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SHORT COMMUNICATIONS

New Route of Reaction of 4-Acyl-1*H*-pyrrole-2,3-diones with 1,3-CH,NH-Binucleophile

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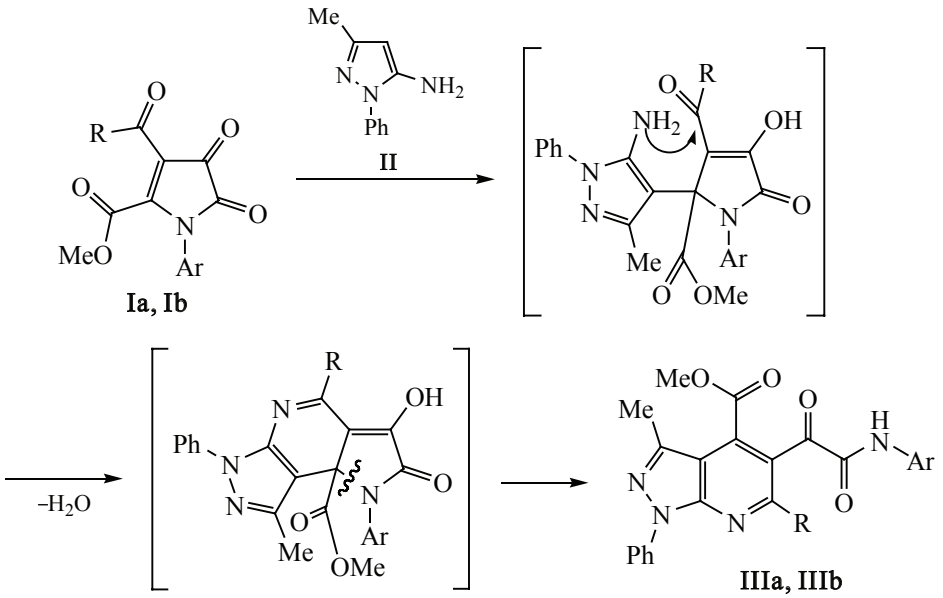
Reactions are described of 1-aryl-4-aroyl-5-methoxycarbonyl-1*H*-pyrrole-2,3-diones with acyclic [1], carbocyclic [2] and heterocyclic [3] 1,3-CH,NH-binucleophiles leading to the formation of spirobisheterocyclic or bridging heterocyclic systems due to the involvement of pyrrolediones in these reactions by atom C^5 and methoxycarbonyl group or atom C^3 respectively.

At boiling substituted 5-methoxycarbonyl-1-(4-tolyl)-1*H*-pyrrole-2,3-diones **Ia, Ib** and 5-amino-3-methyl-1-phenyl-1*H*-pyrazole (**II**) in 1:1 ratio in anhydrous benzene for 1–1.5 h (TLC monitoring) we obtained methyl 6-R-3-methyl-5-[2-oxo-2-(4-tolylamino)acetyl]-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-4-carboxylates **IIIa, IIIb**.

The formation of compounds **IIIa, IIIb** occurs apparently through primary addition of the β-CH group of the enamino fragment of compound **II** to the atom C^5 of pyrrolediones **Ia, Ib** followed by the intramolecular reaction of the primary amino group with the carbonyl group of the acyl substituent in the position *4* and by the opening of the pyrrole ring at the N^1–C^5 bond.

The described reaction is an example of the new route of the reaction between 1-aryl-4-acyl-5-methoxycarbonyl-1*H*-pyrrole-2,3-diones and 1,3-CH,NH-binucleophiles,



Ar = 4-MeC_6H_4, R = Ph (**a**), Ph-CH=CH (**b**).

and also a convenient method of building up the heterocyclic system of 1*H*-pyrazolo[3,4-*b*]pyridine with previously inaccessible combination of substituents.

Methyl 3-methyl-5-[2-oxo-2-(4-tolylamino)-acetyl]-1,6-diphenyl-1*H*-pyrazolo[3,4-*b*]pyridine-4-carboxylate (IIIa). A solution of 1 mmol of compound **Ia** and 1 mmol of amine **II** in 10 ml of anhydrous benzene was boiled for 1 h, cooled, the separated precipitate was filtered off. Yield 84%, mp 195–196°C (benzene). IR spectrum, ν, cm^{-1}: 3364 (NH), 1727 (COOMe), 1698 (C^5–C=O), 1686 (CONH). ^{1}H NMR spectrum, *δ*, ppm: 2.26 s (3H, Me), 2.64 s (3H, Me), 3.94 s (3H, OMe), 7.12–8.24 group of signals (14H, 2Ph + 2C$_6$H$_4$), 10.74 s (1H, NH). ^{13}C NMR spectrum, *δ,* ppm: 14.47 (Me), 20.49 (Me), 53.38 (OMe), 110.45 (C^3–C), 120.40–138.60 (C$_{arom}$), 142.89 (MeC^3), 150.17 (N^{1}C), 158.16 (C^4), 159.24 (C^6), 164.89 (COOMe), 191.48 (C^{5}C=O). Found, %: C 71.42; H 4.79; N 11.10. C$_{30}$H$_{24}$N$_4$O$_4$. Calculated, %: C 71.42; H 4.79; N 11.10.

Methyl 3-methyl-5-[2-oxo-2-(4-tolylamino)-acetyl]-6-styryl-1-phenyl-1*H*-pyrazolo[3,4-*b*]-pyridine-4-carboxylate (IIIb). Yield 80%, mp 219–220°C (toluene). IR spectrum, ν, cm^{-1}: 3328 (NH), 1719 (COOMe), 1697 (C^5–C=O), 1669 (CONH), 1636 (C^6–CH=CH). ^{1}H NMR spectrum, δ, ppm: 2.29 s (3H, Me), 2.64 s (3H, Me), 3.88 s (3H, OMe), 7.19–8.30 group of signals (16H, 2Ph + C$_6$H$_4$ + CH=CH), 10.94 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 15.01 (Me), 20.38 (Me), 53.05 (OMe), 110.43 (C^{3}C), 120.25–138.27 (C$_{arom}$), 143.07 (MeC^3), 150.25 (N^{1}C), 152.86 (C^4), 159.13 (C^6), 164.40 (COOMe), 191.18 (C^{5}C=O). Found, %: C 72.47; H 4.93; N 10.54. C$_{32}$H$_{26}$N$_4$O$_4$. Calculated, %: C 72.44; H 4.94; N 10.56.

IR spectra of compounds obtained were recorded on a spectrophotometer Perkin Elmer Spectrum Two from mulls in mineral oil. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker AM-400 at operating frequencies 400 (^{1}H) and 100 MHz (^{13}C) in DMSO-d_6, internal reference TMS. The homogeneity of compounds synthesized was proved by TLC on Silufol plates, eluent benzene–ethyl acetate, 5 : 1, development in iodine vapor.

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