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SHORT COMMUNICATIONS

Spiro Heterocyclization of Methyl 4,5-Dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylates with Acyclic Enamino Ketones

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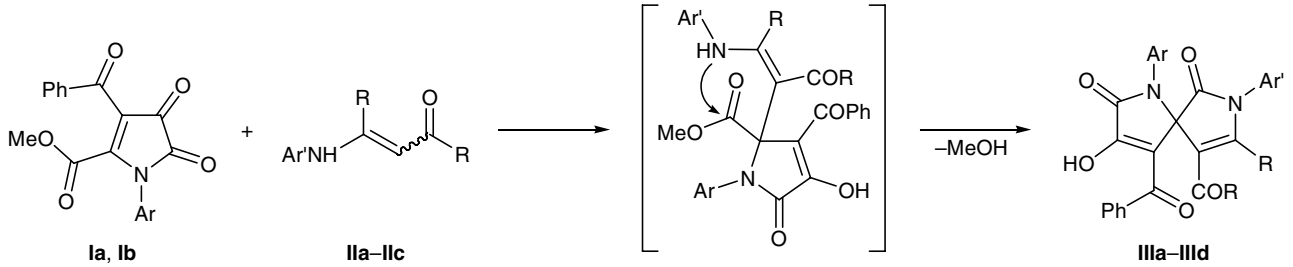
Reactions of monocyclic 2,3-dihydro-1*H*-pyrrole-2,3-diones with acyclic enamino ketones were not studied previously. We examined reactions of methyl 1-aryl-3-benzoyl-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylates **Ia** and **Ib** [1] with equimolar amounts of 4-arylaminopent-3-en-2-ones **IIa** and **IIb** and 3-(4-tolylamino)-1,3-diphenylprop-2-en-1-one (**IIc**). The reactants were heated in boiling anhydrous benzene or *m*-xylene for 2–240 min (until the reaction mixture turned colorless), and the products were the corresponding 9-acetyl-1,7-diaryl-4-benzoyl-3-hydroxy-8-methyl-1,7-diazaspiro[4.4]nona-3,8-diene-2,6-diones **IIIa** and **IIIb** and 9-acetyl-1,7-diaryl-4-benzoyl-3-hydroxy-8-phenyl-1,7-diazaspiro[4.4]nona-3,8-diene-2,6-diones **IIIc** and **IIId**. The spectral parameters of spiro compounds **IIIa**–**IIId** were very similar to those of model octahydrospiro[indole-3,2'-pyrroles] whose structure was proved by X-ray analysis [2, 3].

Presumably, the first stage of the process is addition of the activated β-CH group in the enamino fragment of ketones **IIa**–**IIc** to C^2 of pyrrolediones **Ia** and **Ib**. The subsequent intramolecular nucleophilic attack by the amino group of enamino ketones **IIa**–**IIc** on the ester carbonyl carbon atom at C^2 of pyrroledione **Ia** leads to closure of the second pyrrole ring with elimination of methanol. The described reaction is a rare example of regioselective formation of difficultly accessible spirobipyrrole system having variable functionalities in several positions of both heterorings.

9-Acetyl-4-benzoyl-7-(4-chlorophenyl)-3-hydroxy-8-methyl-1-(4-methylphenyl)-1,7-diazaspiro[4.4]nona-3,8-diene-2,6-dione (IIIa). A solution of 1 mmol of compound **Ia** and 1 mmol of 4-(4-chlorophenylamino)pent-3-en-2-one (IIa) in 10 ml of anhydrous benzene was heated for 2 min under reflux. The mixture was cooled, and the precipitate was filtered off. Yield 86%, mp 254–255°C (decomp., from ethyl acetate–dichloroethane). IR spectrum, ν, cm^{-1}: 3150 br (OH), 1720 (C^2=O, C^6=O), 1655 (COMe), 1626 (COPh). ^{1}H NMR spectrum, δ, ppm: 2.14 s (3H, Me), 2.17 s (3H, COMe), 2.34 s (3H, **Me**C_6H_4), 6.98–7.76 s (13H, H_{arom}), 12.56 br.s (1H, OH). Found, %: C 68.39; H 4.39; Cl 6.72; N 5.31. $C_{30}H_{23}ClN_2O_5$. Calculated, %: C 68.38; H 4.40; Cl 6.73; N 5.32.

9-Acetyl-4-benzoyl-1-(4-chlorophenyl)-3-hydroxy-7-(4-methoxyphenyl)-8-methyl-1,7-diazaspiro[4.4]nona-3,8-diene-2,6-dione (IIIb) was synthesized in a similar way. Yield 82%, mp 220–222°C



Ia, **Ib** **IIa**–**IIc** **IIIa**–**IIId**

I, Ar = 4-MeC_6H_4 (**a**), 4-ClC_6H_4 (**Ib**); **II**, R = Me, Ar' = 4-ClC_6H_4 (**a**), R = Me, Ar' = 4-$MeOC_6H_4$ (**b**), R = Ph, Ar' = 4-MeC_6H_4 (**c**); **III**, R = Me, Ar = 4-MeC_6H_4, Ar' = 4-ClC_6H_4 (**a**), Ar = 4-ClC_6H_4, Ar' = 4-$MeOC_6H_4$ (**b**); R = Ph, Ar = 4-ClC_6H_4, Ar' = 4-MeC_6H_4 (**c**), Ar = Ar' = 4-MeC_6H_4 (**d**).

(decomp., from methanol). IR spectrum, ν, cm^{-1}: 3145 br (OH); 1704, 1748 (C^2=O, C^6=O); 1665 (COMe); 1631, 1610 (COPh). ^{1}H NMR spectrum, δ, ppm: 2.14 s (3H, Me), 2.17 s (3H, COMe), 3.83 s (3H, **Me**OC_6H_4), 7.13–7.75 s (13H, H_{arom}), 12.55 br.s (1H, OH). Found, %: C 66.35; H 4.26; Cl 6.54; N 5.15. $C_{30}H_{23}ClN_2O_6$. Calculated, %: C 66.36; H 4.27; Cl 6.53; N 5.16.

4,9-Dibenzoyl-1-(4-chlorophenyl)-3-hydroxy-7-(4-methylphenyl)-8-phenyl-1,7-diazaspiro[4.4]nona-3,8-diene-2,6-dione (IIIc). A solution of 1 mmol of compound **Ic** and 1 mmol of enamine **IIc** in 50 ml of anhydrous *m*-xylene was heated for 4 h under reflux. The mixture was cooled, and the precipitate was filtered off. Yield 78%, mp 300–302°C (decomp., from ethyl acetate). IR spectrum, ν, cm^{-1}: 3175 br (OH); 1755, 1694 (C^2=O, C^6=O); 1667, 1629, 1613 (COPh). ^{1}H NMR spectrum, δ, ppm: 2.26 s (3H, **Me**C_6H_4), 6.72–7.80 s (23H, H_{arom}), 12.41 br.s (1H, OH). Found, %: C 73.81; H 4.19; Cl 5.47; N 4.31. $C_{40}H_{27}ClN_2O_5$. Calculated, %: C 73.79; H 4.18; Cl 5.44; N 4.30.

4,9-Dibenzoyl-3-hydroxy-1,7-bis(4-methylphenyl)-8-phenyl-1,7-diazaspiro[4.4]nona-3,8-diene-2,6-dione (IIId) was synthesized in a similar way. Yield 81%, mp 335–337°C (decomp., from butyl acetate). IR spectrum, ν, cm^{-1}: 3171 br (OH); 1751, 1692 (C^2=O, C^6=O); 1667, 1630, 1615 (COPh). ^{1}H NMR spectrum, δ, ppm: 2.25 s (3H, **Me**C_6H_4), 2.36 s (3H, **Me**C_6H_4), 6.67–7.81 s (23H, H_{arom}), 12.63 br.s (1H, OH). Found, %: C 78.10; H 4.76; N 4.42. $C_{41}H_{30}N_2O_5$. Calculated, %: C 78.08; H 4.79; N 4.44.

The IR spectra were recorded from samples dispersed in mineral oil on a UR-20 spectrometer. The ^{1}H NMR spectra were measured on a Bruker WP-400 spectrometer from solutions in DMSO-d_6 using TMS as internal reference. The purity of the products was checked by TLC on Silufol plates (eluent ethyl acetate, development with iodine vapor).

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