ISSN 1070-4280, Russian Journal of Organic Chemistry, 2011, Vol. 47, No. 8, pp. 1263–1264. © Pleiades Publishing, Ltd., 2011.
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SHORT COMMUNICATIONS

Three Component Condensation of 1*H*-Pyrrol-2,3-dione with Malononitrile and 4-Hydroxycoumarin

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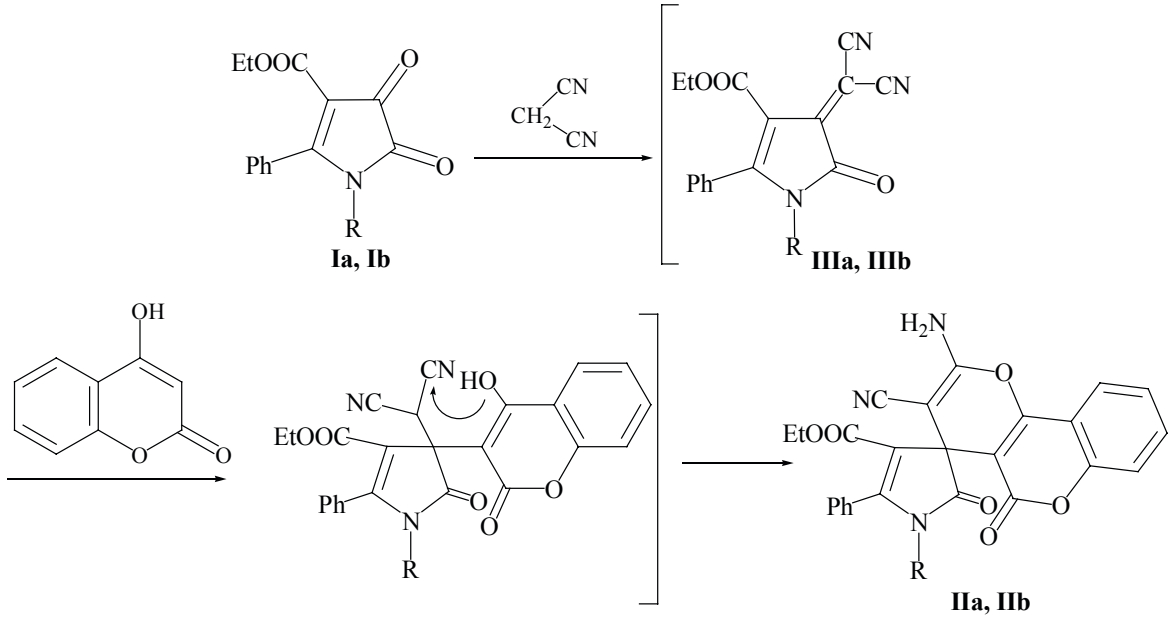
Received November 9, 2010

DOI: 10.1134/S1070428011080288

The spiroheterocyclixation of isatin under the action of malononitrile and 4-hydroxycoumarin was described resulting in the formation of substituted spiro{indole-3,4'-pyrano[3,2-*c*]chromene}-2,5'(1*H*)-diones [1].

We carried out the reaction of 5-phenyl-4-ethoxycarbonyl-1*H*-pyrrole-2,3-diones **Ia** and **Ib** with malononitrile and 4-hydroxy-2*H*-chromen-2-one (4-hydroxycoumarin) in the ratio 1 : 1 : 1 by boiling the solution of the reagents in anhydrous toluene in the presence of the equimolar amount of triethylamine for 25–40 min (TLC monitoring) to obtain ethyl 2-amino-2',5-dioxo-5'-phenyl-3-cyano-1',2'-dihydro-5*H*-spiro{pyrano[3,2-*c*]chromene-4,3'-pyrrole}-4'-carboxylates **IIa** and **IIb**.

In the first stage of the reaction proceeds apparently the condensation of the keto carbonyl group of pyrrolediones **Ia, Ib** with the methylene group of the malononitrile to form pyrrolones **IIIa, IIIb** followed by the successive nucleophilic addition of the β-CH group and the hydroxy group of the enol fragment of the 4-hydroxycoumarin to the carbon atom in the position *3* and to the cyano group



R = CH_2Ph (**a**), Ph (**b**).

of the pyrrolones respectively.

The reaction described is a rare example of the spirobisheterocyclization of monocyclic 1*H*-pyrrole-2,3-dione at the successive condensation with two different nucleophilic reagents, and also an example of the synthesis of difficultly accessible heterocyclic system of spiro{pyrano[3,2-*c*]chromene-4,3'-pyrrole}.

Ethyl 2-amino-1'-benzyl-2',5-dioxo-5'-phenyl-3-cyano-1',2'-dihydro-5*H*-spiro{pyrano[3,2-*c*]-chromen-4,3'-pyrrole}-4'-carboxylate (IIa). To a solution of 1.0 mmol of pyrroledione **Ia** in 20 ml of anhydrous toluene was added 1.0 mmol of malononitrile and 1.0 mmol of triethylamine, the mixture was boiled for 10 min, cooled, and 1.0 mmol of 4-hydroxycoumarin was added, the mixture was boiled for 25 min, cooled, the separated precipitate was filtered off and recrystallized from acetone. Yield 87%, mp 293–294°C. IR spectrum, ν, cm^{-1}: 3426, 3310 (NH_2), 2193 (CN), 1725, 1709, 1686 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.71 т (3H, $C\underline{H}_3CH_2O$, *J* 6.9 Hz), 3.74 m (2H, $CH_3C\underline{H}_2O$), 4.53 d (1H, $C\underline{H}_2Ph$, *J* 16.4 Hz), 4.59 d (1H, $C\underline{H}_2Ph$, *J* 16.4 Hz), 7.12–7.96 group of signals (16H, 2Ph + C_6H_4 + NH_2). Found, %: C 70.39; H 4.21; N 7.66. $C_{32}H_{23}N_3O_6$. Calculated, %: C 70.45; H 4.25; N 7.70.

Ethyl 2-amino-2',5-dioxo-1',5'-diphenyl-3-cyano-1',2'-dihydro-5*H*-spiro{pyrano[3,2-*c*]chromene-4,3'-pyrrole}-4'-carboxylate (IIb) was similarly prepared. Yield 64%, mp 294–296°C (ethyl acetate–acetone, 1 : 1). IR spectrum, *v*, cm^{-1}: 3341 (NH_2), 2199 (CN), 1742, 1705, 1686 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.77 t (3H, $C\underline{H}_3CH_2O$, *J* 6.9 Hz), 3.80 m (2H, $CH_3C\underline{H}_2O$), 7.08–7.97 group of signals (16H, 2Ph + C_6H_4 + NH_2). ^{13}C NMR spectrum, δ, ppm: 13.23 ($\underline{C}H_3CH_2$), 48.53 (C^4), 54.44 (C^3), 59.18 ($CH_3\underline{C}H_2$), 100.74 ($C^{4'}$), 110.43 (C^{10a}), 112.22 (C^7), 116.81 (CN), 116.91 (C^{4a}), 122.36–151.97 (C_{arom}), 155.13 (C^{6a}), 155.42 ($C^{5'}$), 158.74 (C^2), 159.40 (C^5), 161.37 (COO), 176.89 ($C^{2'}$). Found, %: C 69.99; H 3.95; N 7.88. $C_{31}H_{21}N_3O_6$. Calculated, %: C 70.05; H 3.98; N 7.91.

IR spectra of compounds obtained were recorded on a spectrophotometer FSM -1201 from mulls in mineral oil. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker AM-400 [operating frequencies 400 (^{1}H) and 100 (^{13}C) MHz] in DMSO-d_6, internal reference TMS.

ACKNOWLEDGMENTS

The study was performed under the financial support of the Ministry of Education and Science of the Russian Federation (project no. 2.19.10) and the Russian Foundation for Basic Research (grant no. 08-03-01032).

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