Five-membered 2,3-Dioxoheterocycles: LXXIII.* Synthesis and Thermolysis of 3-Acylpyrrolo[1,2-*a*]quinoxaline-1,2,4(5*H*)-triones

I. V. Mashevskaya^a, I. G. Mokrushin^b, K. S. Bozdyreva^b, and A. N. Maslivets^{a,b}

^aInstitute of Natural Sciences at Perm State University, Perm, Russia ^bPerm State University, Perm, 614990 Russia e-mail: koh2@psu.ru

Received April 6, 2010

Abstract—Reactions of (*Z*)-3-(phenacylidene-2-oxo)-3,4-dihydroquinoxalin-2(1*H*)-ones and (*Z*)-3-(3,3-dimethyl-2-oxobutylidene)-3,4-dihydroquinoxalin-2(1*H*)-one with oxalyl chloride led to the formation of 3-acyl-1*H*-pyrrolo[1,2-a]quinoxaline-1,2,4(5*H*)-triones that at the thermal decarbonylation generated acyl(3-oxoquinoxalin-2-yl)ketenes which underwent the intramolecular stabilization giving 3-acylfuro[3,2-b]quinoxalin-2(4*H*)-ones.

DOI: 10.1134/S1070428011020151

The thermal decarbonylation of 4-acyl-substituted 1H-pyrrole-2,3-diones fused with azaheterocycles at the [*a*] side (hetareno[*a*]-pyrrole-2,3-diones) is a convenient method for the generation of acyl(imidoyl)ketenes where the imidoyl fragment is included into the heterocyclic system [2–5].

It was formerly established that the thermolysis of 3-aroyl- and 3-heteroyl-5-phenylpyrrolo[1,2-a] quinoxalin-1,2,4(5H)-triones resulted in the generation of aroyl- and heteroyl(3-oxo-4-phenylquinoxalin-2yl)ketenes which underwent the stabilization through [4+2]-cyclodimerization followed by the [1,3]-acvlotropic shift to provide 4-acyl-3-acyloxy-2-(3-oxo-4-phenyl-2- quinoxalinyl)-6-phenyl-1*H*-pyrido[1,2-*a*] quinoxalin-1,5-diones [4]. Yet even insignificant changes in the structure of the imidoylketene led to the alteration of its stabilization paths. For instance, the 4-unsubstituted 3-oxoquinoxalin-2-yl(ethoxycarbonyl)ketene originating from the thermolysis of 5-unsubstituted 3-ethoxycarbonylpyrrolo[1,2-a]quinoxaline-1,2,4(5H)trione stabilized by the transformation of the quinoxalinone fragment from the amide into the hydroxyimine form with the subsequent intramolecular acylation of the hydroxyimine OH group by the ketene fragment [5].

In order to examine the effect of the structure of

the fuzed quinoxalone fragment of the pyrrolo[1,2-a] quinoxaline-1,2,4(5*H*)-triones on the stabilization routes of the quinoxalinylketenes obtained by the thermolysis of the former we investigated the methods of synthesis and thermolytic transformations of 3-acyl-1*H*-pyrrolo-[1,2-a]quinoxaline-1,2,4(5*H*)-triones, 5-unsubstituted analogs of 3-aroyl- and 3-heteroyl-5-phenylpyrrolo[1,2-a]-quinoxaline-1,2,4-triones [4].

(Z)-3-(2-Oxophenacylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones **Ia–Ig** and (Z)-3-(3,3-dimethyl-2-oxobutylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (**Ih**) were obtained reacting the esters of acylpyruvic acids with *O*-phenylenediamine by the known method [6, 7] (see the scheme).

Compounds **Ia–Ig** are bright yellow crystalline substances of high melting points, readily soluble in DMF and DMSO, sparingly soluble in the common organic solvents, insoluble in water and alkanes.

IR spectra of compounds **Ia–Ig** contain absorption bands of the stretching vibrations of the group N^{*I*}H (3120–3170 cm⁻¹), of N⁴H group involved into an intramolecular hydrogen bond of the H-chelate type (wide band at 3020–3060 cm⁻¹), of amide carbonyl C²=O (1673–1688 cm⁻¹), of the aroyl carbonyl group involved into the intramolecular hydrogen bond (wide band at 1603–1611 cm⁻¹).

^{*} For Communication LXXII, see [1].





 $R = Ph(a), n-MeC_{6}H_{4}(b), n-EtOC_{6}H_{4}(c), n-FC_{6}H_{4}(d), n-ClC_{6}H_{4}(e), n-BrC_{6}H_{4}(f), n-NO_{2}C_{6}H_{4}(g), t-Bu(h).$

In the ¹H NMR spectra of compounds **Ia–Ig** apart the signals of the aromatic protons and the groups linked to the aromatic rings a singlet was observed of the vinyl proton (6.80–6.87 ppm), a singlet of the proton of N^{*I*}H group (11.97–12.18 ppm), and the singlet of the proton of N^{*4*}H group involved into the intramolecular hydrogen bond, downfield at 13.58–13.81 ppm. In the group of the aromatic protons the doublet of two *ortho*-protons of the benzene ring of the ArCO group is shifted downfield to 7.90–8.22 ppm.

The spectral characteristics of compounds **Ia–Ig** show that they exist in the crystalline state and in solution in the form with the *exo*-located double bond and a strong intramolecular hydrogen bond of the H-chelate type between the N⁴H and aroyl group, therefore they are present in the form of Z-isomers characteristic of compounds of this class [8].

The reaction of (*Z*)-3-(2-oxophenacylidene)-3,4dihydroquinoxalin-2(1*H*)-ones **Ia–Ig** with oxalyl chloride at boiling in anhydrous chloroform over 1–2 h (till the end of HCl liberation) afforded in virtually quantitative yields 3-aroylpyrrolo[1,2-*a*]quinoxaline-1,2,4(5*H*)-triones **IIa–IIg**. Pyrroloquinoxalinetriones **IIa–IIg** are dark violet (nearly black) crystalline substances of high melting point, melting with decomposition, readily soluble in DMF and DMSO, sparingly soluble in the common organic solvents, insoluble in alkanes. They react with water and alcohols and suffer decoloration at storage due to the reaction with air moisture.

IR spectra of compounds **IIa–IIg** contain absorption bands of the stretching vibrations of group N⁵H (3120– 3180 cm⁻¹), of lactam carbonyl C¹=O (1754–1774 cm⁻¹), of keto group C²=O (1715–1740 cm⁻¹), of amide carbonyl C⁴=O in the region 1670–1696 cm⁻¹, and of the aroyl carbonyl group of the side chain (1615–1635 cm⁻¹). The range of the stretching vibrations of the carbonyl groups of the pyrroledione ring and also the higher frequency of v(CO) of the lactam carbonyl compared with that of the keto group in the ring are consistent with the published data for these groups in the IR spectra of monocyclic 1*H*-pyrrole-2,3-diones [8].

In the ¹H NMR spectra of compounds **IIa–IIg** apart the signals of the aromatic protons and the groups linked to the aromatic rings a singlet was observed of the proton of the N⁵H group in the region 11.60–11.90 ppm. In the group of the aromatic protons the doublet of two *ortho*protons of the benzene ring of the ArCO group is shifted downfield to 8.03–8.32 ppm, and the multiplet of the proton H⁹ deshielded due to the interaction with the oxygen of the carbonyl group C¹=O appears at 8.36–8.40 ppm.

The heating of 3-aroylsubstituted pyrroloquinoxalinetriones **IIa–IIg** and 3-pivaloylpyrrolo-[1,2-a]quinoxaline-1,2,4(5*H*)-trione (**IIh**) [7] in an inert aprotic solvent (Dowtherm A) at 190–195°C for 1–5 min (till the disappearance of the violet color of the initial pyrroloquinoxalinetriones) furnished in good yields 3-aroyl- and 3-pivaloylfuro[3,2-*b*]-quinoxaline-2(4*H*)-ones **IIIa–IIIh**. After the thermolysis in the reaction mixture according to TLC monitoring initial quinoxalones **Ia–Ih** are present in trace amounts as impurities. They apparently form by hydrolysis of pyrroloquinoxalinetriones **IIa–IIh** with residual water present in the dried solvent. Compounds **IIIa–IIIh** are light-yellow crystalline substances of high melting point, melting with decomposition, readily soluble in DMF and DMSO, sparingly soluble in the common organic solvents, insoluble in water and alkanes.

In the IR spectra of compounds **IIIa–IIIh** the following absorption bands are observed: the wide band of the stretching vibrations of the NH group (3170-3290 cm⁻¹), of lactone group C²=O (1775-1787 cm⁻¹), of aroyl carbonyl group from the side chain (1654-1664 cm⁻¹ for compounds **IIIa–IIIg**), of pivaloyl carbonyl group (1680 cm⁻¹ for compound **IIIh**).

The NMR spectra of compounds **IIIa–IIIh** apart the signals of the aromatic protons and the groups linked to the aromatic rings contain the proton singlet of the N⁴H group in the region 13.73–14.30 ppm. In the group of the aromatic protons the doublet of the proton H⁸ is shifted downfield due to the deshielding because of the interaction with the atom N⁹ (8.18–8.24 ppm).

Evidently the thermolysis of pyrroloquinoxalinetriones **IIa–IIh** led to the decarbonylation and the generation of acyl(3-oxoquinoxalin-2-yl)ketenes **IVa–IVh** undergoing the stabilization by the conversion of the quinoxalone fragment from the amide into the hydroxyimine form **Va–Vh** with the subsequent intramolecular acylation of the hydroxyimine OH group with the ketene fragment. This reaction is a convenient method of the regioselective construction of the functionally-substituted system of furo[3,2-*b*]quinoxaline.

EXPERIMENTAL

IR spectra of compounds obtained were recorded on a spectrophotometer FSM-1201. ¹H and ¹³C NMR spectra were registered on a spectrometer Bruker AM-400 [operating frequencies 400 (¹H) and 100 (¹³C) MHz] in DMSO- d_6 , internal reference TMS. The homogeneity of compounds synthesized was tested by TLC on Silufol plates, eluents benzene–ethyl acetate, 5:1, ethyl acetate, development in iodine vapor or under UV irradiation.

(Z)-3-(2-Oxo-2-phenylethyl idene)-3,4-dihydroquinoxalin-2(1*H*)-one (Ia). A solution of 0.01 mol of methyl benzoylpyruvate and 0.01 mol of *o*-phenylenediamine in 30 ml of dioxane was boiled for 30 min (TLC monitoring), the solvent was removed, the residue was recrystallized from dioxane. Yield 99%, mp 266–267°C [6]. IR spectrum, v, cm⁻¹: 3160 (N¹H), 3070 br (N⁴H), 1688 (C²=O), 1611 br (COPh). ¹H NMR spectrum, δ , ppm: 6.83 s (1H, C³=CH), 7.14–7.61 group of signals (7H, C₆H₃ + H⁵⁻⁸), 7.99 d [2H, 2H^o(PhCO), *J* 8.7 Hz], 12.05 s (N¹H), 13.68 s (N⁴H). Found, %: C 72.77; H 4.60; N 10.63. C₁₆H₁₂N₂O₂. Calculated, %: C 72.72; H 4.58; N 10.60.

Compounds **Ib–Ig** were similarly obtained.

(Z)-3-[2-(4-Methylphenyl)-2-oxoethylidene]-3,4dihydroquinoxalin-2(1*H*)-one (Ib). Yield 98%, mp 229– 230°C. IR spectrum, v, cm⁻¹: 3170 (N¹H), 3030 br (N⁴H), 1680 (C²=O), 1607 br (COC₆H₄). ¹H NMR spectrum, δ , ppm: 2.39 s (3H, Me), 6.81 s (1H, C³=CH), 7.12–7.57 group of signals [6H, 2H^m(COC₆H₄) + H^{5–8}], 7.90 d [2H, 2H^O(COC₆H₄), J 8.2 Hz], 12.02 s (N¹H), 13.63 s (N⁴H). Found, %: C 73.35; H 5.03; N 10.09. C₁₇H₁₄N₂O₂. Calculated, %: C 73.37; H 5.07; N 10.07.

(Z)-3-[2-Oxo-2-(4-ethoxyphenyl)ethylidene]-3,4dihydroquinoxalin-2(1*H*)-one (Ic). Yield 92%, mp 238– 239°C. IR spectrum, v, cm⁻¹: 3120 (N^{*I*}H), 3020 br (N^{*4*}H), 1676 (C²=O), 1610 br (COC₆H₄). ¹H NMR spectrum, δ , ppm: 2.39 s (3H, Me), 6.81 s (1H, C³=CH), 7.12–7.57 group of signals [6H, 2H^{*m*}(COC₆H₄) + H^{5–8}], 7.90 d [2H, 2H^o(COC₆H₄), *J* 8.2 Hz], 11.97 s (N^{*I*}H), 13.58 s (N⁴H). Found, %: C 70.16; H 5.25; N 9.11. C₁₈H₁₆N₂O₃. Calculated, %: C 70.12; H 5.23; N 9.09.

(*Z*)-3-[2-Oxo-2-(4-fluorophenyl)ethylidene]-3,4dihydroquinoxalin-2(1*H*)-one (Id). Yield 89%, mp 257– 258°C. IR spectrum, v, cm⁻¹: 3140 (N^{*I*}H), 3030 br (N^{*4*}H), 1674 (C²=O), 1610 br (COC₆H₄). ¹H NMR spectrum, δ , ppm: 6.80 s (1H, C³=CH), 7.12–7.54 group of signals [6H, 2H^m(COC₆H₄) + H⁵⁻⁸], 8.06 d [2H, 2H^o(COC₆H₄), *J* 8.7 Hz], 12.06 s (N^{*I*}H), 13.62 s (N⁴H). Found, %: C 68.05; H 3.97; F 6.70; N 9.95. C₁₆H₁₁FN₂O₂. Calculated, %: C 68.08; H 3.93; F 6.73; N 9.92.

(Z)-3-[2-Oxo-2-(4-chlorophenyl)ethylidene]-3,4dihydroquinoxalin-2(1*H*)-one (Ie). Yield 94%, mp 271– 272°C. IR spectrum, v, cm⁻¹: 3170 (N^{*I*}H), 3030 br (N^{*4*}H), 1684 (C²=O), 1608 br (COC₆H₄). ¹H NMR spectrum, δ , ppm: 6.80 s (1H, CH), 7.15–7.60 group of signals [6H, 2H^m(COC₆H₄) + H⁵⁻⁸], 8.00 d [2H, 2H^O(COC₆H₄), *J* 8.6 Hz], 12.07 s (N^{*I*}H), 13.65 s (N⁴H). Found, %: C 64.37; H 3.74; Cl 11.85; N 9.32. C₁₆H₁₁ClN₂O₂. Calculated, %: C 64.33; H 3.71; Cl 11.87; N 9.36.

(Z)-3-[2-(4-Bromophenyl)-2-oxoethylidene]-3,4dihydroquinoxalin-2(1*H*)-one (If). Yield 89%, mp 279–

RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 47 No. 2 2011

280°C. IR spectrum, v, cm⁻¹: 3150 (N^{*I*}H), 3040 br (N^{*4*}H), 1673 (C²=O), 1607 br (COC₆H₄). ^{*I*}H NMR spectrum, δ, ppm: 6.80 s (1H, C³=CH), 7.13–7.74 group of signals [6H, 2H^{*m*}(COC₆H₄) + H^{5–8}], 7.92 d [2H, 2H^O(COC₆H₄), *J* 8.6 Hz], 12.09 s (N^{*I*}H), 13.66 s (N⁴H). Found, %: C 56.07; H 3.20; Br 23.30; N 8.14. C₁₆H₁₁BrN₂O₂. Calculated, %: C 56.00; H 3.23; Br 23.28; N 8.16.

(*Z*)-3-[2-(4-Nitrophenyl)-2-oxoethylidene]-3,4dihydroquinoxalin-2(1*H*)-one (Ig). Yield 80%, mp 298– 299°C. IR spectrum, v, cm⁻¹: 3170 (N¹H), 3060 br (N⁴H), 1684 (C²=O), 1603 br (COC₆H₄). ¹H NMR spectrum, δ , ppm: 6.87 s (1H, C³=CH), 7.17–7.61 group of signals (4H, H⁵⁻⁸), 8.22 d [2H, 2H⁰(COC₆H₄), *J* 8.7 Hz], 8.34 d [2H, 2H^m(COC₆H₄), *J* 8.7 Hz], 12.18 s (N¹H), 13.81 s (N⁴H). Found, %: C 62.11; H 3.61; N 13.55. C₁₆H₁₁N₃O₄. Calculated, %: C 62.14; H 3.58; N 13.59.

3-Benzoylpyrrolo[1,2-*a*]quinoxaline-1,2,4(5*H*)trione (IIa). To a dispersion of 0.01 mol of compound Ia in 50 ml of anhydrous chloroform was added dropwise 0.011 mol of freshly distilled oxalyl chloride, the mixture was heated at 40–50°C for 10 min, boiled for 100 min, cooled, the precipitate was filtered off and washed with anhydrous hexane (2 × 10 ml). Yield 92%, mp 220–221°C (decomp). IR spectrum, v, cm⁻¹: 3175 (N⁵H), 1769 (C¹=O), 1730 (C²=O), 1682 (C⁴=O), 1630 (C³C=O). ¹H NMR spectrum, δ , ppm: 7.05–7.85 group of signals (5H, C₆H₃ + H^{6–8}), 8.03 d [2H, 2H^o(COC₆H₄)], 8.36 m (1H, H⁹), 11.60 s (1H, N⁵H). Found, %: C 67.90; H 3.13; N 8.81. C₁₈H₁₀N₂O₄. Calculated, %: C 67.93; H 3.17; N 8.80.

Compounds IIb-IIg were similarly obtained.

3-[(4-Methyl)benzoyl]pyrrolo[1,2-*a***]quinoxaline-1,2,4(5***H***)-trione (IIb). Yield 93%, mp 238–240°C. IR spectrum, v, cm⁻¹: 3180 (N⁵H), 1765 (C¹=O), 1722 (C²=O), 1688 (C⁴=O), 1625 (C³C=O). ¹H NMR spectrum, \delta, ppm: 2.39 s (3H, Me), 7.17–7.77 group of signals [5H, H^{6–8}+2H^m (COC₆H₄)], 7.97 d [2H, 2H⁰(COC₆H₄),** *J* **7.93 Hz], 8.38 m (1H, H⁹), 11.75 s (N¹H). Found, %: C 68.63; H 3.60; N 8.41. C₁₉H₁₂N₂O₄. Calculated, %: C 68.67; H 3.64; N 8.43.**

3-(4-Ethoxybenzoyl)pyrrolo[**1**,**2**-*a*]**quinoxaline-1**,**2**,**4**(*5H*)-**trione (IIc).** Yield 86%, mp 218–220°C. IR spectrum, v, cm⁻¹: 3130 (N⁵H), 1765 (C¹=O), 1740 (C²=O), 1679 (C⁴=O), 1635 (C³C=O). ¹H NMR spectrum, δ , ppm: 1.35 t (3H, CH₂CH₃, *J* 7.0 Hz), 4.14 q (2H, CH₂CH₃, *J* 7.0 Hz), 7.00 d [2H, 2H_m (COC₆H₄), *J* 8.7 Hz], 7.11–7.22 group of signals (3H, H^{6–8}), 8.0 d [H, 2H^o(COC₆H₄), *J* 8.7 Hz], 8.38 m (1H, H⁹), 11.74 s

(N⁵H). Found, %: C 66.28; H 3.85; N 7.70. C₂₀H₁₄N₂O₅. Calculated, %: C 66.30; H 3.89; N 7.73.

3-(4-Fluorobenzoyl)pyrrolo[**1**,**2**-*a*]**quinoxaline-1**,**2**,**4**(**5***H*)-**trione (IId).** Yield 93%, mp 258–259°C. IR spectrum, v, cm⁻¹: 3120 (N⁵H), 1760 (C¹=O), 1730 (C²=O), 1670 (C⁴=O), 1610 (C³C=O). ¹H NMR spectrum, δ , ppm: 7.10–8.09 group of signals [7H, H^{6–8} + C₆H₄], 8.37 m (1H, H⁹), 11.80 s (1H, N⁵H). Found, %: C 64.25; H 2.68; F 5.61; N 8.30. C₁₈H₉FN₂O₄. Calculated, %: C 64.29; H 2.70; F 5.65; N 8.33.

3-(4-Chlorobenzoyl)pyrrolo[**1,2-***a*]**quinoxaline-1,2,4(5***H***)-trione (IIe). Yield 89%, mp 248–250°C. IR spectrum, v, cm⁻¹: 3170 (N⁵H), 1774 (C¹=O), 1737 (C²=O), 1696 (C⁴=O), 1620 (C³C=O). ¹H NMR spectrum, \delta, ppm: 7.14–7.83 group of signals [5H, H⁶⁻ ⁸⁺2H^m(COC₆H₄)], 8.10 d [2H, 2H^o(COC₆H₄), J 8.5 Hz], 8.39 m (1H, H⁹), 11.82 s (1H, N⁵H). Found, %: C 61.26; H 2.53; Cl 11.12; N 7.91. C₁₈H₉ClN₂O₄. Calculated, %: C 61.29; H 2.57; Cl 10.05; N 7.94.**

3-(4-Bromobenzoyl)pyrrolo[**1,2-***a*]**quinoxaline-1,2,4(5***H***)-trione (IIf). Yield 79%, mp 255–257°C. IR spectrum, v, cm⁻¹: 3170 (N⁵H), 1770 (C¹=O), 1740 (C²=O), 1680 (C⁴=O), 1615 (C³C=O). ¹H NMR spectrum, \delta, ppm: 7.06–7.80 group of signals [5H, H⁶⁻ ⁸⁺2H^m(COC₆H₄)], 8.01 d [2H, 2H^O(COC₆H₄), J 8.7 Hz], 8.37 m (1H, H⁹), 11.78 s (1H, N⁵H). Found, %: C 54.40; H 2.23; Br 20.07; N 7.09. C₁₈H₉BrN₂O₄. Calculated, %: C 54.43; H 2.28; Br 20.12; N 7.05.**

3-(4-Nitrobenzoyl)pyrrolo[1,2-*a*]quinoxaline-1,2,4(5*H*)-trione (IIg). To a solution of 0.01 mol of compound Ig in 50 ml of anhydrous O 1,2-dichloroethene was added 0.011 mol of freshly distilled oxalyl chloride, the mixture was heated at 40–50°C for 10 min, boiled for 100 min, cooled, the precipitate was filtered off, washed with anhydrous hexane (2×10 ml), and dried in air for 3 min. Yield 86%, mp 290–292°C (decomp). IR spectrum, v, cm⁻¹: 3180 (N⁵H), 1780 (C¹=O), 1732 (C²=O), 1693 (C⁴=O), 1618 (C³C=O). ¹H NMR spectrum, δ , ppm: 7.09–7.30 group of signals (3H, H^{6–8}), 8.32 m (4H, C₆H₄), 8.40 m (1H, H⁹), 11.90 s (1H, N⁵H). Found, %: C 59.50; H 2.47; N 11.54. C₁₈H₉N₃O₆. Calculated, %: C 59.51; H 2.50; N 11.57.

3-Benzoylfuro[3,2-b]quinoxalin-2(4H)-one (IIIa). A solution of 2.5 mmol of compound **IIa** in 8 ml of Dow-therm A was heated on a metal bath at 195–200°C for 1.5 mandH (till the disappearance of the bright violet color of initial compound **IIa**). The reaction mixture was cooled, the separated precipitate was filtered off. Yield 95%, mp

274–275°C (ethyl acetate). IR spectrum, ν, cm⁻¹: 3170 br (NH), 1776 (C²=O), 1656 (COPh). ¹H NMR spectrum, δ, ppm: 7.50–7.87 group of signals (8H, H^{5–7+} Ph), 8.21 d (1H, H⁸, J 8.2 Hz), 14.05 s (1H, N⁴H). ¹³C NMR spectrum, δ, ppm: 91.7 (C³), 118.6–142.0 (C^{Ar}, C⁹a), 154.7 (C^{3a}), 164.0 (C²), 188.5 (<u>C</u>OPh). Found, %: C 70.30; H 3.43; N 9.62. C₁₇H₁₀N₂O₃. Calculated, %: C 70.34; H 3.47; N 9.65.

Compounds IIIb-IIIh were similarly obtained.

3-(4-Methylbenzoyl)furo[**3**,**2**-*b*]**quinoxalin-2(4***H***)one (IIIb**). Yield 93%, mp 239–240°C. IR spectrum, v, cm⁻¹: 3190 br (NH), 1787 (C²=O), 1657 (COC₆H₄). ¹H NMR spectrum, δ , ppm: 2.40 s (3H, Me), 7.30–7.87 group of signals (7H, H⁵⁻⁷+ C₆H₄CO), 8.19 d (1H, H⁸, *J* 8.2 Hz), 14.00 s (1H, N⁴H). Found, %: C 71.01; H 3.93; N 9.20. C₁₈H₁₂N₂O₃. Calculated, %: C 71.05; H 3.97; N 9.21.

3-(4-Ethoxybenzoyl)furo[3,2-*b***]quinoxalin-2(4***H***)one (IIIc). Yield 95%, mp 246–247°C. IR spectrum, v, cm⁻¹: 3290 br (NH), 1775 (C²=O), 1658 (COC₆H₄). ¹H NMR spectrum, \delta, ppm: 1.37 t (3H, Me,** *J* **7.0 Hz), 4.14 q (2H, CH₂O,** *J* **7.0 Hz), 7.03–7.92 group of signals (7H, H^{5–7+} C₆H₄CO), 8.18 d (1H, H⁸,** *J* **8.3 Hz), 13.92 s (1H, N⁴H). Found, %: C 68.22; H 4.20; N 8.34. C₁₉H₁₄N₂O₃. Calculated, %: C 68.26; H 4.22; N 8.38.**

3-(4-Fluorobenzoyl)furo[**3**,2-*b*]quinoxalin-2(*4H*)one (**IIId**). Yield 89%, mp 258–259°C. IR spectrum, v, cm⁻¹: 3216 (NH), 1775 (C²=O), 1658 (COC₆H₄). ¹H NMR spectrum, δ , ppm: 7.34–7.96 group of signals (7H, H⁵⁻⁷⁺ C₆H₄CO), 8.21 d (1H, H⁸, *J* 8.3 Hz), 14.06 s (1H, N⁴H). Found, %: C 66.20; H 2.91; F 6.14; N 9.04. C₁₇H₉FN₂O₃. Calculated, %: C 66.23; H 2.94; F 6.16; N 9.08.

3-(4-Chlorobenzoyl)furo[**3**,2-*b*]quinoxalin-2(4*H*)one (**IIIe**). Yield 95%, mp 257–259°C. IR spectrum, v, cm⁻¹: 3282 (NH), 1797 (C²=O), 1654 (COC₆H₄). ¹H NMR spectrum, δ , ppm: 7.56–7.89 group of signals (7H, H⁵⁻⁷⁺ C₆H₄CO), 8.21 d (1H, H⁸, *J* 8.3 Hz), 14.12 s (1H, N⁴H). Found, %: C 62.85; H 2.74; Cl 10.89; N 8.61. C₁₇H₉ClN₂O₃. Calculated, %: C 62.88; H 2.79; Cl 10.92; N 8.63.

3-(4-Bromobenzoyl)furo[3,2-b]quinoxalin-2(4H)one (IIIf). Yield 90%, mp 271–272°C. IR spectrum, v, cm⁻¹: 3285 (NH), 1778 (C²=O), 1664 (COC₆H₄). ¹H NMR spectrum, δ , ppm: 7.56–7.88 group of signals (7H, H⁵⁻⁷+ C₆H₄CO), 8.21 d (1H, H⁸, *J* 8.2 Hz), 14.12 s (1H, N⁴H). Found, %: C 55.28; H 2.43; Br 21.60; N 7.55. C₁₇H₉BrN₂O₃. Calculated, %: C 55.31; H 2.46; Br 21.64; N 7.59.

3-(4-Nitrobenzoyl)furo[3,2-b]quinoxalin-2(4H)one (IIIg). Yield 69%, mp 278–279°C. IR spectrum, v, cm⁻¹: 3267 (NH), 1786 (C²=O), 1657 (COC₆H₄). ¹H NMR spectrum, δ , ppm: 7.58–8.37 group of signals (7H, H⁵⁻⁷⁺ C₆H₄CO), 8.23 d (1H, H⁸, *J* 8.3 Hz), 14.30 s (1H, N⁴H). Found, %: C 60.87; H 2.69; N 12.50. C₁₇H₉N₃O₄. Calculated, %: C 60.90; H 2.71; N 12.53.

3-Pivaloylfuro[3,2-*b***]quinoxalin-2(4***H***)-one (IIIh). Yield 61%, mp 239–240°C. IR spectrum, v, cm⁻¹: 3180 (NH), 1781 (C²=O), 1680 (COCMe₃). ¹H NMR spectrum, \delta, ppm: 1.33 s (9H, CMe₃), 7.55 m (3H, H^{5–7}), 8.24 d (1H, H⁸,** *J* **8.4 Hz), 13.73 s (1H, N⁴H). Found, %: C 66.60; H 5.19; N 10.32. C₁₅H₁₄N₂O₄. Calculated, %: C 66.66; H 5.22; N 10.36.**

ACKNOWLEDGMENTS

The study was carried out under the financial support of the Russian Foundation for Basic Research (grant no. 08-03-01032).

REFERENCES

- 1. Dmitriev, M.V., Silaichev, P.S., and Maslivets, A.N. Zh. Org. Khim., 2011, vol. 47, p. 94.
- Aliev, Z.G., Krasnykh, O.P., Maslivets, A.N., Andreichikov, Yu.S., and Atovmyan, L.O., *Izv. Akad. Nauk, Ser. Khim.*, 1993, p. 1633.
- Aliev, Z.G., Krasnykh, O.P., Maslivets, A.N., Andreichikov, Yu.S., and Atovmyan, L.O., *Izv. Akad. Nauk, Ser. Khim.*, 1999, p. 2154.
- Bozdyreva, K.S., Cmirnova, I.V., and Maslivets, A.N., *Zh.* Org. Khim., 2005, vol. 41, p. 1101.
- 5. Maslivets, A.N., Golovnina, O.V, Krasnykh, O.P., and Aliev, Z.G., *Khim. Geterotsikl. Soedin.*, 2000, p. 418.
- Andreichikov, Yu.S., Pitirimova, S.G., Saraeva, R.F., Gein, V.L., Plakhina, G.D., and Voronova, L.A. *Khim. Geterotsikl. Soedin.*, 1978, p. 407.
- Bozdyreva, K.S., Aliev, Z.G., and Maslivets, A.N., *Zh. Org. Khim.*, 2008, vol. 44, p. 612.
- Maslivets, A.N., Cmirnova, L.I., and Andreichikov, Yu.S., *Zh. Org. Khim.*, 1992, vol. 28, p. 2141.