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## Five-Membred 2,3-Dioxoheterocycles: LXXXI.\* Reactions of 4,5-Bis(methoxycarbonyl)-1*H*-pyrrole-2,3-diones with N-Substituted 3-Amino-5,5-dimethyl-2-cyclohex-2-en-1-ones. Crystal and Molecular Structure of Methyl 4'-Hydroxy-6,6-dimethyl-1,1'-bis(4-methylphenyl)-2,4,5'-trioxo-1,1',2,4,5,5',6,7octahydrospiro[indole-3,2'-pyrrole]-3'-carboxylate

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**Abstract**—1-Aryl-4,5-bis(methoxycarbonyl)-1*H*-pyrrole-2,3-diones react with N-substituted 3-amino-5,5-dimethylcyclohex-2-en-1-ones affording methyl 1,1'-diaryl-4'-hydroxy-6,6-dimethyl-2,4,5'-trioxo-1,1',2,4,5,5',6,7-octahydrospiro[indole-3,2'-pyrrole]-3'-carboxylates whose structure was proved by XRD analysis.

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It was shown formerly that the direction of the reaction between monocyclic 1*H*-pyrrole-2,3-diones with enamines was governed by the structure of the substituents in the pyrroledione ring [2–5].

The reaction of 1-alkyl-5-phenyl-4-ethoxycarbonyl-1*H*-pyrrole-2,3-diones with *N*-aryl-substituted enamines proceeds as a successive addition of the groups of the *ortho*-CH of aryl substituent and  $\beta$ -CH of the enamine fragment to the C<sup>3</sup> atom of pyrrolediones [2, 3]. 4-Isopropoxalyl-1,5-diphenyl-1*H*-pyrrole-2,3-dione reacted with enamine adding the NH and  $\beta$ -CH groups of the enamine fragment to atoms C<sup>2</sup> and C<sup>3</sup> of pyrroledione followed by the cleavage of the pyrroledione ring and by subsequent cyclization [4]. In the reaction of 1-aryl-4aroyl-5-methoxycarbonyl-1*H*-pyrrole-2,3-diones with enamines the process proceeds along three directions. Firstly, successive addition occurs of  $\beta$ -CH and NH groups of the enamine fragment to atoms C<sup>5</sup> and C<sup>3</sup> of the pyrrolediones, secondly, the similar addition to atom C<sup>5</sup> and COOMe group in the position 5 of the heterocycle. The third, minor, direction is the addition of NH and  $\beta$ -CH groups of the enamine fragment to atoms C<sup>2</sup> and C<sup>3</sup> of the pyrrolediones with the cleavage of the pyrroledione ring and the subsequent cyclization [5].

In order to investigate the effect on the reactivity of 1H-pyrrole-2,3-diones of introduction of two methoxycarbonyl fragments into the positions 4 and 5 we studied the reactions of 1-aryl-4,5-bis(methoxycarbonyl)-1H-pyrrole-2,3-diones Ia-Ic with 1,3-CH,NHbinucleophiles, 3-arylamino-5,5-di-methyl-2-cyclohex-2-en-1-ones IIa-IIf. N-Substituted dimedone imines **IIa–IIf** existing in the enamine form were chosen as CH,NH-binucleophiles due to their preparative availability [6] and the ease of the variation of substituents at the nitrogen atom. These cyclic enaminoketones exist in the form of (*E*)-isomers with the location of  $\beta$ -CH and NH groups of the enamine fragment on the same side of the double bond favoring their participation in reactions as binucleophiles. The wide range of electron-donor and electron-acceptor substituents at the nitrogen atom in

<sup>\*</sup> For communication LXXX, see [1].

Scheme.



I,  $R^1 = Ph(a)$ ,  $C_6H_4Me-4(b)$ ,  $C_6H_4OMe-4(c)$ ; II,  $R^2 = CH_2=CH-CH_2(a)$ , Ph(b),  $C_6H_4Me-4(c)$ ,  $C_6H_4OMe-4(d)$ ,  $C_6H_4Br-4(e)$ , (e), 1-naphthyl (f); III,  $R^1 = Ph$ ,  $R^2 = 1$ -naphthyl (a);  $R^1 = C_6H_4Me-4$ :  $R^2 = CH_2=CH-CH_2(b)$ , Ph(c),  $C_6H_4OMe-4(e)$ ,  $C_6H_4Br-4(f)$ ;  $R^1 = R^2 = C_6H_4Me-4(d)$ ;  $C_6H_4OMe-4(i)$ ;  $R^1 = C_6H_4OMe-4$ ,  $R^2 = Ph(g)$ ,  $C_6H_4Me-4(h)$ , 1-naphthyl (j).

enaminoketones **IIa–IIf** was used in order to estimate their effect on the reaction course.

The reaction of pyrrolediones **Ia–Ic** with enamines **IIa–IIf** in equimolar ratio at boiling the reagents solution in anhydrous toluene over 2–4 h furnished in good yields methyl 1,1'-diaryl-4'hydroxy-6,6-dimethyl-2,4,5'-trioxo-1,1',2,4,5,5',6,7octahydrospiro[indole-3,2'-pyrrole]-3'-carboxylates **IIIa–IIIj** (see the scheme) whose structure was proved by XRD analysis of compound **IIId**.

Compounds **IIIa–IIIj** are colorless crystalline substances of high melting points, easily soluble in DMF and DMSO, sparingly soluble in the common organic solvents, insoluble in alkanes and water, with a positive test (cherry color) for the presence of an enol hydroxy group with the alcohol solution of iron(III) chloride.

The IR spectra of compounds **IIIa–IIIj** contain characteristic absorption bands of the stretching vibrations of the enol hydroxy group in the region 3130–3280 cm<sup>-1</sup>, of the methoxycarbonyl group at 1750–1759 cm<sup>-1</sup>, of two lactam and of a ketone carbonyl groups in the region 1701–1732 and 1613–1634 cm<sup>-1</sup> respectively.

In the <sup>1</sup>H NMR spectra of compounds **IIIa–IIIj** alongside the proton signals of the aromatic rings and the groups attached to them two six-proton singlets appear corresponding to two nonequivalent methyl groups in the position 6 of the cyclohexenone fragment (0.56–0.93 ppm) and four four-proton doublets belonging to two nonequivalent methylene groups in the positions 5 and 7 of the cyclohexenone fragment (1.79–2.38 ppm), a three-proton singlet from the methoxycarbonyl group (3.63–3.78 ppm), and a broadened singlet from the pro-

ton of the enol hydroxy group (12.40–12.69 ppm). In the <sup>1</sup>H NMR spectrum of compound **IIIb** alongside the above mentioned signals the proton signals of the allyl substituent are observed in the region 4.18–5.72 ppm. In the spectra of 1-( $\alpha$ -naphthyl) derivatives **IIIa**, **IIIj** a double set of signals appears from the protons of methyl, methylene, and methoxycarbonyl groups apparently due to the existence of these compounds as a mixture of two relatively stable conformers because of the hindrance to



General appearance of the molecule of methyl 4'-hydroxy-6,6-dimethyl-1,1'-bis-(4-methylphenyl)-2,4,5'-trioxo-1,1',2,4,5,5',6,7-octahydrospiro-[indole-3,2'-pyrrole]-3'carboxylate (**IIId**) shown in thermal ellipsoids of 50% probability according to XRD data.

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the free rotation of the bulky naphthyl substituent around the C–N bond.

In the <sup>13</sup>C NMR spectrum of compound **IIIc** alongside the carbon signals from the atoms of the aromatic and aliphatic substituents the signals are present from the carbon atom of the keto (C<sup>4</sup>=O), two lactam (C<sup>5</sup>=O and C<sup>2</sup>=O) and ester carbonyl groups at 190.56, 165.04, 155.04, and 161.99 ppm respectively, and also the signal from the spirocarbon atom at 68.31 ppm.

According to XRD data compound **IIId** (see the figure) crystallized from acetone as a solvate in the ratio 1:1 in a centrosymmetric space group of symmetry. The OH group of the hydroxypyrrolone fragment is involved into an intramolecular hydrogen bond with the methoxycarbonyl group  $[O^4-H^4 \, 86(2), H^4\cdots O^2 \, 2.21(2), O^4\cdots O^2 \, 2.838(2)$  Å, angle  $O^4H^4O^2 \, 130(1)^\circ]$  and an intermolecular hydrogen bond with the keto group of the cyclohexenone fragment  $(H^4\cdots O^1 \, [-x, -y + 1, -z + 1] \, 2.02(2), O^4\cdots O^1 \, [-x, -y + 1, -z + 1] \, 2.743(2)$  Å, angle  $O^4H^4O^2 \, 140(1)^\circ$  Å). By the hydrogen bonds the molecules are joined into dimers.

The formation of compounds IIIa-IIIj proceeds along the scheme similar to that described in [5]. As a result of the initial addition of the activated  $\beta$ -CH group of the enamine fragment of compounds IIa-IIf to the carbon atom in the position 5 of pyrrolediones Ia-Ic with the formation of intermediate compounds IVa-IVj followed by the intramolecular closure of a pyrrole ring due to the nucleophilic attack of the amino group of the enamine fragment on the carbonyl of the ester substituent in the position 5 of pyrrolediones and methanol elimination compounds IIIa-IIIj are obtained. The reaction of pyrroledione Ib with N-alkyl-substituted enamine IIa proceeded notably faster as showed the TLC monitoring of the reaction mixture than the reactions with N-aryl-substituted enamines IIb-IIf. At the same time the introduction of electron-donor or electron-acceptor substituents into the aryl ring attached to the nitrogen of N-aryl-substituted enamines IIb-IIf did not affect the rate of their reaction with pyrrolediones Ia-Ic.

## EXPERIMENTAL

IR spectra of compounds synthesized were recorded on a spectrophotometer FSM-1201 from mulls in mineral oil. NMR spectra were registered on a spectrometer Bruker AM-400 [operating frequencies 400 (<sup>1</sup>H), 100 MHz (<sup>13</sup>C)] in DMSO- $d_6$ , internal reference TMS. The homogeneity of compounds obtained was confirmed by TLC of Silufol plates, eluent benzene–ethyl acetate, 5 : 1, development in iodine vapor.

Methyl 4'-hydroxy-6,6-dimethyl-1-naphthyl-2,4,5'-trioxo-1'-phenyl-1,1',2,4,5,5',6,7-octahydrospiro[indole-3,2'-pyrrole]-3'-carboxylate (IIIa). A olution of 1.0 mmol of pyrroledione Ia and 1.0 mmol of enamine IIf in 20 mi of anhydrous toluene was boiled over 4 h (TLC monitoring) and cooled. The separated precipitate was filtered off and recrystallized from toluene. Yield 76%, mp 190–192°C (toluene). IR spectrum, v, cm<sup>-1</sup>: 3150 (OH), 1744 (COOMe), 1719 (C<sup>2</sup>=O, C<sup>5</sup>'=O), 1636 (C<sup>4</sup>=O). <sup>1</sup>H NMR spectrum, δ, ppm: 0.73 s (3H, Me), 0.92 s (3H, Me), 1.79 d (1H, C<sup>7</sup>H<sub>2</sub>, J 15.8 Hz), 2.18-2.30 group of signals (3H, C<sup>7</sup>H<sub>2</sub>, C<sup>5</sup>H<sub>2</sub>), 3.78 s (3H, OMe), 6.47-8.14 group of signals (11H, C<sub>6</sub>H<sub>4</sub>, C<sub>10</sub>H<sub>7</sub>), 12.69 br.s (1H, OH); 0.51 c (3H, Me), 088 s (3H, Me), 2.03 d (1H, C7H<sub>2</sub>, J15.8 Hz), 2.16-2.30 group of signals (3H, C7H<sub>2</sub>, C5H<sub>2</sub>), 3.82 s (3H, OMe), 6.47-8.14 group of signals (12H, Ph, C<sub>10</sub>H<sub>7</sub>), 12.69 br.s (1H, OH). Found, %: C 71.21; H 5.06; N 5.39. C<sub>30</sub>H<sub>26</sub>N<sub>2</sub>O<sub>6</sub>. Calculated, %: C 71.25; H 5.02; N 5.36.

Compounds IIIb-IIIj were obtained similarly.

Methyl 1-allyl-4'-hydroxy-6,6-dimethyl-1'-(4-methylphenyl)-2,4,5'-trioxo-1,1',2,4,5,5',6,7octahydrospiro[indole-3,2'-pyrrole]-3'-carboxylate (IIIb). Yield 77%, mp 243–244°C (toluene). IR spectrum, v, cm<sup>-1</sup>: 3175 (OH), 1746, 1701 (C<sup>2</sup>=O, C<sup>5</sup>'=O, COOMe), 1641 (C<sup>4</sup>=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.70 s (3H, Me), 0.99 s (3H, Me), 2.04 d (1H, C<sup>7</sup>H<sub>2</sub>, J 16.4 Hz), 2.14 d (1H, C<sup>5</sup>H<sub>2</sub>, J 18.3 Hz), 2.28 s (3H, Me), 2.34 d (1H, C<sup>7</sup>H<sub>2</sub>, J 16.4 Hz), 2.54 d (1H, C<sup>5</sup>H<sub>2</sub>, J 18.3 Hz), 3.63 s (3H, OMe), 4.18 s (2H, -CH<sub>2</sub>-), 4.79 d (1H, =CH<sub>2</sub>, J 17.3 Hz ), 5.04 d (1H, =CH<sub>2</sub>, J 10.6 Hz), 5.72 m (1H, -CH<sub>2</sub>=), 6.80 d (2H<sub>arom</sub>, J 8.0 Hz), 7.19 d (2H<sub>arom</sub>, J 8.0 Hz), 12.40 br.s (1H, OH). Found, %: C 69.15; H 5.34; N 5.77. C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>O<sub>6</sub>. Calculated, %: C 69.12; H 5.39; N 5.76.

Methyl 4'-hydroxy-6,6-dimethyl-1'-(4methylphenyl)-2,4,5'-trioxo-1-phenyl-1,1',2,4,5,5',6,7octahydrospiro[indole-3,2'-pyrrole]-3'-carboxylate (IIIc). Yield 75%, mp 240–241°C (toluene). IR spectrum, v, cm<sup>-1</sup>: 3170 (OH), 1750, 1701 (C<sup>2</sup>=O, C<sup>5</sup>=O, COOMe), 1628 (C<sup>4</sup>=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.55 s (3H, Me), 0.93 s (3H, Me), 2.00 d (1H, C<sup>7</sup>H<sub>2</sub>, J 16.3 Hz), 2.11 d (1H, C<sup>5</sup>H<sub>2</sub>, J 18.5 Hz), 2.18 d (1H, C<sup>7</sup>H<sub>2</sub>, J 16.3 Hz), 2.10 s (3H, Me), 2.38 d (1H, C<sup>5</sup>H<sub>2</sub>, J 18.5 Hz), 3.70 s (3H, OMe), 6.94–7.60 group of signals (9H, Ph, C<sub>6</sub>H<sub>4</sub>), 12.08 br.s (1H, OH). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 20.63 (Me), 26.51 (C<sup>6</sup><u>Me</u>), 27.85 (C<sup>6</sup><u>Me</u>), 33.82 (C<sup>6</sup>), 35.86 (C<sup>7</sup>), 50.48 (C<sup>5</sup>), 51.56 (OMe), 68.31 (C<sup>3</sup>), 107.94 (C<sup>3</sup>a), 109.52 (C<sup>3</sup>), 125.26–138.03 (C<sub>arom</sub>), 155.05 (C<sup>2</sup>), 161.99 (COO), 165.04 (C<sup>5</sup>), 174.45 (C<sup>4</sup>), 190.56 (C<sup>4</sup>). Found, %: C 69.15; H 5.34; N 5.77.  $C_{28}H_{26}N_2O_6$ . Calculated, %: C 69.12; H 5.39; N 5.76.

Methyl 4'-hydroxy-6,6-dimethyl-1,1'-bis(4methylphenyl)-2,4,5'-trioxo-1,1',2,4,5,5',6,7octahydrospiro[indole-3,2'-pyrrole]-3'-carboxylate (IIId). Yield 78%, mp 234–236°C (toluene). IR spectrum, v, cm<sup>-1</sup>: 3280 (OH), 1759, 1719 (C<sup>2</sup>=O, C<sup>5</sup>=O, COOMe), 1613 (C<sup>4</sup>=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.56 s (3H, Me), 0.93 s (3H, Me), 2.00 d (1H, C<sup>7</sup>H<sub>2</sub>, J 16.2 Hz), 2.10 d (1H, C<sup>3</sup>H<sub>2</sub>, J 18.0 Hz), 2.17 d (1H, C<sup>7</sup>H<sub>2</sub>, J 16.2 Hz), 2.30 s (3H, Me), 2.34 d (1H, C<sup>5</sup>H<sub>2</sub>, J 18.0 Hz), 2.37 s (3H, Me), 3.70 s (3H, OMe), 6.93–7.37 group of signals (8H, 2C<sub>6</sub>H<sub>4</sub>), 12.53 br.s (1H, OH). Found, %: C 69.60; H 5.61; N 5.66. C<sub>29</sub>H<sub>28</sub>N<sub>2</sub>O<sub>6</sub>. Calculated, %: C 69.59; H 5.64; N 5.60.

**XRD** analysis of compound IIId was carried out on a diffractometer Xcalibur-3 with a CCD detector  $[\lambda(MoK_{\alpha}) 0.71073]$ , graphite monochromator,  $\omega$ -scanning, scanning step 1°, T 295(2) K]. The analysis was performed using a fragment of a colorless crystal of the size  $0.25 \times 0.20 \times 0.15$  mm. The correction for extinction was not applied due to its negligible value ( $\mu$  0.088 mm<sup>-1</sup>). The structure was solved by the direct method using SHELXS-97 software and it was refined using SHELXL-97 program [7]. The positions and thermal parameters of nonhydrogen atoms were refined first in isotropic and then in nonisotropic approximation by the full-matrix least-squares method. The hydrogen atoms were localized from the electron density maxima and included into the refinement in the *rider* model. The main data of the structural experiment: crystal triclinic, space group P-1, a 9.8911(9), b 10.9834(6), c 13.8528(10) Å,  $\alpha$  83.825(6),  $\beta$  88.581(7),  $\gamma$  88.163(6) deg,  $d_{calc}$  1.241 g cm<sup>-3</sup>, V 1495.09(19) Å<sup>3</sup>, Z 2. At scanning angles 2.82  $< \theta < 28.28^{\circ}$  8857 reflections were collected, among them 7108 independent ( $R_{int}$  0.0202), 3788 at  $I > 2\sigma(I)$ . Completeness for  $\theta$  26.00° 97.2%. The final parameters of refinement:  $R_1$  0.0419,  $wR_2$  0.1006 [for  $I > 2\sigma(I)$ ],  $R_1$ 0.0897,  $wR_2$  0.1082 (for all reflections) at S 1.006, maximum and minimum peaks of the spatial electron density 0.221, -0.226 ē/Å<sup>3</sup>.

The XRD results were deposited into the Cambridge Cristallographic Datacenter under the number CCDC 846265. These materials are available at the address www. ccdc.cam.ac.uk/data\_request/cif. Methyl 4'-hydroxy-6,6-dimethyl-1'-(4methylphenyl)-1-(4-methoxyphenyl)-2,4,5'-trioxo-1,1',2,4,5,5',6,7-octahydrospiro[indole-3,2'-pyrrole]-3'-carboxylate (IIIe). Yield 76%, mp 236–238°C (toluene). IR spectrum, v, cm<sup>-1</sup>: 3205 (OH), 1753, 1721 ( $C^{2=}O, C^{5'=}O, COOMe$ ), 1620 ( $C^{4=}O$ ). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.56 s (3H, Me), 0.93 s (3H, Me), 1.99 d (1H,  $C^{7}H_{2}$ , J 16.1 Hz), 2.08 d (1H,  $C^{5}H_{2}$ , J 17.9 Hz), 2.17 d (1H,  $C^{7}H_{2}$ , J 16.1 Hz), 2.30 s (3H, Me), 2.32 d (1H,  $C^{5}H_{2}$ , J 16.1 Hz), 3.70 s (3H, OOMe), 3.81 s (3H, OMe), 6.92–7.26 group of signals (8H, 2C<sub>6</sub>H<sub>4</sub>), 12.54 br.s (1H, OH). Found, %: C 67.45; H 5.42; N 5.39. C<sub>29</sub>H<sub>28</sub>N<sub>2</sub>O<sub>7</sub>. Calculated, %: C 67.43; H 5.46; N 5.42.

Methyl 1-(4-bromophenyl)-4'-hydroxy-6,6-dimethyl-1'-(4-methylphenyl)-2,4,5'-trioxo-1,1',2,4,5,5',6,7-octahydrospiro[indole-3,2'-pyrrole]-3'-carboxylate (IIIf). Yield 76%, mp 236–238°C (toluene). IR spectrum, v, cm<sup>-1</sup>: 3209 (OH), 1757, 1719 (C<sup>2</sup>=O, C<sup>5</sup>=O, COOMe), 1619 (C<sup>4</sup>=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.56 s (3H, Me), 0.93 s (3H, Me), 2.00 d (1H, C<sup>7</sup>H<sub>2</sub>, J 16.1 Hz), 2.17 d (1H, C<sup>5</sup>H<sub>2</sub>, J 18.1 Hz), 2.19 d (1H, C<sup>7</sup>H<sub>2</sub>, J 16.1 Hz), 2.17 d (1H, C<sup>5</sup>H<sub>2</sub>, J 18.1 Hz), 2.40 d (1H, C<sup>5</sup>H<sub>2</sub>, J 18.1 Hz), 3.70 s (3H, OOMe), 6.92 d (2H<sub>arom</sub>, J 8.1 Hz), 7.18 d (2H<sub>arom</sub>, J 8.8 Hz), 7.25 d (2H<sub>arom</sub>, J 8.1 Hz), 7.78 d (2H<sub>arom</sub>, J 8.8 Hz), 12.62 br.s (1H, OH). Found, %: C 57.45; H 5.42; Br 10.14; N 5.39. C<sub>29</sub>H<sub>28</sub>BrN<sub>2</sub>O<sub>7</sub>. Calculated, %: C 57.43; H 5.46; Br 10.17; N 5.42.

Methyl 4'-hydroxy-6,6-dimethyl-1'-(4-methoxyphenyl)-2,4,5'-trioxo-1-phenyl-1,1',2,4,5,5',6,7octahydrospiro[indole-3,2'-pyrrole]-3'-carboxylate (IIIg). Yield 78%, mp 236–237°C (toluene). IR spectrum, v, cm<sup>-1</sup>: 3130 (OH), 1754, 1727 (C<sup>2</sup>=O, C<sup>5</sup>'=O, COOMe), 1636 (C<sup>4</sup>=O). <sup>1</sup>H NMR spectrum, δ, ppm: 0.59 s (3H, Me), 0.94 s (3H, Me), 2.02 d (1H, C<sup>7</sup>H<sub>2</sub>, J 15.7 Hz), 2.10 d (1H, C<sup>5</sup>H<sub>2</sub>, J 18.0 Hz), 2.20 d (1H, C<sup>7</sup>H<sub>2</sub>, J 15.7 Hz), 2.10 d (1H, C<sup>5</sup>H<sub>2</sub>, J 18.0 Hz), 2.20 d (1H, C<sup>7</sup>H<sub>2</sub>, J 15.7 Hz), 2.38 s (1H, C<sup>5</sup>H<sub>2</sub>, J 18.0 Hz), 3.70 c (3H, OOMe), 6.96–7.59 group of signals (9H, Ph, C<sub>6</sub>H<sub>4</sub>), 12.57 br.s (1H, OH). Found, %: C 68.01; H 3.94; N 10.11. C<sub>28</sub>H<sub>26</sub>N<sub>2</sub>O<sub>7</sub>. Calculated, %: C 68.05; H 3.90; N 10.15.

Methyl 4'-hydroxy-6,6-dimethyl-1-(4-methylphenyl)-1'-(4-methoxyphenyl)-2,4,5'-trioxo-1,1',2,4,5,5',6,7-octahydrospiro[indole-3,2'-pyrrole]-3'-carboxylate (IIIh). Yield 79%, mp 236–238°C (toluene). IR spectrum, v, cm<sup>-1</sup>: 3254 (OH), 1759, 1725 (C<sup>2</sup>=O, C<sup>5'</sup>=O, COOMe), 1626 (C<sup>4</sup>=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.59 s (3H, Me), 0.93 s (3H, Me), 2.02 d (1H, C<sup>7</sup>H<sub>2</sub>, J 15.9 Hz), 2.09 d (1H, C<sup>5</sup>H<sub>2</sub>, J 17.4 Hz), 2.18 d (1H, C<sup>7</sup>H<sub>2</sub>, J 15.9 Hz), 2.30 (C<sup>5</sup>H<sub>2</sub>, J 17.4 Hz),

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2.37 s (3H, Me), 3.70 s (3H, OMe), 3.75 s (3H, OMe), 6.94–7.36 group of signals (8H,  $2C_6H_4$ ), 12.54 br.s (1H, OH). Found, %: C 67.41; H 5.42; N 5.47.  $C_{29}H_{28}N_2O_7$ . Calculated, %: C 67.43; H 5.46; N 5.42.

Methyl 4'-hydroxy-6,6-dimethyl-1,1'-bis(4methoxyphenyl)-2,4,5'-trioxo-1,1',2,4,5,5',6,7octahydrospiro[indole-3,2'-pyrrole]-3'-carboxylate (IIIi). Yield 71%, mp 246–248°C (toluene). IR spectrum, v, cm<sup>-1</sup>: 3200 (OH), 1752, 1727 (C<sup>2</sup>=O, C<sup>5</sup>=O, COOMe), 1631 (C<sup>4</sup>=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.59 s (3H, Me), 0.94 s (3H, Me), 2.01 d (1H, C<sup>7</sup>H<sub>2</sub>, J 15.9 Hz), 2.09 d (1H, C<sup>5</sup>H<sub>2</sub>, J 17.9 Hz), 2.18 d (1H, C<sup>7</sup>H<sub>2</sub>, J 15.9 Hz), 2.33 s (C<sup>5</sup>H<sub>2</sub>, J 17.9 Hz), 3.70 s (3H, OMe), 3.75 s (3H, OMe), 3.81s (3H, OOMe), 6.94–7.16 group of signals (8H, 2C<sub>6</sub>H<sub>4</sub>), 12.54 br.s (1H, OH). Found, %: C 65.60; H 5.19; N 5.41. C<sub>29</sub>H<sub>28</sub>N<sub>2</sub>O<sub>8</sub>. Calculated, %: C 65.41; H 5.30; N 5.26.

Methyl 4'-hydroxy-6,6-dimethyl-1-naphthyl-1'-(4-methoxyphenyl)-2,4,5'-trioxo-1,1',2,4,5,5',6,7octahydrospiro[indole-3,2'-pyrrole]-3'-carboxylate (IIIj). Yield 72%, mp 229–231°C (toluene). IR spectrum, v, cm<sup>-1</sup>: 3195 (OH), 1759, 1719 (C<sup>2</sup>=O, C<sup>5</sup>=O, COOMe), 1634 (C<sup>4</sup>=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.78 s (3H, Me), 0.93 s (3H, Me), 1.91 d (1H, C<sup>7</sup>H<sub>2</sub>, J 16.4 Hz), 2.16– 2.30 group of signals (3H, C<sup>7</sup>H<sub>2</sub>, C<sup>5</sup>H<sub>2</sub>), 3.77 s (3H, OMe), 3.87 (3H, OMe), 6.46–8.15 group of signals (11H, C<sub>6</sub>H<sub>4</sub>,  $C_{10}H_7$ ), 12.61 br.s (1H, OH); 0.59 s (3H, Me), 0.90 s (3H, Me), 1.79 d (1H, C<sup>7</sup>H<sub>2</sub>, *J* 16.2 Hz), 2.16–2.30 group of signals (3H, C<sup>7</sup>H<sub>2</sub>, C<sup>5</sup>H<sub>2</sub>), 3.80 s (3H, OMe), 3.81 s (3H, OMe), 6.98–8.15 group of signals (12H, Ph, C<sub>10</sub>H<sub>7</sub>), 12.61 br.s (1H, OH). Found, %: C 69.60; H 5.29; N 5.01.  $C_{31}H_{28}N_2O_7$ . Calculated, %: C 69.56; H 5.11; N 5.07.

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