

SHORT
COMMUNICATIONS

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

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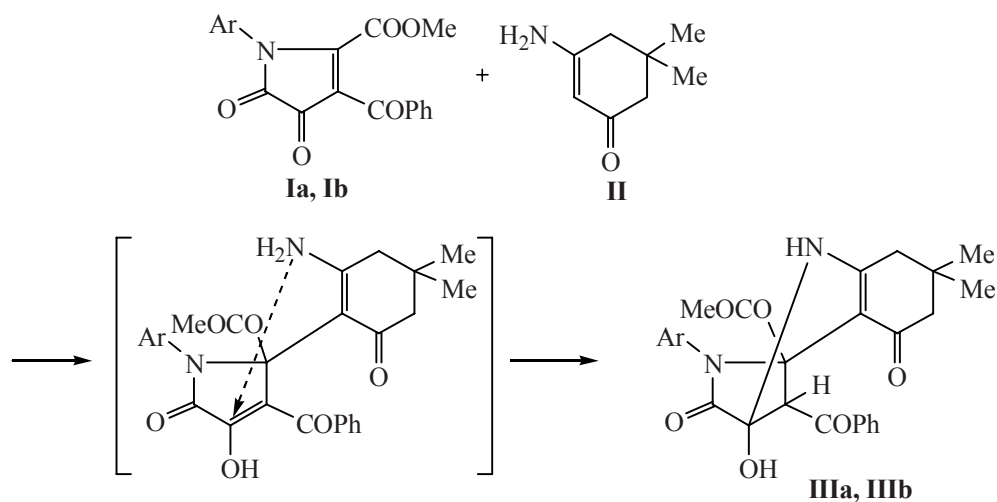
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A reaction is described of substituted 1*H*-pyrrole-2,3-diones (methyl 1-aryl-3-aryl-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylates) with N-alkyl- and N-aryl-substituted 3-amino-5,5-dimethyl-2-cyclohexen-1-ones providing 1-alkyl- and 1-aryl-substituted 6,6-dimethyl-2,4-dioxo-2,3,4,5,6,7-hexahydro-1*H*-indole-3-spiro-2'-(1'-aryl-3'-aryl-4'-hydroxy-5'-oxo-2',5'-dihydro-1*H*-pyrroles) [1, 2]. The reaction proceeds as successive attacks of β -CH and NH groups of the enamino fragment of the carbocyclic enamines first on the carbon atom in the position 2 and then on the carbonyl group of the methoxycarbonyl moiety (substituent in the position 2) of pyrrolediones followed by methanol elimination.

In reaction of methyl 1-aryl-3-benzoyl-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylates **Ia** and **Ib** with N-un-

substituted 3-amino-5,5-dimethyl-2-cyclohexen-1-one (**II**) taken in a ratio 1:1 performed by boiling in anhydrous benzene for 1–2 min (to the disappearance of the bright red color of initial compounds **Ia** and **Ib**) we unexpectedly obtained methyl 11-aryl-12-benzoyl-9-hydroxy-5,5-dimethyl-3,10-dioxo-8,11-diazatricyclo[7.2.1.0^{2,7}]dodec-2(7)-ene-1-carboxylates **IIIa** and **IIIb**. 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 confirmed by XRD analysis [3].

Evidently the bridged compounds **IIIa** and **IIIb** formed by the addition of β -CH and NH₂ groups of the enamino fragment of carbocyclic enamine **II** to atoms C² and C⁴ respectively of monocyclic pyrrolediones **Ia** and **Ib**.



Ar = Ph (**a**), 4-ClC₆H₄ (**b**).

The described reaction is a new procedure for preparation of difficultly accessible functionalized bridged heterocyclic system of 8,11-diazatricyclo-[7.2.1.0^{2,7}]dodecane and also is the first example of nucleophilic [3+3]-addition of an enamine to monocyclic 1*H*-pyrrole-2,3-diones.

Methyl 12-benzoyl-9-hydroxy-5,5-dimethyl-3,10-dioxo-11-phenyl-8,11-diazatricyclo-[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 5 ml of anhydrous benzene was boiled for 1 min, then cooled, the separated precipitate was filtered off. Yield 79%, mp 179–180°C (from ethyl acetate). IR spectrum, ν , cm⁻¹: 3384 (NH), 3090 br (OH), 1751 (C³=O), 1731 (COOMe), 1663 (C¹⁰=O), 1630 (COPh). ¹H NMR spectrum, δ , ppm: 0.73 s (3H, Me), 0.86 s (3H, Me), 1.91, 1.98 d.d (2H, C⁶H₂, *J* 16.1 Hz), 2.18, 2.29 d.d (2H, C⁴H₂, *J* 16.5 Hz), 3.79 s (3H, OMe), 5.15 s (1H, C¹²H), 6.75 s (1H, OH), 7.44 s (1H, NH), 7.12–7.82 group of signals (10H, 2Ph). Found, %: C 68.38; H 5.50; N 5.92. C₂₇H₂₆N₂O₆. Calculated, %: C 68.34; H 5.52; N 5.90.

Methyl 12-benzoyl-9-hydroxy-5,5-dimethyl-3,10-dioxo-11-*p*-chlorophenyl-8,11-diazatricyclo-[7.2.1.0^{2,7}]dodec-2(7)-ene-1-carboxylate (IIIb). Yield 75%, mp 183–184°C (from methanol). IR spectrum, ν , cm⁻¹: 3330 (NH), 3130 br (OH), 1756 (C³=O), 1726

(COOMe), 1659 (C¹⁰=O), 1623 (COPh). ¹H NMR spectrum, δ , ppm: 0.72 s (3H, Me), 0.85 s (3H, Me), 1.90, 1.98 d.d (2H, C⁶H₂, *J* 16.3 Hz), 2.18, 2.30 d.d (2H, C⁴H₂, *J* 16.7 Hz), 3.79 s (3H, OMe), 5.11 s (1H, C¹²H), 6.81 s (1H, OH), 7.47 s (1H, NH), 7.16–7.82 group of signals (9H, Ph + C₆H₄). Found, %: C 63.77; H 4.91; Cl 6.99; N 5.54. C₂₇H₂₅ClN₂O₆. Calculated, %: C 63.72; H 4.95; Cl 6.97; N 5.50.

IR spectra of compounds synthesized 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 proved by TLC on Silufol plates, eluent ethyl acetate, development in iodine vapor.

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