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SHORT COMMUNICATIONS

Spiro Heterocyclization of 1*H*-Pyrrole-2,3-dione in the Reactions with 3-Arylamino-5,5-dimethylcyclohex-2-en-1-ones

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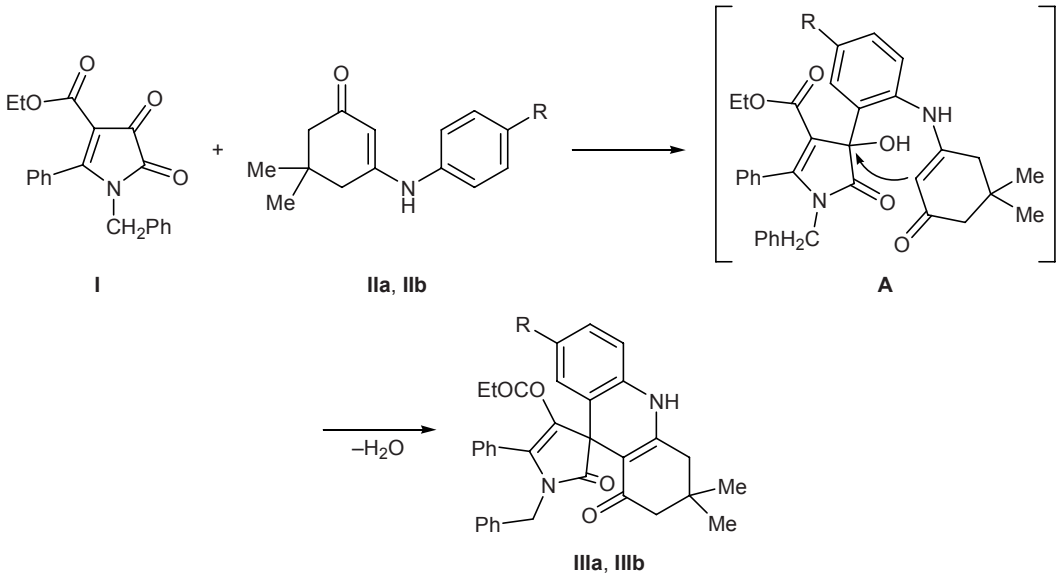
We previously reported on [3+3]-nucleophilic addition [1] and spiro heterocyclization [2] of substituted 1*H*-pyrrole-2,3-diones in reactions with cyclic enamines; in both cases, the latter acted as 1,3-C,N-binucleophiles.

We now report on the reactions of ethyl 1-benzyl-4,5-dioxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**I**) [3] with 3-arylamino-5,5-dimethylcyclohex-2-en-1-ones **IIa** and **IIb**. These reactions were carried out by heating equimolar amounts of the reactants in anhydrous *m*-xylene at 139–140°C over a period of 5–6 h, and their progress was monitored by chromatography. As a result we isolated in good yields ethyl 1′-benzyl-3,3-dimethyl-1,2′-dioxo-5′-phenyl-1′,2,2′,3,-4,10-hexahydro-1*H*-spiro[acridine-9,3′-pyrrole]-4′-carboxylates **IIIa** and **IIIb** whose structure was determined by X-ray analysis.

Presumably, compounds **IIIa** and **IIIb** are formed via initial addition of the *ortho*-carbon atom in the aryl substituent of cyclic enamine **IIa** or **IIb** at the carbonyl carbon atom in position *4* of the pyrrole ring, followed by intramolecular cyclization of intermediate **A** with participation of the =CH group in the enamine fragment.

The described reaction is the first example of direct spiro heterocyclization of substituted 1*H*-pyrrole-2,3-dione by the action of N-aryl-substituted cyclic enamines which act as 1,5-C,C-binucleophiles. It opens



I **IIa**, **IIb** **A** **IIIa**, **IIIb**

R = Me (**a**), MeO (**b**).

a synthetic route to difficultly accessible spiro[acridine-9,3′-pyrrole] heterocyclic system.

Ethyl 1′-benzyl-3,3,7-trimethyl-1,2′-dioxo-5′-phenyl-1′,2,2′,3,4,10-hexahydro-1*H*-spiro[acridine-9,3′-pyrrole]-4′-carboxylate (IIIa). A solution of 1.0 mmol of compound **I** and 1.0 mmol of enamine **IIa** in 15 ml of anhydrous *m*-xylene was heated for 5 h under reflux. The mixture was cooled, and the precipitate was filtered off. Yield 73%, mp 263–264°C (from toluene). IR spectrum, ν, cm^{-1}: 3264 br (NH), 1687 (4′-C=O, $C^{2'}$=O), 1624 (C^1=O). ^{1}H NMR spectrum, δ, ppm: 0.74 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.2 Hz), 0.99 s (3H, Me), 1.08 s (3H, Me), 2.06 d (1H, 2-H, *J* = 16.0 Hz), 2.12 s (3H, Me) 2.20 d (1H, 2-H, *J* = 16.0 Hz), 2.30 d and 2.55 d (1H each, 4-H, *J* = 16.4 Hz), 3.59 m (2H, OCH_2), 4.38 d and 4.66 d (1H each, NCH_2, *J* = 16.0 Hz), 6.59 s (1H, 8-H), 6.82 d (1H, 5-H, *J* = 8.4 Hz), 6.95 d (1H, 6-H, *J* = 8.4 Hz), 7.06–7.45 m (10H, H_{arom}), 9.62 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.22 ($\mathbf{C}H_3CH_2$), 20.32 (7-Me), 26.25 (Me), 28.89 (Me), 31.89 (C^3), 40.72 (C^4), 43.77 (C^9), 50.07 ($N\mathbf{C}H_2$), 51.78 (C^2), 58.35 (OCH_2), 103.16–153.09 (C_{arom}, C^{4a}, C^{10a}, $C^{4'}$, $C^{5'}$), 161.93 ($C^{2'}$), 181.41 (4′-C=O), 191.59 (C^1). Found, %: C 76.75; H 6.39; N 5.03. $C_{35}H_{34}N_2O_4$. Calculated, %: C 76.90; H 6.27; N 5.12.

Ethyl 1′-benzyl-7-methoxy-3,3-dimethyl-1,2′-dioxo-5′-phenyl-1′,2,2′,3,4,10-hexahydro-1*H*-spiro[acridine-9,3′-pyrrole]-4′-carboxylate (IIIb) was synthesized in a similar way. Yield 78%, mp 268–269°C (from toluene). IR spectrum, ν, cm^{-1}: 3256 br (NH), 1687 (4′-C=O, $C^{2'}$=O), 1626 (C^1=O). ^{1}H NMR spectrum, δ, ppm: 0.74 t (3H, $CH_2C\mathbf{H}_3$, *J* = 6.8 Hz), 0.99 s (3H, Me), 1.08 s (3H, Me), 2.06 d and 2.20 d (1H each, 2-H, *J* = 16.4 Hz), 2.30 d and 2.55 d (1H each, 4-H, *J* = 16.6 Hz), 3.56 s (3H, OMe), 3.60 m (2H, OCH_2), 4.36 d and 4.65 d (1H each, NCH_2, *J* = 15.6 Hz), 6.33 s (1H, 8-H), 6.78 d (1H, 6-H, *J* = 8.8 Hz), 6.89 d (1H, 5-H, *J* = 8.8 Hz), 7.06–7.46 m (10H, H_{arom}), 9.63 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.23 ($\mathbf{C}H_3CH_2$), 26.26 (Me), 28.89 (Me), 31.90 (C^3), 40.72 (C^4), 43.82 (C^9), 50.08 (NCH_2), 52.20 (C^2), 54.88 (OMe), 58.37 (OCH_2), 102.22–155.10 (C_{arom}, C^{4a}, C^{10a}, $C^{4'}$, $C^{5'}$), 161.86 ($C^{2'}$), 181.29 (4′-C=O), 191.46 (C^1). Found, %: C 74.80; H 6.03; N 5.00. $C_{35}H_{34}N_2O_5$. Calculated, %: C 74.71; H 6.09; N 4.98.

The IR spectra were measured on an FSM-1201 spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 instrument at 400 and 100 MHz, respectively, using DMSO-d_6 as solvent and tetramethylsilane as internal reference.

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