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Five-Membered 2,3-Dioxo Heterocycles: C.* Reaction of Methyl 1-Aryl-3-cinnamoyl-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carbocylates with Acyclic Enamines

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Abstract—Methyl 1-aryl-3-cinnamoyl-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carbocylates react with N-substituted ethyl 3-amino-3-phenylprop-2-enoates, ethyl 3-aminobut-2-enoates, 3-amino-1,3-diphenylprop-2-en-1-ones, and dimethyl 2-arylaminofumarates to give 9-ethoxycarbonyl-, 9-benzoyl-, and 8,9-bis(methoxycarbonyl)-4-cinnamoyl-1,7-diazaspiro[4.4]nona-3,8-dienes.

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Nucleophilic heterocyclizations and recyclizations of monocyclic 1*H*-pyrrole-2,3-diones by the action of binucleophiles underlie convenient methods of synthesis of various five-, six-, and seven-membered nitrogen heterocycles and fused, bridged, and spiro heterocyclic systems [2, 3]. We previously showed that methyl 3-acyl-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylates react with acyclic enamino ketones [4, 5] and enamino esters [6] to give substituted 1,7-diazaspiro-[4.4]nonanes as a result of nucleophilic attack on C^2 and subsequent cyclization with participation of the ester carbonyl carbon atom. Reactions of methyl 1-aryl-3-cinnamoyl-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carbocylates with enamines and enamino esters possessing functional groups in the α- and β-positions of the enamino fragment were not reported previously.

In the present work we examined reactions of methyl 1-aryl-3-cinnamoyl-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carbocylates **Ia**–**Id** with acyclic enamines **IIa**–**IIc**, **IIIa**, **IIIb**, and **IVa**–**IVc**. Compounds **Ia** and **Id** were synthesized by reaction of methyl (2*Z*,5*E*)-2-arylamino-4-oxo-6-phenylhexa-2,5-dienoates with oxalyl chloride, and esters **Ib** and **Ic** were prepared as described in [7].

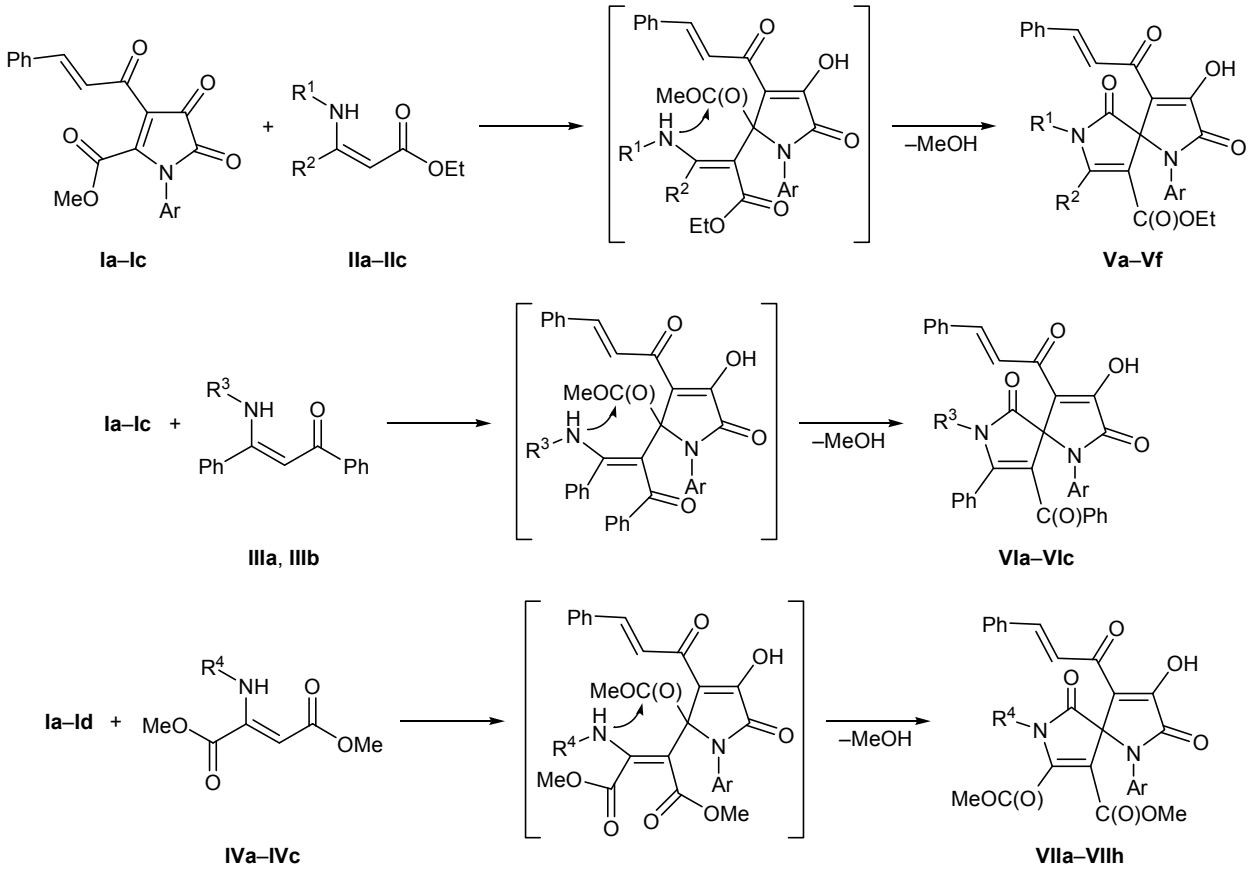
The reactions of **Ia**–**Id** with N-substituted ethyl 3-amino-3-phenylprop-2-enoate **IIa**, ethyl 3-aminobut-2-enoates **IIb** and **IIc**, 3-amino-1,3-diphenylprop-2-en-1-ones **IIIa** and **IIIb**, and dimethyl 2-aminofumarates **IVa**–**IVc** were carried out by heating equimolar amounts of the reactants in boiling anhydrous toluene or benzene (with compounds **IVa**–**IVc**) for 2–4 h (until the bright red color typical of initial pyrrolediones disappeared). As a result, we isolated in good yields the corresponding substituted ethyl 4-cinnamoyl-1,7-diazaspiro[4.4]nona-3,8-diene-9-carboxylates **Va**–**Vf**, 9-benzoyl-4-cinnamoyl-8-phenyl-1,7-diazaspiro[4.4]-nona-3,8-dienes **VIa**–**VIc**, and dimethyl 4-cinnamoyl-1,7-diazaspiro[4.4]nona-3,8-diene-8,9-dicarboxylates **VIIa**–**VIIh**.

Compounds **Va**–**Vf**, **VIa**–**VIc**, and **VIIa**–**VIIh** are colorless or light yellow substances which melt at high temperature with decomposition; they are readily soluble in DMFA and DMSO, poorly soluble in alcohols and haloalkanes, and insoluble in alkanes and water. The presence of a enolic hydroxy group in their molecules is confirmed by positive color test (cherry color) with an alcoholic solution of $FeCl_3$.

The IR spectra of **Va**–**Vf**, **VIa**–**VIc**, and **VIIa**–**VIIh** contained absorption bands due to stretching vibrations of the enolic OH group (3169–3458 cm^{-1}), two lactam carbonyl groups (1689–1755 cm^{-1}), and ketone carbonyl group in the cinnamoyl fragment (1639–1649 cm^{-1}). In addition, compounds **Va**–**Vf** displayed in the IR spectra ester carbonyl absorption band at 1671–1677 cm^{-1}, compounds **VIa**–**VIc** showed ketone carbonyl band at 1669–1672 cm^{-1} (benzoyl fragment);

* For communication XCIX, see [1].

Scheme 1.



I, Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**), 4-BrC_6H_4 (**d**); **II**, R^1 = $PhCH_2$, R^2 = Ph (**a**), Me (**b**); R^1 = Ph, R^2 = Me (**c**); **III**, R^3 = $PhCH_2$ (**a**), 4-MeC_6H_4 (**b**); **IV**, R^4 = 4-MeC_6H_4 (**a**), 4-BrC_6H_4 (**b**), 4-ClC_6H_4 (**c**); **V**, Ar = Ph, R^1 = $PhCH_2$, R^2 = Me (**a**); Ar = 4-MeC_6H_4, R^1 = $PhCH_2$, R^2 = Ph (**b**), Me (**c**); Ar = 4-$MeOC_6H_4$, R^1 = $PhCH_2$, R^2 = Ph (**d**), Me (**e**); R^1 = Ph, R^2 = Me (**f**); **VI**, Ar = Ph, R^3 = $PhCH_2$ (**a**); Ar = R^3 = 4-MeC_6H_4 (**b**); Ar = 4-$MeOC_6H_4$, R^3 = 4-MeC_6H_4 (**c**); **VII**, Ar = Ph, R^4 = 4-MeC_6H_4 (**a**), 4-BrC_6H_4 (**b**), 4-ClC_6H_4 (**c**); Ar = 4-MeC_6H_4, R^4 = 4-MeC_6H_4 (**d**), 4-ClC_6H_4 (**e**); Ar = 4-$MeOC_6H_4$, R^4 = 4-MeC_6H_4 (**f**), 4-BrC_6H_4 (**g**); Ar = R^4 = 4-BrC_6H_4 (**h**).

and diesters **VIIa**–**VIIh** gave rise to absorption in the region 1670–1703 cm^{-1}, corresponding to vibrations of two ester groups.

In the ^1H NMR spectra of **Va**–**Vf**, **VIa**–**VIc**, and **VIIa**–**VIIh** we observed signals from protons in the aromatic rings and substituents therein, two doublets at δ 7.60–7.78 ppm from protons in the cinnamoyl fragment with the coupling constant ^3J = 15.4–16.4 Hz typical of *trans* configuration of the double bond [8], and a broadened singlet from the enolic hydroxy proton at δ 12.23–13.35 ppm. In the spectra of **Va**–**Vf**, protons in the ester ethoxy group resonated as a triplet at δ 0.82–1.16 ppm (CH_3) and a multiplet at δ 3.81–4.07 ppm (CH_2). The spectra of **Va**, **Vc**, **Ve**, and **Vf** contained a singlet at δ 2.11–2.45 ppm from the 8-CH_3 group, and singlets from the ester methoxy groups in **VIIa**–**VIIh** were located at δ 3.60–3.66 ppm.

Compounds **Vb**, **VIc**, and **VIId** displayed in the ^{13}C NMR spectra signals from carbon atoms in the exocyclic ethene fragment, aromatic rings and substituents therein, ketone carbonyl group of the cinnamoyl substituent (δ_C 181.93–183.03 ppm), and lactam carbonyl groups C^2=O (δ_C 165.66–165.71 ppm) and C^6=O (δ_C 156.62–158.38 ppm). The spiro carbon atom resonated at δ_C 69.58–70.88 ppm. In addition, signals from the ethoxycarbonyl fragment in **Vb** (δ_C 13.37, 58.96, 160.91 ppm), benzoyl carbonyl carbon atom in **VIc** (δ_C 190.86 ppm), and methoxycarbonyl fragments in **VIId** (δ_C 51.94, 53.35, 160.10, 160.52 ppm) were present.

The spectral parameters of **Va**–**Vf**, **VIa**–VIc, and **VIIa**–**VIIh** were very similar to those found for 4-methyl 9-ethyl 7-benzyl-3-hydroxy-1-(4-methoxyphenyl)-8-methyl-2,6-dioxo-1,7-diazaspiro[4.4]nona-

3,8-diene-4,9-dicarboxylate [9] whose structure was unambiguously determined by X-ray analysis.

Presumably, compounds **Va**–**Vf**, **VIa**–**VIc**, and **VIIa**–**VIIh** are formed via initial addition of the activated β-CH group of the enamine fragment in **II**–**IV** to C^2 of pyrrole **I**, followed by *Z*/*E* isomerization of the enamine fragment and closure of new pyrrole ring as a result of attack by the secondary amino group on the ester carbonyl carbon atom, by analogy with the scheme proposed previously [6].

EXPERIMENTAL

The IR spectra were recorded on a Perkin Elmer Spectrum Two spectrometer from samples dispersed in mineral oil. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker AM-400 instrument at 400 and 100 MHz, respectively, from solutions in DMSO-d_6 using tetramethylsilane as internal reference. The purity of the isolated compounds was checked by ultra-HPLC (Acquity UPLC BEH C18 column, grain size 1.7 μm; eluent aqueous methanol or aqueous acetonitrile, flow rate 0.3–0.5 mL/s; ESI MS Xevo TQD detector).

Methyl 3-cinnamoyl-4,5-dioxo-1-phenyl-4,5-dihydro-1*H*-pyrrole-2-carboxylate (Ia). Aniline, 0.1 mol, and acetic acid, 2 mL, were added to a solution of 0.1 mol of methyl (2*Z*,5*E*)-2-hydroxy-4-oxo-6-phenylhexa-2,5-dienoate in 200 mL of toluene, 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 (Silicagel L, 100–400 μm) using toluene–isooctane (1:1) as eluent. The first bright red fraction was collected. Removal of the solvent gave oily methyl 4-oxo-2-(4-phenylamino)-6-phenylhexa-2,5-dienoate which was used without additional purification.

The product, 0.05 mol, was dissolved in 30 mL of anhydrous benzene, 0.05 mol of oxalyl chloride was added, the mixture was heated for 70 min under reflux, 30 mL of anhydrous hexane was added, the mixture was cooled, and the precipitate was filtered off and recrystallized. Yield 86%, mp 188–189°C (from benzene–hexane, 1:1). IR spectrum, ν, cm^{-1}: 1784 (C^5=O), 1736 (C=O, ester), 1717 (C^4=O), 1659 (3-C=O). ^{1}H NMR spectrum, δ, ppm: 3.59 s (3H, OMe), 7.15–7.79 m (12H, H_{arom}, CH=CH). Found, %: C 69.76; H 4.16; N 3.82. $C_{21}H_{15}NO_5$. Calculated, %: C 69.80; H 4.18; N 3.88.

Compound **Id** was synthesized in a similar way.

Methyl 1-(4-bromophenyl)-3-cinnamoyl-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylate (Id). Yield 82%, mp 207–208°C (from benzene–hexane, 1:1). IR spectrum, ν, cm^{-1}: 1783 (C^5=O), 1736 (C=O, ester), 1679 (C^4=O), 1658 (3-C=O). ^{1}H NMR spectrum, δ, ppm: 3.60 s (3H, OMe), 7.31–7.86 m (11H, H_{arom}, CH=CH). Found, %: C 57.31; H 3.25; N 3.16. $C_{21}H_{14}BrNO_5$. Calculated, %: C 57.29; H 3.21; N 3.18.

Ethyl 7-benzyl-4-cinnamoyl-3-hydroxy-8-methyl-2,6-dioxo-1-phenyl-1,7-diazaspiro[4.4]nona-3,8-diene-9-carboxylate (Va). A solution of 1.0 mmol of enamine **IIb** in 5 mL of anhydrous toluene was added to a solution of 1.0 mmol of compound **Ia** in 20 mL of anhydrous toluene. The mixture was heated for 2 h under reflux and cooled, and the precipitate was filtered off and recrystallized from toluene. Yield 70%, mp 197–198°C. IR spectrum, ν, cm^{-1}: 3428 (OH), 1726 (C^6=O), 1696 (C^2=O), 1673 (9-C=O), 1638 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 1.13 t (3H, $CH_3C\mathbf{H}_2$, *J* = 7.0 Hz), 2.25 s (3H, Me), 4.04 m (2H, OCH_2), 4.76 d and 4.91 d (1H each, $C\mathbf{H}_2$Ph, *J* = 16.4 Hz), 6.94–7.69 m (15H, Ph), 7.62 d (1H, COC**H**=CHPh, *J* = 16.0 Hz), 7.73 d (1H, COCH=C**H**Ph, *J* = 16.0 Hz), 13.36 br.s (1H, OH). Found, %: C 72.19; H 5.12; N 5.10. $C_{33}H_{28}N_2O_6$. Calculated, %: C 72.25; H 5.14; N 5.11.

Compounds **Vb**–**Vf** were synthesized in a similar way.

Ethyl 7-benzyl-4-cinnamoyl-3-hydroxy-1-(4-methylphenyl)-2,6-dioxo-8-phenyl-1,7-diazaspiro[4.4]nona-3,8-diene-9-carboxylate (Vb). Yield 68%, mp 209–210°C. IR spectrum, ν, cm^{-1}: 3417 (OH), 1723 (C^6=O), 1698 (C^2=O), 1671 (9-C=O), 1644 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 0.83 t (3H, $C\mathbf{H}_3CH_2$, *J* = 7.1 Hz), 2.41 s (3H, Me), 3.81 m (2H, OCH_2), 4.27 d and 4.69 d (1H each, $C\mathbf{H}_2$Ph, *J* = 15.9 Hz), 6.52–7.71 m (19H, H_{arom}), 7.70 d (1H, COC**H**=CHPh, *J* = 15.5 Hz), 7.78 d (1H, COCH=C**H**Ph, *J* = 15.5 Hz), 13.24 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 13.37 ($CH_2\mathbf{C}H_3$), 20.64 (Me), 43.85 ($\mathbf{C}H_2$Ph), 58.96 (OCH_2), 70.21 (C^5), 105.09 (C^9), 117.88 (C^4), 123.92–138.22 (C_{arom}, C^8), 142.14 (COCH=**C**HPh), 158.38 (C^6), 160.91 (9-C=O), 165.71 (C^2), 173.73 (C^3), 183.03 (4-C=O). Found, %: C 74.93; H 5.17; N 4.46. $C_{39}H_{32}N_2O_6$. Calculated, %: C 74.99; H 5.16; N 4.48.

Ethyl 7-benzyl-4-cinnamoyl-3-hydroxy-8-methyl-1-(4-methylphenyl)-2,6-dioxo-1,7-diazaspiro[4.4]-

nona-3,8-diene-9-carboxylate (Vc). Yield 71%, mp 236–238°C. IR spectrum, ν, cm^{-1}: 3170 (OH), 1725 (C^6=O), 1696 (C^2=O), 1675 (9-C=O), 1647 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 1.12 t (3H, C**H**$_3$CH$_2$, *J* = 7.0 Hz), 2.24 s (3H, Me), 2.35 s (3H, 8-Me), 4.04 m (2H, OCH$_2$), 4.75 d and 4.90 d (1H each, C**H**$_2$Ph, *J* = 16.8 Hz), 6.87–7.68 m (14H, H$_{arom}$), 7.60 d (1H, COC**H**=CHPh, *J* = 16.1 Hz), 7.77 d (1H, COCH=C**H**Ph, *J* = 16.1 Hz), 13.33 br.s (1H, OH). Found, %: C 72.53; H 5.34; N 4.99. $C_{34}H_{30}N_2O_6$. Calculated, %: C 72.58; H 5.37; N 4.98.

Ethyl 7-benzyl-4-cinnamoyl-3-hydroxy-1-(4-methoxyphenyl)-2,6-dioxo-8-phenyl-1,7-diazaspiro[4.4]nona-3,8-diene-9-carboxylate (Vd). Yield 75%, mp 199–200°C. IR spectrum, ν, cm^{-1}: 3431 (OH), 1723 (C^6=O), 1690 (C^2=O), 1677 (9-C=O), 1649 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 0.82 t (3H, C**H**$_3$CH$_2$, *J* = 7.0 Hz), 3.82 m (2H, OCH$_2$), 3.84 s (3H, OMe), 4.25 d and 4.70 d (1H each, C**H**$_2$Ph, *J* = 16.5 Hz), 6.49–7.71 m (19H, H$_{arom}$), 7.69 d (1H, COC**H**=CHPh, *J* = 16.0 Hz), 7.77 d (1H, COCH=C**H**Ph, *J* = 16.0 Hz), 13.30 br.s (1H, OH). Found, %: C 73.15; H 5.00; N 4.32. $C_{39}H_{32}N_2O_7$. Calculated, %: C 73.11; H 5.03; N 4.37.

Ethyl 7-benzyl-4-cinnamoyl-3-hydroxy-1-(4-methoxyphenyl)-8-methyl-2,6-dioxo-1,7-diazaspiro[4.4]nona-3,8-diene-9-carboxylate (Ve). Yield 69%, mp 235–236°C. IR spectrum, ν, cm^{-1}: 3458 (OH), 1721 (C^6=O), 1696 (C^2=O), 1671 (9-C=O), 1644 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 1.13 t (3H, C**H**$_3$CH$_2$, *J* = 7.0 Hz), 2.45 s (3H, Me), 3.80 s (3H, OMe), 4.06 m (2H, OCH$_2$), 4.73 d and 4.90 d (1H each, C**H**$_2$Ph, *J* = 16.5 Hz), 6.89–7.68 m (14H, H$_{arom}$), 7.60 d (1H, COC**H**=CHPh, *J* = 16.2 Hz), 7.72 d (1H, COCH=C**H**Ph, *J* = 16.2 Hz), 13.32 br.s (1H, OH). Found, %: C 70.54; H 5.26; N 4.81. $C_{34}H_{30}N_2O_7$. Calculated, %: C 70.58; H 5.23; N 4.84.

Ethyl 4-cinnamoyl-3-hydroxy-1-(4-methoxyphenyl)-8-methyl-2,6-dioxo-7-phenyl-1,7-diazaspiro[4.4]nona-3,8-diene-9-carboxylate (Vf). Yield 73%, mp 236–237°C. IR spectrum, ν, cm^{-1}: 3169 (OH), 1727 (C^6=O), 1703 (C^2=O), 1674 (9-C=O), 1645 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 1.16 t (3H, C**H**$_3$CH$_2$, *J* = 7.0 Hz), 2.11 s (3H, Me), 3.80 s (3H, OMe), 4.07 m (2H, OCH$_2$), 7.06–7.71 m (14H, H$_{arom}$), 7.67 d (1H, COC**H**=CHPh, *J* = 15.7 Hz), 7.74 d (1H, COCH=C**H**Ph, *J* = 15.7 Hz), 13.35 br.s (1H, OH). Found, %: C 70.16; H 5.03; N 4.93. $C_{33}H_{28}N_2O_7$. Calculated, %: C 70.20; H 5.00; N 4.96.

9-Benzoyl-7-benzyl-4-cinnamoyl-3-hydroxy-1,8-diphenyl-1,7-diazaspiro[4.4]nona-3,8-diene-2,6-dione (VIa). Enamine **IIIa**, 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 3 h under reflux and cooled, and the precipitate was filtered off and recrystallized from ethyl acetate–dichloroethane. Yield 78%, mp 274–275°C. IR spectrum, ν, cm^{-1}: 3180 (OH), 1722 (C^6=O), 1713 (C^2=O), 1672 (9-C=O), 1642 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 4.54 d and 4.73 d (1H, C**H**$_2$Ph, *J* = 16.4 Hz), 6.65–7.71 m (25H, Ph), 7.71 d (1H, COC**H**=CHPh, *J* = 15.9 Hz), 7.78 d (1H, COCH=C**H**Ph, *J* = 15.9 Hz), 13.13 br.s (1H, OH). Found, %: C 78.43; H 4.67; N 4.38. $C_{42}H_{30}N_2O_5$. Calculated, %: C 78.49; H 4.70; N 4.36.

Compounds **VIb** and **VIc** were synthesized in a similar way.

9-Benzoyl-4-cinnamoyl-3-hydroxy-1,7-bis(4-methylphenyl)-8-phenyl-1,7-diazaspiro[4.4]nona-3,8-diene-2,6-dione (VIb). Yield 82%, mp 281–283°C. IR spectrum, ν, cm^{-1}: 3178 (OH), 1728 (C^6=O), 1689 (C^2=O), 1669 (9-C=O), 1647 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 2.24 s and 2.35 s (3H each, Me), 6.70–7.72 m (23H, H$_{arom}$), 7.73 d (1H, COC**H**=CHPh, *J* = 16.0 Hz), 7.78 d (1H, COCH=C**H**Ph, *J* = 16.0 Hz), 13.05 br.s (1H, OH). Found, %: C 78.67; H 4.89; N 4.23. $C_{43}H_{32}N_2O_5$. Calculated, %: C 78.64; H 4.91; N 4.27.

9-Benzoyl-4-cinnamoyl-3-hydroxy-1-(4-methoxyphenyl)-7-(4-methylphenyl)-8-phenyl-1,7-diazaspiro[4.4]nona-3,8-diene-2,6-dione (VIc). Yield 79%, mp 277–278°C. IR spectrum, ν, cm^{-1}: 3205 (OH), 1731 (C^6=O), 1695 (C^2=O), 1671 (9-C=O), 1646 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 2.24 s (3H, Me), 3.78 s (3H, OMe), 6.70–7.74 m (23H, H$_{arom}$), 7.73 d (1H, COC**H**=CHPh, *J* = 15.4 Hz), 7.73 d (1H, COCH=C**H**Ph, *J* = 15.4 Hz), 13.05 br.s (1H, OH). ^{13}C NMR spectrum, δ$_C$, ppm: 20.50 (Me), 55.44 (OMe), 71.88 (C^5), 113.27 (C^9), 114.56–138.16 (C$_{arom}$, C^4, C^8), 142.23 (COCH=**C**HPh), 157.22 (C^6), 159.11 (**C**OMe), 165.66 (C^2), 173.99 (C^3), 182.62 (4-C=O), 190.86 (**C**OPh). Found, %: C 76.84; H 4.74; N 4.14. $C_{43}H_{32}N_2O_6$. Calculated, %: C 76.77; H 4.79; N 4.16.

Dimethyl 4-cinnamoyl-3-hydroxy-7-(4-methylphenyl)-2,6-dioxo-1-phenyl-1,7-diazaspiro[4.4]nona-3,8-diene-8,9-dicarboxylate (VIIa). Enamine **IVa**, 1.0 mmol, was added to a solution of 1.0 mmol of compound **Ia** in 20 mL of anhydrous benzene, the

mixture was heated for 3–4 h under reflux and cooled, and the precipitate was filtered off and recrystallized from ethyl acetate. Yield 82%, mp 262–264°C. IR spectrum, ν, cm^{-1}: 3331 (OH), 1755 (C^6=O), 1728 (C^2=O), 1703 (8-C=O), 1674 (9-C=O), 1647 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 2.35 s (3H, Me), 3.60 s and 3.62 s (3H each, COOMe), 7.06–7.73 m (14H, H_{arom}), 7.70 d (1H, COC**H**=CHPh, *J* = 16.0 Hz), 7.75 d (1H, COCH=C**H**Ph, *J* = 16.0 Hz), 12.24 br.s (1H, OH). Found, %: C 68.52; H 4.55; N 4.90. $C_{33}H_{26}N_2O_8$. Calculated, %: C 68.51; H 4.53; N 4.84.

Compounds **VIIb**–**VIIh** were synthesized in a similar way.

Dimethyl 7-(4-bromophenyl)-4-cinnamoyl-3-hydroxy-2,6-dioxo-1-phenyl-1,7-diazaspiro[4.4]nona-3,8-diene-8,9-dicarboxylate (VIIb). Yield 79%, mp 264–265°C. IR spectrum, ν, cm^{-1}: 3285 (OH), 1767 (C^6=O), 1725 (C^2=O), 1689 (8-C=O), 1670 (9-C=O), 1645 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 3.65 s and 3.66 s (3H each, COOMe), 7.15–7.80 m (14H, H_{arom}), 7.69 d (1H, COC**H**=CHPh, *J* = 15.8 Hz), 7.75 d (1H, COCH=C**H**Ph, *J* = 15.8 Hz), 12.30 br.s (1H, OH). Found, %: C 59.69; H 3.64; N 4.38. $C_{32}H_{23}BrN_2O_8$. Calculated, %: C 59.73; H 3.60; N 4.35.

Dimethyl 7-(4-chlorophenyl)-4-cinnamoyl-3-hydroxy-2,6-dioxo-1-phenyl-1,7-diazaspiro[4.4]nona-3,8-diene-8,9-dicarboxylate (VIIc). Yield 80%, mp 271–273°C. IR spectrum, ν, cm^{-1}: 3287 (OH), 1767 (C^6=O), 1726 (C^2=O), 1690 (8-C=O), 1671 (9-C=O), 1645 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 3.63 s and 3.64 s (3H each, COOMe), 7.12–7.79 m (14H, H_{arom}), 7.69 d (1H, COC**H**=CHPh, *J* = 15.9 Hz), 7.75 d (1H, COCH=C**H**Ph, *J* = 16.0 Hz), 12.26 br.s (1H, OH). Found, %: C 64.13; H 3.91; N 4.64. $C_{32}H_{23}ClN_2O_8$. Calculated, %: C 64.17; H 3.87; N 4.68.

Dimethyl 4-cinnamoyl-3-hydroxy-1,7-bis-(4-methylphenyl)-2,6-dioxo-1,7-diazaspiro[4.4]-nona-3,8-diene-8,9-dicarboxylate (VIId). Yield 83%, mp 251–252°C. IR spectrum, ν, cm^{-1}: 3291 (OH), 1759 (C^6=O), 1727 (C^2=O), 1698 (8-C=O), 1674 (9-C=O), 1644 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 2.35 s and 2.36 s (3H each, Me), 3.61 s and 3.62 s (3H each, COOMe), 7.00–7.72 m (13H, H_{arom}), 7.71 d (1H, COC**H**=CHPh, *J* = 15.9 Hz), 7.75 d (1H, COCH=C**H**Ph, *J* = 15.9 Hz), 12.31 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 20.70 and 20.72 (Me), 51.94 and 53.35 (OCH_3), 69.58 (C^5), 104.92 (C^9), 117.52 (C^4), 123.59–139.13 (C_{arom}), 142.78 (COCH=**C**HPh), 149.36 (C^8), 156.62 (C^6), 160.10 (8-C=O), 160.52 (9-C=O), 165.69 (C^2), 172.97 (C^3), 181.93 (4-C=O). Found, %: C 68.93; H 4.71; N 4.70. $C_{34}H_{28}N_2O_8$. Calculated, %: C 68.91; H 4.76; N 4.73.

Dimethyl 7-(4-chlorophenyl)-4-cinnamoyl-3-hydroxy-1-(4-methylphenyl)-2,6-dioxo-1,7-diazaspiro-[4.4]nona-3,8-diene-8,9-dicarboxylate (VIIe). Yield 78%, mp 249–250°C. IR spectrum, ν, cm^{-1}: 3286 (OH), 1768 (C^6=O), 1724 (C^2=O), 1688 (8-C=O), 1670 (9-C=O), 1639 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 2.35 s (3H, Me), 3.63 s and 3.65 s (3H each, COOMe), 7.00–7.80 m (13H, H_{arom}), 7.69 d (1H, COC**H**=CHPh, *J* = 16.0 Hz), 7.75 d (1H, COCH=C**H**Ph, *J* = 16.0 Hz), 12.28 br.s (1H, OH). Found, %: C 64.69; H 4.08; N 4.58. $C_{33}H_{25}ClN_2O_8$. Calculated, %: C 64.66; H 4.11; N 4.57.

Dimethyl 4-cinnamoyl-3-hydroxy-1-(4-methoxyphenyl)-7-(4-methylphenyl)-2,6-dioxo-1,7-diazaspiro[4.4]nona-3,8-diene-8,9-dicarboxylate (VIIf). Yield 81%, mp 247–249°C. IR spectrum, ν, cm^{-1}: 3264 (OH), 1767 (C^6=O), 1732 (C^2=O), 1698 (8-C=O), 1674 (9-C=O), 1644 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 2.35 s (3H, Me), 3.62 s and 3.64 s (3H each, COOMe), 3.80 s (3H, OMe), 7.02–7.72 m (13H, H_{arom}), 7.70 d (1H, COC**H**=CHPh, *J* = 16.0 Hz), 7.75 d (1H, COCH=C**H**Ph, *J* = 16.0 Hz), 12.30 br.s (1H, OH). Found, %: C 67.07; H 4.60; N 4.65. $C_{34}H_{28}N_2O_9$. Calculated, %: C 67.10; H 4.64; N 4.60.

Dimethyl 7-(4-bromophenyl)-4-cinnamoyl-3-hydroxy-1-(4-methoxyphenyl)-2,6-dioxo-1,7-diazaspiro[4.4]nona-3,8-diene-8,9-dicarboxylate (VIIg). Yield 78%, mp 249–250°C. IR spectrum, ν, cm^{-1}: 3280 (OH), 1767 (C^6=O), 1731 (C^2=O), 1698 (8-C=O), 1676 (9-C=O), 1645 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 3.65 s and 3.66 s (3H each, COOMe), 3.80 s (3H, OMe), 7.02–7.79 m (13H, H_{arom}), 7.69 d (1H, COC**H**=CHPh, *J* = 15.8 Hz), 7.75 d (1H, COCH=C**H**Ph, *J* = 15.8 Hz), 12.23 br.s (1H, OH). Found, %: C 58.88; H 3.69; N 4.17. $C_{33}H_{25}BrN_2O_9$. Calculated, %: C 58.85; H 3.74; N 4.16.

Dimethyl 1,7-bis(4-bromophenyl)-4-cinnamoyl-3-hydroxy-2,6-dioxo-1,7-diazaspiro[4.4]nona-3,8-diene-8,9-dicarboxylate (VIIh). Yield 79%, mp 270–271°C. IR spectrum, ν, cm^{-1}: 3271 (OH), 1764 (C^6=O), 1734 (C^2=O), 1699 (8-C=O), 1679 (9-C=O), 1644 (4-C=O). ^{1}H NMR spectrum, δ, ppm: 3.62 s and 3.66 s (3H, COOMe), 7.06–7.86 m (13H, H_{arom}), 7.68 d (1H, COC**H**=CHPh, *J* = 15.8 Hz), 7.75 d (1H, COCH=C**H**Ph, *J* = 15.8 Hz), 12.34 br.s (1H, OH). Found, %: C 53.23; H 3.04; N 3.85. $C_{32}H_{22}Br_2N_2O_8$. Calculated, %: C 53.21; H 3.07; N 3.88.

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