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SHORT COMMUNICATIONS

Double Spiro-bis-heterocyclization of 5-Methoxycarbonyl-2,3-dihydro-2,3-pyrroledione by Treatment with N-Aryl-Substituted Dimedone Imine

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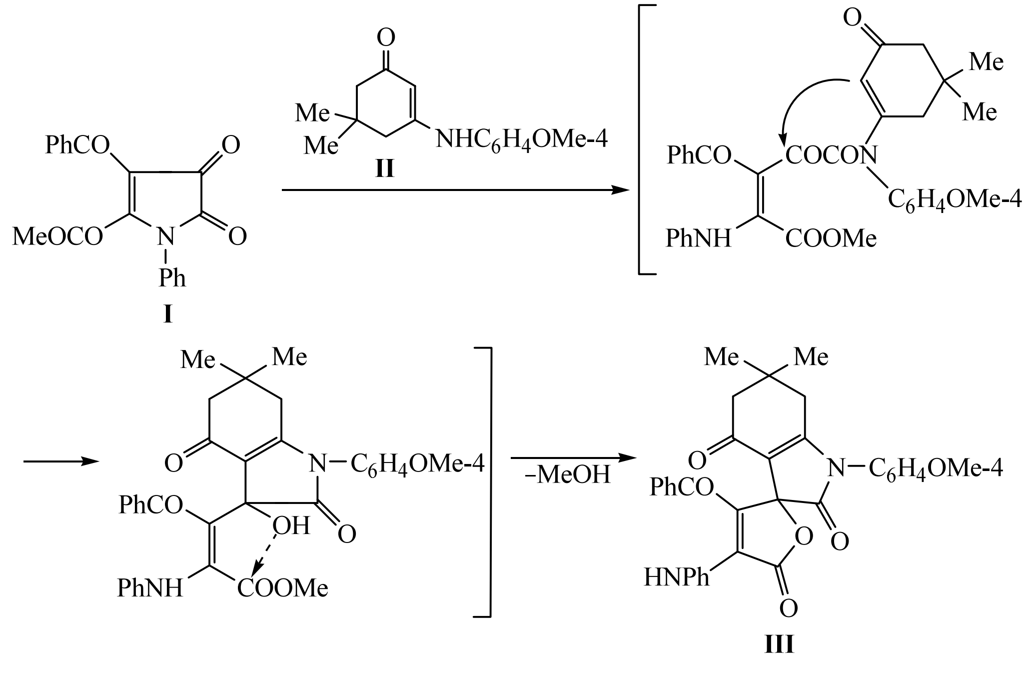
We formerly reported on reactions of 1-aryl-4-aroyl-5-methoxycarbonyl-2,3-dihydro-2,3-pyrolediones with CH,NH-binucleophiles, cyclic enamines (3-alkylamino- and 3-arylamino-5,5-dimethyl-2-cyclohexen-1-ones), occurring as a successive attack by the β-CH and NH groups of the enamino fragment from the reagents on the carbon atoms in position *5* and in the carbonyl group of the methoxycarbonyl moiety, the substituent in position *5* of pyrolediones, and affording substituted 6,6-dimethyl-2,4-dioxo-2,3,4,5,6,7-hexahydro-1*H*-indole-3-spiro-2-(1-aryl-3-aroyl-4-hydroxyθ-5-oxo-2,5-dihydro-1*H*-pyrroles) [1, 2].

The reaction of 4-benzoyl-1-phenyl-5-methoxycarbonyl-2,3-dihydro-2,3-pyrroledione (**I**) with 5,5-dimethyl-3-*p*-methoxyphenylamino-2-cyclohexen-1-one (**II**) instead of the expected colorless 6,6-dimethyl-1-*p*-methoxyphenyl-2,4-dioxo-2,3,4,5,6,7-hexahydro-1*H*-indole-3-spiro-2-(3-benzoyl-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1*H*-pyrrole) gave rise unexpectedly to bright-yellow 6,6-dimethyl-1-*p*-methoxyphenyl-2,4-dioxo-2,3,4,5,6,7-hexahydro-1*H*-indole-3-spiro-2-(3-benzoyl-5-oxo-4-phenylamino-2,5-dihydrofuran) (**III**), whose structure was proved by spectral data and X-ray diffraction analysis.



Apparently in the first stage the activated NH group of enamine **II** added to the carbon atom in position *2* of pyrroledione **I** with subsequent pyrroledione ring opening at the N^1–C^2 bond, intramolecular nucleophilic attack of the β-CH group of the enamine on the ketone carbonyl group and a “second” intramolecular cyclization involving the formed CH group and the ester carbonyl accompanied by methanol molecule elimination. It should be emphasized that the reaction described is the first example of a “double” nucleophilic cyclization of the product of enamine addition to monocyclic pyrrolediones, and also a very seldom instance of building up of a difficultly accessible spiro-bisheterocyclic system indole–spirofuran with purposeful varied functional substituents in several positions of both heterocycles.

6,6-Dimethyl-1-*p*-methoxyphenyl-2,4-dioxo-2,3,4,5,6,7-hexahydro-1*H*-indole-3-spiro-2-(3-benzoyl-5-oxo-4-phenylamino-2,5-dihydrofuran) (III). A solution of 1.0 mmol of compound **I** and 1.0 mmol of enamine **II** in 10 ml of anhydrous benzene was boiled for 1 min, cooled, and the separated precipitate was filtered off. Yield 86%, mp 185–187°C (decomp, from ethyl acetate). IR spectrum, cm^{-1}: 3283 (NH), 1790 (C^5=O), 1761 (C^2=O), 1655 (C^4=O), 1626 (COPh). ^1H NMR spectrum, δ, ppm: 0.69 s (3H, Me), 1.01 s (3H, Me), 1.98, 2.36 d.d (2H, C^7H_2, *J* 16.0 Hz), 2.16, 2.70 d.d (2H, C^5H_2, *J* 18.4 Hz), 3.85 s (3H, $C_6H_4O\underline{Me}$-4), 6.71–7.45 group of s (14H, 2Ph + C_6H_4), 9.31 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 28.86 (C^6), 33.95 (Me), 35.96 (C^7), 50.21 (C^5), 55.50 (MeO), 83.05 (spiro-C), 108.52, 114.95, 117.94, 120.16, 123.28, 125.16, 128.04, 128.36, 128.70, 132.84, 132.96, 137.23, 140.55, 159.58 (α-C–OMe), 167.97 (C^{7a}), 169.07 ($C^{5'}$), 173.16 (C^2), 190.11 (Ph$\underline{C}$O), 190.62 (C^4O). Found, %: C 72.26; H 5.15; N 5.13. $C_{33}H_{28}N_2O_6$. Calculated, %: C 72.25; H 5.14; N 5.11.

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 DMSO-d_6, internal reference TMS. The homogeneity of compounds synthesized was proved by TLC on Silufol plates, eluent ethyl acetate, development in iodine vapor.

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