ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 4, pp. 561–565. © Pleiades Publishing, Ltd., 2012. Original Russian Text © P.S. Silaichev, V.O. Filimonov, P.A. Slepukhin, A.N. Maslivets, 2012, published in Zhurnal Organicheskoi Khimii, 2012, Vol. 48, No. 4, pp. 563–567.

## Five-Membered 2,3-Dioxo Heterocycles: LXXXV.\* Synthesis of Methyl 1-Aryl-4,5-dioxo-3-(1-oxo-3-phenylprop-2-en-1-yl)-4,5-dihydro-1*H*-pyrrole-2-carboxylates and Their Reaction with 3-Amino-5,5-dimethylcyclohex-2-en-1-ones. Molecular and Crystalline Structure of 4'-Hydroxy-1'-(4-methoxyphenyl)-6,6-dimethyl-3'-(1-oxo-3-phenylprop-2-en-1-yl)-1-phenyl-6,7-dihydrospiro[indole-3,2'-pyrrole]-2,4,5'(1*H*,1'*H*,5*H*)-trione

P. S. Silaichev<sup>a, b</sup>, V. O. Filimonov<sup>b</sup>, P. A. Slepukhin<sup>c</sup>, and A. N. Maslivets<sup>a, b</sup>

<sup>a</sup> Institute of Natural Sciences, Perm State University, ul. Genkelya 4, Perm, 614990 Russia e-mail: koh2@psu.ru

<sup>b</sup> Perm State University, ul. Bukireva 15, Perm, 614990 Russia

<sup>c</sup> Postovskii Institute of Organic Synthesis, Ural Division, Russian Academy of Sciences, ul. S. Kovalevskoi/Akademicheskaya 22/20, Yekaterinburg, 620041 Russia

Received June 29, 2011

**Abstract**—Treatment of methyl 2-arylamino-4-oxo-6-phenylhexa-2,5-dienoates with oxalyl chloride gave methyl 1-aryl-4,5-dioxo-3-(1-oxo-3-phenylprop-2-en-1-yl)-4,5-dihydro-1*H*-pyrrole-2-carboxylates which reacted with 3-benzylamino- and 3-arylamino-5,5-dimethylcyclohex-2-en-1-ones to produce 1'-aryl-1-benzyl- and 1,1'-diaryl-4'-hydroxy-6,6-dimethyl-3'-(1-oxo-3-phenylprop-2-en-1-yl)-6,7-dihydrospiro[indole-3,2'-pyrrole]-2,4,5'(1*H*,1'*H*,5*H*)-triones.

DOI: 10.1134/S1070428012040173

It is known that the direction of reactions of 1*H*-pyrrole-2,3-diones with carbocyclic enamines is determined by the nature of substituents in the pyrrole ring. Reactions of ethyl 1-alkyl-4,5-dioxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylates with N-arylsubstituted enamines involve successive addition of the ortho-carbon atom in the aryl substituent and β-carbon atom in the enamino fragment to the C<sup>4</sup>=O carbonyl carbon atom in dioxopyrrole [2, 3]. Isopropyl (1-aryl-4,5-dioxo-2-phenyl-4,5-dihydro-1H-pyrrol-3-yl)oxoacetates react via addition of the NH and  $\beta$ -CH groups in the enamine to  $C^5$  and  $C^4$  in the pyrrole ring, opening of the latter, and subsequent cyclization [4]. Dimethyl 1-aryl-4,5-dioxo-4,5-dihydro-1H-pyrrole-2,3dicarboxylates react with enamines via successive addition of the  $\beta$ -CH and NH groups in the enamine to  $C^2$  and ester carbonyl carbon atom at  $C^2$  in the initial

pyrrole [5]. Reactions of methyl 3-aroyl-1-aryl-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylates with enamines take three reaction paths: successive addition of the  $\beta$ -CH and NH groups in the enamine to C<sup>2</sup> and C<sup>4</sup> or C<sup>2</sup> and 2-C=O and (minor path) addition of the NH and  $\beta$ -CH groups in the enamine to C<sup>5</sup> and C<sup>4</sup>, followed by pyrrole ring opening and cyclization [6].

In the present work we examined the reaction of methyl 1-aryl-4,5-dioxo-3-(1-oxo-3-phenylprop-2-en-1-yl)-4,5-dihydro-1*H*-pyrrole-2-carboxylates **Ia** and **Ib** with carbocyclic enamines, 3-benzylamino- and 3-aryl-amino-5,5-dimethylcyclohex-2-en-1-ones **IIa–IIe**, with a view to elucidate how introduction of a cinnamoyl fragment into position 3 of dioxopyrroles **I** affects their reactivity. Compounds **Ia** and **Ib** were synthesized from methyl (2Z,5E)-2-arylamino-4-oxo-6-phenylhexa-2,5-dienoates **IIIa** and **IIIb** which were prepared in turn by reaction of methyl (2Z,5E)-2-hydroxy-4-oxo-6-phenylhexa-2,5-dienoate with aromatic

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





I, III, Ar =  $4 - MeC_6H_4$  (a),  $4 - MeOC_6H_4$  (b); II, R = Ph (a),  $4 - MeC_6H_4$  (b),  $4 - MeOC_6H_4$  (c),  $4 - BrC_6H_4$  (d), PhCH<sub>2</sub> (e); IV, Ar =  $4 - MeC_6H_4$ , R = Ph (a),  $4 - MeC_6H_4$  (b),  $4 - MeC_6H_4$  (c); Ar =  $4 - MeOC_6H_4$ , R = Ph (d),  $4 - MeC_6H_4$  (e),  $4 - MeOC_6H_4$  (f),  $4 - BrC_6H_4$  (g), PhCH<sub>2</sub> (h).

amines. Compounds **IIIa** and **IIIb** were isolated as red oily liquids, which are readily soluble in common organic solvents, poorly soluble in alkanes, and insoluble in water. They were brought into reaction with oxalyl chloride without additional purification. By heating enamines **IIIa** and **IIIb** with an equimolar amount of oxalyl chloride in boiling anhydrous benzene over a period of 70–80 min (until hydrogen chloride no longer evolved) we obtained desired dioxopyrroles **Ia** and **Ib** as orange crystalline substances which melted with decomposition at a high temperature. Compounds **Ia** and **Ib** were readily soluble in common organic solvent and insoluble in alkanes; they



Structure of the molecule of 4'-hydroxy-1'-(4-methoxyphenyl)-6,6-dimethyl-3'-(1-oxo-3-phenylprop-2-en-1-yl)-1-phenyl-6,7-dihydrospiro[indole-3,2'-pyrrole]-2,4,5'(1H,1H',5H)trione (**IVd**) according to the X-ray diffraction data.

lost their color on storage due to reaction with atmospheric moisture. The IR spectra of **Ia** and **Ib** contained absorption bands due to stretching vibrations of the lactam (1773–1775 cm<sup>-1</sup>) and ketone carbonyl groups (1725–1727 cm<sup>-1</sup>) in the pyrrole ring, ester carbonyl group (1744–1745 cm<sup>-1</sup>), and carbonyl group in the cinnamoyl fragment (1659–1663 cm<sup>-1</sup>).

Compounds Ia and Ib reacted with enamines IIa– IIe at a ratio of 1:1 in boiling anhydrous toluene (reaction time 15–20 min; until the color intrinsic to initial compounds I disappeared) to give 1-substituted 1'-aryl-4'-hydroxy-6,6-dimethyl-3'-(1-oxo-3-phenylprop-2-en-1-yl)-6,7-dihydrospiro[indole-3,2'-pyrrole]-2,4,5'(1H,1'H,5H)-triones IVa–IVh (Scheme 1). Compounds IVa–IVh were isolated as colorless or light yellow high-melting crystalline substances, which were readily soluble in DMF and DMSO, poorly soluble in other common organic solvents, and insoluble in alkanes and water. The products showed a positive color test for enolic hydroxy group upon treatment with an alcoholic solution of iron(III) chloride.

The IR spectra of **IVa–IVh** contained absorption bands belonging to stretching vibrations of the enolic O–H group (3167–3306 cm<sup>-1</sup>), lactam carbonyl groups  $C^2=O$  (1755–1761 cm<sup>-1</sup>) and  $C^{5'}=O$  (1719–1730 cm<sup>-1</sup>), and ketone carbonyl groups  $C^4=O$  (1659–1669 cm<sup>-1</sup>) and 3'-C=O (1640–1645 cm<sup>-1</sup>). Compounds **IVa–IVh** displayed in the <sup>1</sup>H NMR spectra signals from protons in the aromatic rings and substituents attached thereto, two singlets from nonequivalent methyl groups at  $\delta$  0.53–0.96 ppm, four doublets from methylene protons at  $\delta$  1.97–2.54 ppm (<sup>2</sup>J<sub>HH</sub> = 16–18 Hz), doublets from protons at the double bond in the cinnamoyl substituent at  $\delta$  7.59–7.72 ppm with a coupling constant typical of *trans*-configured double bond (<sup>3</sup>J<sub>trans</sub> = 15.7–16.2 Hz) [7], and a broadened signal at  $\delta$  13.08–13.48 ppm from the enolic hydroxy proton.

In the <sup>13</sup>C NMR spectrum of compound IVd, apart from signals typical of carbon atoms in the aromatic rings, substituents therein, methyl and methylene groups, and vinylene fragment, we observed signals from carbonyl carbon atoms at  $\delta_C$  190.58 (C<sup>4</sup>), 182.39 (3'-C=O), 164.87 (C<sup>2</sup>), and 165.73 ppm (C<sup>5'</sup>); signals from  $C^{3'}$  and  $C^{4'}$  were located at  $\delta_C$  118.20 and 174.60 ppm, respectively; the spiro carbon atom resonated at  $\delta_C$  68.63 ppm; and signals at  $\delta_C$  109.80 and 137.24 ppm were assigned to  $C^{3a}$  and  $C^{7a}$ , respectively. The chemical shifts of carbon nuclei in the 6,7-dihydrospiro[indole-3,2'-pyrrole] heterocyclic system were consistent with those observed for methyl 4'-hydroxy-6,6-dimethyl-1'-(4-methylphenyl)-2,4,5'-trioxo-1phenyl-1,1',2,4,5,5',6,7-octahydrospiro[indole-3,2'pyrrole]-3'-carboxylate,  $\delta_{\rm C}$ , ppm: 190.56 (C<sup>4</sup>), 161.99 (C<sup>2</sup>), 165.04 (C<sup>5'</sup>), 107.94 (C<sup>3'</sup>), 174.45 (C<sup>4'</sup>), 68.31 (C<sub>spiro</sub>), 109.52 (C<sup>3a</sup>), 138.03 (C<sup>7a</sup>) [5]. An appreciable shift of the  $C^{3'}$  signal of **IVd** (by 10.26 ppm) may be rationalized in terms of stronger electron-acceptor power of the cinnamoyl group compared to methoxycarbonyl.

According to the X-ray diffraction data, compound **IVd** (see figure) crystallized in centrosymmetric point symmetry group as a 1:1 solvate with toluene. The bond lengths and bond angles in molecule **IVd** are similar to the corresponding standard values. Molecules **IVd** in crystal a linked to dimers through intermolecular hydrogen bonds  $O^1-H^1\cdots O^4$  [-*x*, -*y*, -*z*] [ $O^1-H^1 0.92(2), O^1\cdots O^4 2.593(2)$  Å,  $\angle O^1H^1O^4$  148(1)°].

Presumably, compounds **IVa–IVh** are formed via initial addition of the activated  $\beta$ -CH group in the enamine fragment of **II** to the C<sup>2</sup>=O carbon atom in **I**, followed by closure of new pyrrole ring as a result of nucleophilic addition of the secondary amino group at the ester carbonyl group and elimination of methanol according to a scheme analogous to that described previously [5, 6]. In this case, intramolecular cyclization due to reaction of the enolic hydroxy group at the activated double bond in the cinnamoyl substituent does not occur.

## EXPERIMENTAL

The IR spectra were recorded on an FSM-1201 spectrometer from samples dispersed in mineral oil. The NMR spectra were measured on a Bruker AM-400 instrument at 400 (<sup>1</sup>H) and 100 MHz (<sup>13</sup>C) from solutions in DMSO- $d_6$  using tetramethylsilane as internal reference.

Methyl 1-(4-methylphenyl)-4,5-dioxo-3-(1-oxo-3-phenylprop-2-en-2-yl)-4,5-dihydro-1H-pyrrole-2carboxylate (Ia). Methyl (2Z,5E)-2-hydroxy-4-oxo-6phenylhexa-2,5-dienoate, 0.1 mol, was dissolved in 200 ml of toluene, 0.1 mol of *p*-toluidine was added, and the mixture was heated for 5 h under reflux in a flask equipped with a Dean-Stark trap until water no longer separated. The solvent was removed under reduced pressure, and the residue was passed through a column charged with silica gel (L 100-400 µm) using toluene-isooctane (1:1) as eluent. The first bright red fraction was collected, the solvent was removed under reduced pressure, and the residue, oily methyl 4-oxo-2-(4-methylphenylamino)-6-phenylhexa-2,5-dienoate (IIIa), was used without additional purification. Com-pound IIIa, 0.05 mol, was dissolved in 30 ml of anhydrous benzene, 0.05 mol of oxalyl chloride was added dropwise, and the mixture was heated for 70 min under reflux, diluted with 30 ml of anhydrous hexane, and cooled. The precipitate was filtered off and recrystallized from benzene-hexane (1:1). Yield 76%, mp 201–202°C. IR spectrum, v, cm<sup>-1</sup>: 1773  $(C^{5}=O)$ , 1744 (C=O, ester), 1725 (C<sup>4</sup>=O), 1659 (3-C=O). <sup>1</sup>H NMR spectrum, δ, ppm: 2.36 s (3H, Me), 3.78 s (3H, OMe), 7.23–7.78 m (11H, H<sub>arom</sub>, CH=CH). Found, %: C 70.32; H 4.52; N 3.70. C<sub>22</sub>H<sub>17</sub>NO<sub>5</sub>. Calculated, %: C 70.39; H 4.56; N 3.73.

Methyl 1-(4-methoxyphenyl)- 4,5-dioxo-3-(1-oxo-3-phenylprop-2-en-2-yl)-4,5-dihydro-1*H*-pyrrole-2carboxylate (Ib) was synthesized in a similar way. Yield 84%, mp 193–194°C (from benzene–hexane, 1:1). IR spectrum, v, cm<sup>-1</sup>: 1775 (C<sup>5</sup>=O), 1745 (C=O, ester), 1727 (C<sup>4</sup>=O), 1663 (3-C=O). <sup>1</sup>H NMR spectrum, δ, ppm: 3.78 s (3H, COOMe), 3.80 s (3H, OMe), 7.00–7.78 m (11H, H<sub>arom</sub>, CH=CH). Found, %: C 67.48; H 4.36; N 3.52. C<sub>22</sub>H<sub>17</sub>NO<sub>6</sub>. Calculated, %: C 67.52; H 4.38; N 3.58.

4'-Hydroxy-6,6-dimethyl-1'-(4-methylphenyl)-3'-(1-oxo-3-phenylprop-2-en-2-yl)-1-phenyl-6,7-dihydrospiro[indole-3,2'-pyrrole]-2,4,5'(1H,1'H,5H)trione (IVa). Enamine IIa, 1.0 mmol, was added to a solution of 1.0 mmol of compound Ia in 15 ml of anhydrous toluene, the mixture was heated for 20 min under reflux and cooled, and the precipitate was filtered off and recrystallized from toluene. Yield 79%, mp 252–253°C. IR spectrum, v, cm<sup>-1</sup>: 3167 (OH), 1755 (C<sup>2</sup>=O), 1721 (C<sup>5'</sup>=O), 1669 (C<sup>4</sup>=O), 1642 (3'-C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.53 s and 0.92 s (3H each, 6-Me), 1.98 d (1H, 7-H, *J* = 16.1 Hz), 2.10 d (1H, 5-H, *J* = 18.1 Hz), 2.16 d (1H, 7-H, *J* = 16.1 Hz), 2.31 s (3H, Me), 2.37 d (1H, 5-H, *J* = 18.1 Hz), 6.98– 7.74 m (14H, H<sub>arom</sub>), 7.64 d (1H, 2"-H, *J* = 15.8 Hz), 7.72 d (1H, 3"-H, *J* = 15.8 Hz), 13.40 br.s (1H, OH). Found, %: C 75.22; H 5.37; N 5.06. C<sub>35</sub>H<sub>30</sub>N<sub>2</sub>O<sub>5</sub>. Calculated, %: C 75.25; H 5.41; N 5.01.

Compounds **IVb–IVh** were synthesized in a similar way.

**4'-Hydroxy-6,6-dimethyl-1,1'-bis(4-methylphen-yl)-3'-(1-oxo-3-phenylprop-2-en-2-yl)-6,7-dihydrospiro[indole-3,2'-pyrrole]-2,4,5'(1***H***,1'***H***,5***H***)-trione (<b>IVb).** Yield 84%, mp 256–257°C (from toluene). IR spectrum, v, cm<sup>-1</sup>: 3181 (OH), 1759 (C<sup>2</sup>=O), 1725 (C<sup>5'</sup>=O), 1667 (C<sup>4</sup>=O), 1644 (3'-C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.53 s and 0.91 s (3H each, 6-Me), 1.97 d (1H, 7-H, J = 16.0 Hz), 2.08 d (1H, 5-H, J = 18.4 Hz), 2.14 d (1H, 7-H, J = 16.0 Hz), 2.39 s (3H, Me), 6.96–7.70 m (13H, H<sub>arom</sub>), 7.63 d (1H, 2"-H, J = 15.8 Hz), 7.71 d (1H, 3"-H, J = 15.8 Hz), 13.37 br.s (1H, OH). Found, %: C 75.47; H 5.67; N 4.85. C<sub>36</sub>H<sub>32</sub>N<sub>2</sub>O<sub>5</sub>. Calculated, %: C 75.51; H 5.63; N 4.89.

4'-Hydroxy-1-(4-methoxyphenyl)-6,6-dimethyl-1'-(4-methylphenyl)-3'-(1-oxo-3-phenylprop-2-en-2-yl)-6,7-dihydrospiro[indole-3,2'-pyrrole]-2,4,5'(1*H*,1'*H*,5*H*)-trione (IVc). Yield 78%, mp 244– 246°C (from toluene). IR spectrum, v, cm<sup>-1</sup>: 3306 (OH), 1757 (C<sup>2</sup>=O), 1719 (C<sup>5</sup>=O), 1669 (C<sup>4</sup>=O), 1640 (3'-C=O). <sup>1</sup>H NMR spectrum, δ, ppm: 0.53 s and 0.92 s (3H each, 6-Me), 1.97 d (1H, 7-H, J = 16.4 Hz), 2.07 d (1H, 5-H, J = 18.4 Hz), 2.14 d (1H, 7-H, J = 16.4 Hz), 2.30 s (3H, Me), 2.33 d (1H, 5-H, J = 18.4 Hz), 3.83 s (3H, OMe), 6.97–7.70 m (13H, H<sub>arom</sub>), 7.62 d (1H, 2"-H, J = 15.8 Hz), 7.71 d (1H, 3"-H, J = 15.8 Hz), 13.48 br.s (1H, OH). Found, %: C 73.47; H 5.44; N 4.73. C<sub>36</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>. Calculated, %: C 73.45; H 5.48; N 4.76.

4'-Hydroxy-1'-(4-methoxyphenyl)-6,6-dimethyl-3'-(1-oxo-3-phenylprop-2-en-2-yl)-1-phenyl-6,7-dihydrospiro[indole-3,2'-pyrrole]-2,4,5'(1H,1'H,5H)trione (IVd). Yield 75%, mp 242–243°C (from toluene). IR spectrum, v, cm<sup>-1</sup>: 3181 (OH), 1761 (C<sup>2</sup>=O), 1723 (C<sup>5'</sup>=O), 1669 (C<sup>4</sup>=O), 1644 (3'-C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.57 s and 0.93 s (3H each, 6-Me), 1.99 d (1H, 7-H, J = 16.1 Hz), 2.10 d (1H, 5-H, J =18.4 Hz), 2.13 d (1H, 7-H, J = 16.1 Hz), 2.39 d (1H, 5-H, J = 18.4 Hz), 3.76 s (3H, OMe), 6.99–7.71 m (14H, H<sub>arom</sub>), 7.62 d (1H, 2"-H, J = 15.7 Hz), 7.71 d (1H, 3'-H, J = 15.7 Hz), 13.34 br.s (1H, OH). <sup>13</sup>C NMR spectrum,  $\delta_{\rm C}$ , ppm: 26.44 and 27.98 (6-Me), 33.78 (C<sup>6</sup>), 35.85 (C<sup>7</sup>), 50.43 (C<sup>5</sup>), 55.34 (OMe), 68.63 (C<sup>3</sup>), 109.80 (C<sup>3a</sup>), 114.59 (C<sup>o</sup> in C<sub>6</sub>H<sub>4</sub>OMe-4), 118.20 (C<sup>3'</sup>), 123.86 (C<sup>2"</sup>), 125.25–134.39, 137.24 (C<sup>7a</sup>), 142.23 (C<sup>3"</sup>), 159.05 (COMe), 164.87 (C<sup>2</sup>), 165.73 (C<sup>5'</sup>) 174.60 (C<sup>4'</sup>), 182.39 (3'-CO), 190.58 (C<sup>4</sup>). Found, %: C 73.18; H 5.21; N 4.85. C<sub>35</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>. Calculated, %: C 73.16; H 5.26; N 4.88.

X-Ray analysis of compound IVd was performed on an Xcalibur-3 automatic four-circle diffractometer with a CCD detector  $[\lambda(MoK_{\alpha}) 0.71073 \text{ Å}, \text{ temperature}$ 295(2) K, graphite monochromator,  $\omega$ -scanning through a step of 1°]. A fragment of a  $0.25 \times 0.20 \times$ 0.15-mm colorless prism was used. No correction for absorption was introduced taking into account its low value ( $\mu = 0.082 \text{ mm}^{-1}$ ). Total of 19826 reflection intensities were measured in the range  $2.94 < \theta < 33.34^{\circ}$ ; 11424 reflections were independent ( $R_{int} = 0.0435$ ), and 3560 reflections were characterized by  $I > 2\sigma(I)$ . The completeness was 81.8% for  $\theta < 33.34^{\circ}$  and 96.6% for  $\theta < 26.00^\circ$ . Triclinic crystal system, space group P-1; unit cell parameters: a = 10.1696(8), b =13.3383(9), c = 13.5975(13) Å;  $\alpha = 83.622(7)$ ,  $\beta =$  $80.102(7), \gamma = 85.880(6)^{\circ}$ . The structure was solved and refined using SHELXTL 5.1 software package [8]. The positions and temperature parameters of non-hydrogen atoms were refined against  $F^2$  first in isotropic and then in anisotropic approximation by the fullmatrix least-squares procedure. Hydrogen atoms (except for the OH hydrogen atom) were localized by the electron density maxima and were included in the refinement in isotropic approximation according to the riding model. The OH hydrogen atom was refined independently in isotropic approximation. The final divergence factors were  $R_1 = 0.0627$ ,  $wR_2 = 0.1218$ [for reflections with  $I > 2\sigma(I)$ ] and  $R_1 = 0.1751$ ,  $wR_2 =$ 0.1320 (for all reflections); goodness of fit S = 0.991. The crystallographic data for compound IVd were deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 872845) and are available at www.ccdc.cam.ac.uk/data request/cif upon request.

4'-Hydroxy-1'-(4-methoxyphenyl)-6,6-dimethyl-1-(4-methylphenyl)-3'-(1-oxo-3-phenylprop-2-en-2-yl)-6,7-dihydrospiro[indole-3,2'-pyrrole]-2,4,5'(1H,1'H,5H)-trione (IVe). Yield 81%, mp 258– 259°C (from toluene). IR spectrum, v, cm<sup>-1</sup>: 3174 (OH), 1757 (C<sup>2</sup>=O), 1727 (C<sup>5'</sup>=O), 1661 (C<sup>4</sup>=O), 1645 (3'-C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.57 s and 0.92 s (3H each, 6-Me), 1.98 d (1H, 7-H, J = 16.3 Hz), 2.09 d (1H, 5-H, J = 18.4 Hz), 2.15 d (1H, 7-H, J = 16.3 Hz), 2.33 d (1H, 5-H, J = 18.4 Hz), 2.39 s (3H, Me), 3.76 s (3H, OMe), 6.97–7.70 m (13H, H<sub>arom</sub>), 7.62 d (1H, 2"-H, J = 16.2 Hz), 7.70 d (1H, 3"-H, J = 16.2 Hz), 13.08 br.s (1H, OH). Found, %: C 73.46; H 5.50; N 4.82. C<sub>36</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>. Calculated, %: C 73.45; H 5.48; N 4.76.

4'-Hydroxy-1,1'-bis(4-methoxyphenyl)-6,6-dimethyl-3'-(1-oxo-3-phenylprop-2-en-2-yl)-6,7-dihydrospiro[indole-3,2'-pyrrole]-2,4,5'(1H,1'H,5H)trione (IVf). Yield 78%, mp 237–238°C (from toluene). IR spectrum, v, cm<sup>-1</sup>: 3243 (OH), 1755 (C<sup>2</sup>=O), 1721 (C<sup>5'</sup>=O), 1667 (C<sup>4</sup>=O), 1642 (3'-C=O). <sup>1</sup>H NMR spectrum, δ, ppm: 0.57 s and 0.92 s (3H each, 6-Me), 1.98 d (1H, 7-H, J = 16.1 Hz), 2.08 d (1H, 5-H, J =18.2 Hz), 2.15 d (1H, 7-H, J = 16.1 Hz), 2.32 d (1H, 5-H, J = 18.2 Hz), 3.76 s and 3.83 s (3H each, OMe), 6.98–7.71 m (13H, H<sub>arom</sub>), 7.64 d (1H, 2"-H, J =15.7 Hz), 7.71 d (1H, 3"-H, J = 15.7 Hz), 13.26 br.s (1H, OH). Found, %: C 71.54; H 5.28; N 4.64. C<sub>36</sub>H<sub>32</sub>N<sub>2</sub>O<sub>7</sub>. Calculated, %: C 71.51; H 5.33; N 4.63.

1-(4-Bromophenyl)-4'-hydroxy-1'-(4-methoxyphenyl)-6,6-dimethyl-3'-(1-oxo-3-phenylprop-2en-2-yl)-6,7-dihydrospiro[indole-3,2'-pyrrole]-2,4,5'(1*H*,1'*H*,5*H*)-trione (IVg). Yield 87%, mp 265– 266°C (from toluene). IR spectrum, v, cm<sup>-1</sup>: 3170 (OH), 1757 (C<sup>2</sup>=O), 1730 (C<sup>5'</sup>=O), 1659 (C<sup>4</sup>=O), 1644 (3'-C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.58 s and 0.93 s (3H each, 6-Me), 2.00 d (1H, 7-H, *J* = 16.1 Hz), 2.16 d (1H, 5-H, *J* = 18.5 Hz), 2.17 d (1H, 7-H, *J* = 16.1 Hz), 2.39 d (1H, 5-H, *J* = 18.5 Hz), 3.76 s (3H, OMe), 6.98–7.81 m (13H, H<sub>arom</sub>), 7.63 d (1H, 2"-H, *J* = 15.8 Hz), 7.71 d (1H, 3"-H, *J* = 15.8 Hz), 13.38 br.s (1H, OH). Found, %: C 64.28; H 4.51; N 4.31. C<sub>35</sub>H<sub>29</sub>BrN<sub>2</sub>O<sub>6</sub>. Calculated, %: C 64.32; H 4.47; N 4.29. **1-Benzyl-4'-hydroxy-1'-(4-methoxyphenyl)-6,6dimethyl-3'-(1-oxo-3-phenylprop-2-en-2-yl)-6,7-dihydrospiro[indole-3,2'-pyrrole]-2,4,5'(1***H***,1'***H***,5***H***)trione (<b>IVh**). Yield 75%, mp 233–234°C (from toluene). IR spectrum, v, cm<sup>-1</sup>: 3179 (OH), 1757 (C<sup>2</sup>=O), 1723 (C<sup>5'</sup>=O), 1669 (C<sup>4</sup>=O), 1645 (3'-C=O). <sup>1</sup>H NMR spectrum, δ, ppm: 0.70 s and 0.96 s (3H each, 6-Me), 2.07 d (1H, 7-H, J = 16.0 Hz), 2.11 d (1H, 7-H, J =16.0 Hz), 2.16 d (1H, 5-H, J = 18.0 Hz), 2.54 d (1H, 5-H, J = 18.0 Hz), 3.77 s (3H, OMe), 4.75 d and 4.91 d (1H each, C**H**<sub>2</sub>Ph, J = 16.1 Hz), 6.84–7.68 m (14H, H<sub>arom</sub>), 7.59 d (1H, 2"-H, J = 15.8 Hz), 7.70 d (1H, 3"-H, J = 15.8 Hz), 13.31 br.s (1H, OH). Found, %: C 73.48; H 5.43; N 4.77. C<sub>36</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>. Calculated, %: C 73.45; H 5.48; N 4.76.

This study was performed under financial support by the Ministry of Education and Science of the Russian Federation (project no. 2.19.10).

## REFERENCES

- Silaichev, P.S., Kudrevatykh, N.V., Aliev, Z.G., and Maslivets, A.N., *Russ. J. Org. Chem.*, 2012, vol. 48, p. 253.
- Silaichev, P.S., Aliev, Z.G., and Maslivets, A.N., *Russ. J.* Org. Chem., 2009, vol. 45, p. 1114.
- Silaichev, P.S., Dmitriev, M.V., Aliev, Z.G., and Maslivets, A.N., *Russ. J. Org. Chem.*, 2010, vol. 46, p. 1173.
- Silaichev, P.S., Aliev, Z.G., and Maslivets, A.N., *Russ. J.* Org. Chem., 2009, vol. 45, p. 126.
- Silaichev, P.S., Chudinova, M.A., Slepukhin, P.A., and Maslivets, A.N., *Russ. J. Org. Chem.*, 2011, vol. 47, p. 1718.
- 6. Denislamova, E.S. and Maslivets, A.N., *Russ. J. Org. Chem.*, 2010, vol. 46, p. 389.
- Kazitsyna, L.A. and Kupletskaya, N.B., Primenenie UF, IK, YaMR i mass-spektroskopii v organicheskoi khimii (Application of UV, IR, NMR, and Mass Spectroscopy in Organic Chemistry), Moscow: Vysshaya Shkola, 1971.
- Sheldrick, G.M., Acta Crystallogr., Sect. A, 2008, vol. 64, p. 112.