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Synthesis of New Heterocyclic Enamines and Their Cyclization with Oxalyl Chloride

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Substituted furan-2,3-diones are convenient synthons exhibiting high reactivity and unusual chemical behavior toward various reagents [1, 2]. Heterocyclic ensembles derived from these compounds were found to possess versatile biological activity [3]. Functionally substituted furan-2,3-diones can be synthesized by reaction of heterocyclic β -enaminoketones with oxalyl chloride [4–6].

By reaction of diaroylacetylenes **Ia** and **Ib** with biphenyl-3,3',4,4'-tetraamine (**II**) according to the procedure described in [7] we obtained new heterocyclic enamines, 2,2'-(3,3'-diaryl-1,1',2,2'-tetrahydro-6,6'-biquinoxaline-2,2'-diylidene)bis(1-arylethanones) **IIIa** and **IIIb** (Scheme 1). Heating of compounds **IIIa** and **IIIb** with oxalyl chloride in boiling anhydrous chloroform led to the formation of new representatives of the furan-2,3-dione series, 4,4'-(3,3'-diaryl-6,6'-biquinoxaline-2,2'-diyl)bis(5-aryl-2,3-dihydrofuran-2,3-diones) **IVa** and **IVb** (Scheme 2).

Presumably, bis-furanciones IVa and IVb are formed via initial acylation of compounds IIIa and IIIb with oxalyl chloride at the exocyclic =CH fragments to give intermediate acyl chlorides [8] which are converted into hydroxyenimine structure with subsequent intramolecular cyclization.

2,2'-(3,3'-Diphenyl-1,1',2,2'-tetrahydro-6,6'-biquinoxaline-2,2'-divlidene)bis(1-phenylethanone) (IIIa). A solution of 4.68 g (20 mmol) of compound Ia in 10 ml of acetonitrile was added to a solution of 2.14 g (10 mmol) of tetraamine II in 20 ml of acetonitrile, and the mixture was heated to the boiling point and cooled. The precipitate was filtered off and recrystallized from acetonitrile. Yield 5.75 g (89%), orange– red crystals, mp 252–254°C (from acetone). IR spectrum, v, cm⁻¹: 3034 br (NH), 1580 br (C=O). ¹H NMR spectrum, δ , ppm: 6.29 s (2H, CH), 6.93–7.90 m (26H, H_{arom}), 15.70 s (2H, NH). Found, %: C 81.74; H 4.60; N 8.67. C₄₄H₃₀N₄O₂. Calculated, %: C 81.71; H 4.68; N 8.66.

2,2'-[3,3'-Bis(4-methylphenyl)-1,1',2,2'-tetrahydro-6,6'-biquinoxaline-2,2'-diylidene]bis[1-(4-methylphenyl)ethanone] (IIIb) was synthesized in a similar way. Yield 5.98 g (85%), orange-red crystals, mp 223-225°C (from acetone). IR spectrum, v, cm⁻¹: 3024 br (NH), 1586 br (C=O). ¹H NMR spectrum, δ , ppm: 2.34 s (6H, Me), 2.50 s (6H, Me), 6.35 s (2H, CH), 6.90-7.92 m (22H, H_{arom}), 15.76 s (2H, NH). Found, %: C 82.09; H 5.43; N 7.95. C₄₈H₃₈N₄O₂. Calculated, %: C 82.03; H 5.45; N 7.97.

4,4'-(3,3'-Diphenyl-6,6'-biquinoxaline-2,2'-diyl)bis(5-phenyl-2,3-dihydrofuran-2,3-dione) (IVa). Oxalyl chloride, 2.52 g (20 mmol), was added to a solution of 6.47 g (10 mmol) of compound **IIIa** in 40 ml of anhydrous chloroform. The mixture was heated for







100 min under reflux, evaporated to a volume of 20 ml, diluted with anhydrous hexane, and cooled, and the precipitate was filtered off. Yield 6.03 g (80%), yellow crystals, decomposition point 289–291°C (from chloroform–hexane, 2:3). IR spectrum, v, cm⁻¹: 1830 (C²=O), 1719 (C³=O). ¹H NMR spectrum: δ 7.13–8.25 ppm, m (26H, H_{arom}). Found, %: C 76.36; H 3.46; N 7.77. C₄₈H₂₆N₄O₆. Calculated, %: C 76.39; H 3.47; N 7.42.

4,4'-[3,3'-Bis(4-methylphenyl)-6,6'-biquinoxaline-2,2'-diyl]bis[5-(4-methylphenyl)-2,3-dihydrofuran-2,3-dione] (IVb) was synthesized in a similar way. Yield 6.48 g (80%), yellow crystals, decomposition point 319–320°C (from chloroform–hexane, 2:3). IR spectrum, v, cm⁻¹: 1830 (C²=O), 1715 (C³=O). ¹H NMR spectrum, δ , ppm: 2.34 s (6H, Me), 2.46 s (6H, Me), 7.19–8.30 m (22H, H_{arom}). Found, %: C 77.00; H 4.26; N 6.94. C₅₂H₃₄N₄O₆. Calculated, %: C 77.03; H 4.23; N 6.91.

The IR spectra were recorded from samples dispersed in mineral oil on an FSM-1201 spectrometer. The ¹H NMR spectra were measured on a Varian Mercury Plus-300 instrument at 300 MHz using DMSO- d_6 as solvent and HMDS as internal reference. The elemental compositions were determined on a Leco CHNS-932 automatic analyzer. The purity of the isolated compounds was checked, and the progress of reactions was monitored, by TLC on Silufol UV-254 plates using hexane–ethyl acetate (5:1) as eluent.

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