$. Calculated, %: C 61.22; H 4.52; N 11.42.

Methyl 12-*p*-bromobenzoyl-9-hydroxy-4,6-dimethyl-3,5,10-trioxo-11-*p*-tolyl-4,6,8,11-tetraazatricyclo[7.2.1.0^{2,7}]dodec-2(7)-ene-1-carboxylate (IIIb). Yield 73%, mp 220–221°C (decomp., ethyl acetate). IR spectrum, ν, cm^{-1}: 3306 (NH), 3180 br (OH), 1780 (C^{5}=O), 1761 (C^{3}=O), 1727 (COOMe), 1708 (C^{10}=O), 1628 (COPh). ^1H NMR spectrum, δ, ppm: 2.28 s (3H, C_6H_4Me-4), 3.14 s (6H, 2Me), 3.37 s (3H, COOMe), 4.83 s (1H, $C^{12}H$), 7.08–7.93 group of signals (8H, $2C_6H_4$), 7.77 s (1H, OH), 8.52 s (1H, NH). Found, %: C 53.66; H 4.09; Br 13.52; N 9.55. $C_{26}H_{23}BrN_4O_7$. Calculated, %: C 53.53; H 3.97; Br 13.70; N 9.60.

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

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REFERENCES

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