Chemistry of acyl(imidoyl)ketenes
7.* Synthesis and thermolysis of 5-aryl-4-quinoxalinyl-2,3-dihydrofuran-2,3-diones

A. N. Maslivets,[a]★ N. Yu. Lisovenko,[a] O. P. Krasnykh,[a] O. P. Tarasova,[a] Z. G. Aliev,[b] and L. O. Atovmyan[b]

[a]*Perm State University,*
15 ul. Bukireva, 614000 Perm, Russian Federation.
Fax: +7 (342 2) 39 6367. E-mail: koh@psu.ru
[b]*Institute of Problems of Chemical Physics, Russian Academy of Sciences,*
14 Institutskii prosp., 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588. E-mail: aliev@icp.ac.ru

3-Aryl-*Z*-2-aroylmethylidene-1,2-dihydroquinoxalines react with oxalyl chloride to form 3-aryl-2-(2-aryl-4,5-dioxo-4,5-dihydro-3-furyl)quinoxalines, whose thermal decarbonylation generate 5-aryl-2-3(arylquinoxalin-2-yl)-4-aroyl-3-aroyloxy-1*H*-pyrido[1,2-*a*]quinoxalin-1-ones. The crystal and molecular structures of one of them (Ar = Ph) were established by X-ray diffraction analysis.

Key words: 2,3-dihydrofuran-2,3-diones, aroyl(imidoyl)ketene, cycloaddition, crystal structure, molecular structure, X-ray diffraction analysis.

The reaction of primary β-enamino ketones with oxalyl chloride is the most common method for the synthesis of substituted 4-acyl-2,3-dihydropyrrole-2,3-diones.[2] This method was used to synthesize substituted 4-acyl-2,3-dihydropyrrole-2,3-diones from heterocyclic enamino ketones, *viz.*, substituted 1-acylmethylidene-1,2,3,4-tetrahydroisoquinolines,[3] 3-acylmethylidene-3,4-dihydro-2*H*-1,4-benzoxazin-2-ones,[4] 2-acylmethylidene-3,4-dihydro-2*H*-1,3-benzoxazin-4-ones,[5] and 3-acylmethylidene-1,2,3,4-tetrahydro-2-quinoxalones.[6]

This work is devoted to the study of an unusual route of the reaction of enamino ketones with oxalyl chloride, which resulted in the preparation of the first representatives of the class of 5-aryl-4-heteryl-2,3-dihydrofuran-2,3-diones, and to the study of their thermolysis.

Results and Discussion

The reaction of 3-aryl-*Z*-2-aroylmethylidene-1,2-dihydroquinoxalines (**1a—c**) with oxalyl chloride affords 3-aryl-2-(2-aryl-4,5-dioxo-4,5-dihydro-3-furyl)quinoxalines (**3a—c**)** (Scheme 1) instead of the expected 4-aryl-3-aroyl-1,2-dihydropyrrolo[1,2-*a*]quinoxaline-1,2-diones (**2a—c**). The spectroscopic characteristics of furandiones **3a—c** (see Experimental) and substituted 2,3-dihydrofuran-2,3-diones[8—14] are in good agreement.

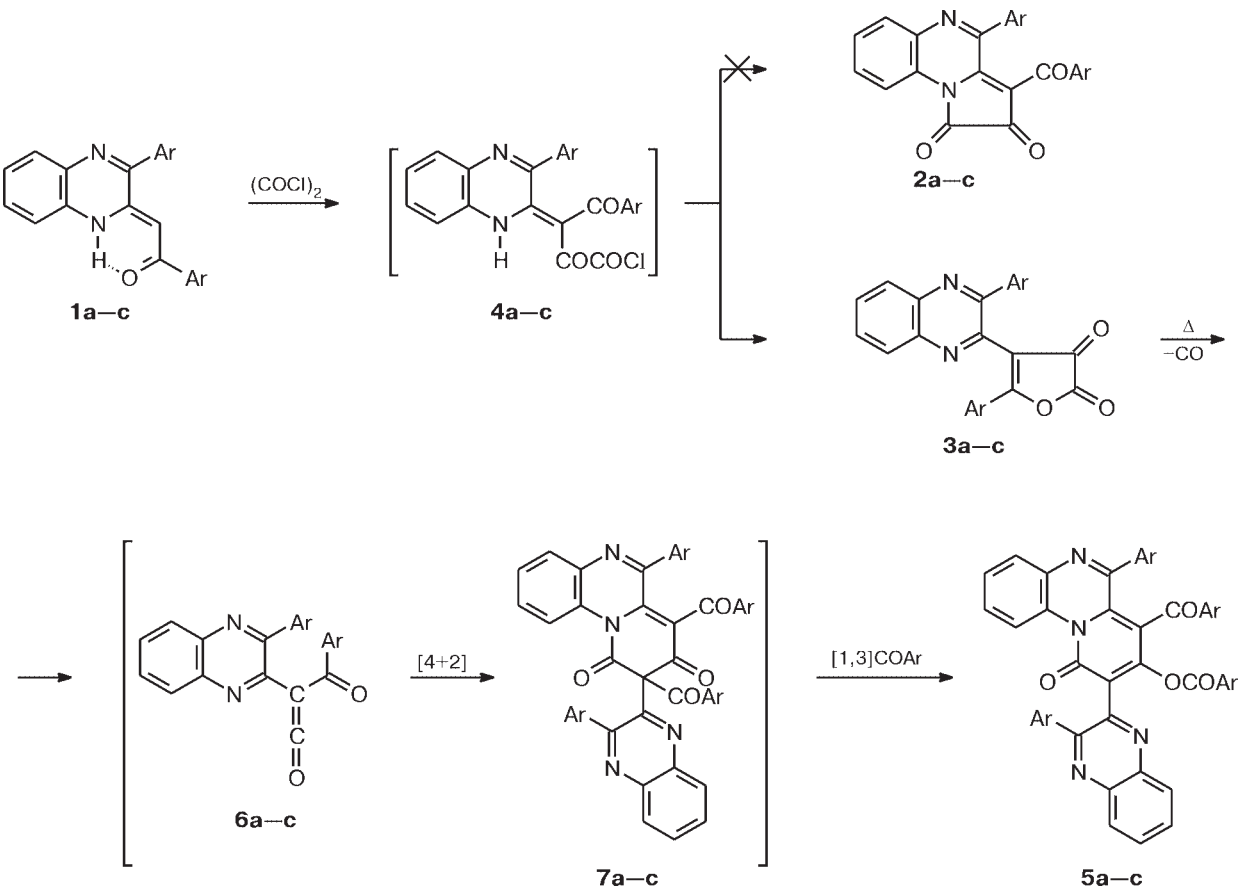
It is most likely that the first stage of the reaction is the acylation of the CH group of the enamino ketone fragment in compounds **1a—c**, which is characteristic of β-enamino ketones, followed by the intramolecular ring closure of acid chlorides **4a—c** to furandiones **3a—c**. The ring closure of acid chlorides **4a—c** to pyrrolediones **2a—c** does not occur, likely, due to steric hindrances from the bulky aryl and aroyl groups. This reaction is the first example of the synthesis of 2,3-dihydrofuran-2,3-diones containing the heterocyclic substituent in position 4.

It is known that the modes of stabilization of acylketenes generated by decarbonylation of 2,3-dihydrofuran-2,3-diones depend on the character of substituents in the furan ring. For example, aroylketenes formed from 5-aryl-,[8] 5-aryl-4-halogen-,[9] 5-aryl-4-methyl-,[10] 4-benzoyl-5-phenyl-,[11] and 4,5-diaryl-2,3-dihydrofuran-2,3-diones[12] are stabilized by intermolecular [4+2]-cycloaddition, and in one ketene molecule the ArCOC=C fragment plays the role of a heterodiene, while in another molecule the C=C bond of ketene plays the role of a dienophile. In the case of cycloadducts from 5-aryl-, 4-benzoyl-5-phenyl-, 4,5-diaryl-2,3-dihydrofuran-2,3-diones, the reaction is usually accompanied by the [1,3]-migration of the proton or aroyl group. The similar [4+2]-cyclodimerization of dipivaloylketene formed from 5-*tert*-butyl-4-pivaloyl-2,3-dihydrofuran-2,3-dione involves the C=O bond of the pivaloyl or ketene fragments.[13] Aroyl(imidoyl)ketenes formed from

* For Part 6, see Ref. 1.
** For preliminary report, see Ref. 7.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 785—788, May, 2002.

Scheme 1



Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 2,5-$Me_2C_6H_3$ (**c**)

4-[α-(arylimino)benzyl]-5-phenyl-2,3-dihydrofuran-2,3-diones undergo intramolecular ring closure due to the acylation of the *ortho*-position of the *N*-aryl ring by the ketene fragment.[14] This type of intramolecular ring closure is impossible for 3-aryl-2-quinoxalinyl(aroyl)ketenes (**5a—c**) generated by the thermolytic decarbonylation of furandiones **3a—c** but other methods of participation in intermolecular cycloaddition are available.

When solutions of furandiones **3a—c** are kept in *p*-xylene at 138—140 °C for 20 min, 4-aroyl-3-aroyloxy-5-aryl-2-(3-aryl-2-quinoxalinyl)-1*H*-pyrido[1,2-*a*]quinoxalin-1-ones (**5a—c**) are formed.* Ketenes **6a—c** formed by the thermal decarbonylation of furandiones **3a—c** are most likely stabilized through [4+2]-cyclodimerization followed by the [1,3]-migration of the aroyl group in cycloadducts **7a—c**.

The structure of compound **5a** was established by X-ray diffraction analysis. The general view of molecule **5a** is shown in Fig. 1. The bond lengths N(6)—C(14) 1.301(3), N(7)—C(41) 1.321(2), and N(8)—C(42) 1.317(2) Å correspond to the double C=C bond lengths. The distances C(10)—C(11) 1.362(3) and C(12)—C(13) 1.375(3) Å are much longer than the standard value for the C=C double bond (1.34 Å), which can indicate considerable delocalization of the double bonds in the pyridine ring of the tricyclic fragment of the molecule. At the same time, this ring has an envelope conformation: the inflection along the N(5)...C(10) line is 19.5°, and the deviation of the C(9) atom from the plane of other five atoms is 0.26 Å. Taking into account that the ordinary C(11)—C(12) bond of 1.410 Å is also strongly shortened and the N(5)—C(13) bond of 1.402 Å corresponds to the ordinary bond, we can assume that delocalization takes place in the C(10)...C(11)...C(12)...C(13) chain. Other bond lengths in the molecule do not differ from standard values. The pyrazine ring fused with pyridine has a boat conformation: the inflections along the N(5)...C(14) and N(6)...C(16) lines are 18.4° and 10.3°, and the deviations of the C(13) and C(15) atoms are 0.24 and 0.12 Å, respectively.

* For preliminary report, see Ref. 12.

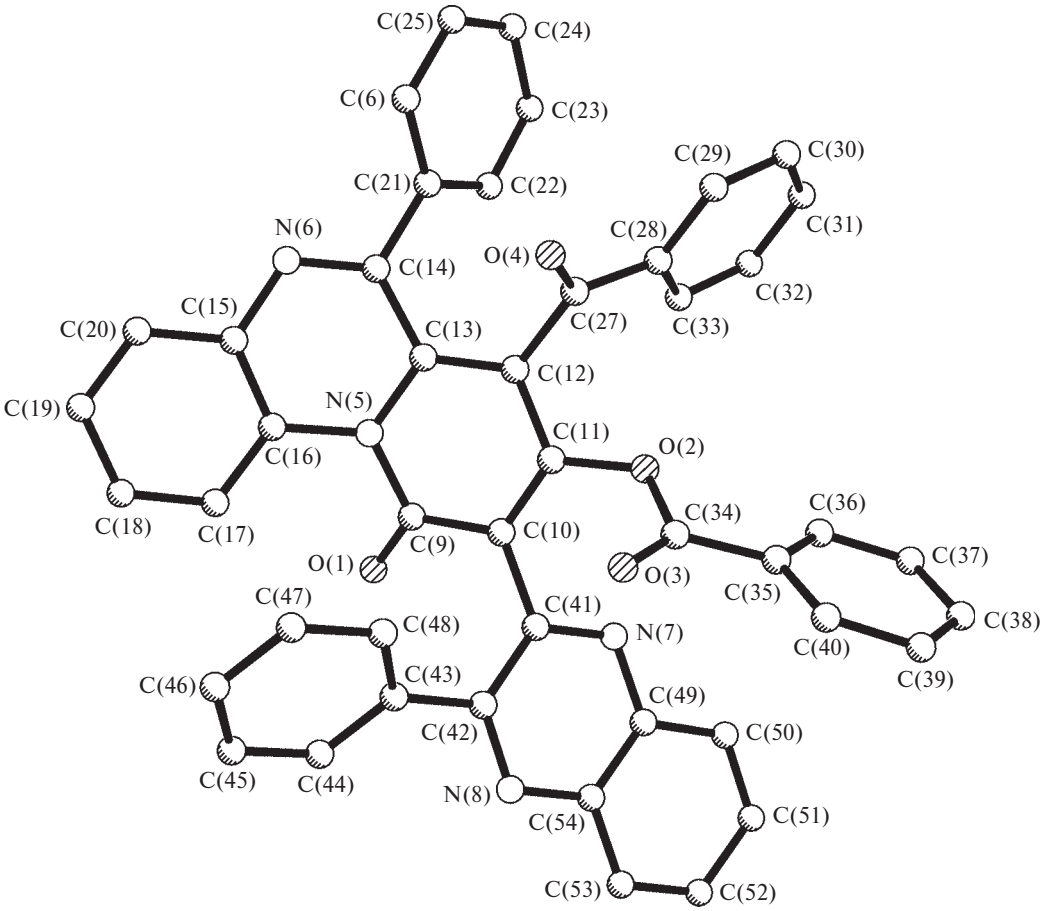


Fig. 1. Molecular structure of compound **5a**.

Experimental

IR spectra of the compounds synthesized were recorded on a UR-20 instrument in Nujol. ^{1}H NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz) in $CDCl_3$ or DMSO-d_6 using Me_4Si as the internal standard. Mass spectra were obtained on an MKh-1310 instrument (70 eV).

Compounds **1a—c** were synthesized by the reaction of diaroylacetylenes with *o*-phenylenediamine according to a previously described method.[15]

2-(4,5-Dioxo-2-phenyl-4,5-dihydro-3-furyl)-3-phenylquinoxaline (3a). A solution of compound **1a** (3.00 g, 10 mmol) and oxalyl chloride (0.85 mL, 10 mmol) in dry $CHCl_3$ (40 mL) was refluxed for ~1.5 h and concentrated to half its volume. Dry hexane (50 mL) was added, the solvent was distilled off to a volume of 20 mL, the resulting solution was cooled, the precipitate that formed was filtered off, and quinoxaline **3a** was obtained in 87% yield (3.29 g), m.p. 142—143 °C (with decomp., from a 1 : 3 chloroform—hexane mixture). Found (%): C, 76.03; H, 3.74; N, 7.42. $C_{24}H_{14}N_2O_3$. Calculated (%): C, 76.18; H, 3.73; N, 7.40. IR, ν/cm^{-1}: 1825 (C(2)=O_{furan}); 1730 (C(3)=O_{furan}). ^{1}H NMR, δ: 7.03 (d, 1 H, *o*-CH, J = 7.0 Hz); 7.15—8.25 (m, 13 H). MS, m/z (I_{rel} (%)): M^+ 378 (10), 350 (35), 321 (100), 305 (10), 293 (30), 105 (25), 77 (20).

2-[(4,5-Dioxo-2-(4-tolyl)-4,5-dihydro-3-furyl)]-3-(4-tolyl)quinoxaline (3b) was synthesized similarly in 90% yield, m.p. 170—171 °C (with decomp., from a 1 : 3 chloroform—hexane mixture). Found (%): C, 76.68; H, 4.45; N, 7.02. $C_{26}H_{18}N_2O_3$. Calculation (%): C, 76.83; H, 4.46; N, 6.89. IR, ν/cm^{-1}: 1830 (C(2)=O_{furan}); 1720 (C(3)=O_{furan}). ^{1}H NMR, δ: 2.30, 2.36 (both s, 3 H, Me); 6.70—8.10 (m, 12 H).

2-[2-(2,5-Dimethylphenyl)-4,5-dioxo-4,5-dihydro-3-furyl]-3-(2,5-dimethylphenyl)quinoxaline (3c) was prepared similarly in 90% yield, m.p. 132—133 °C (with decomp., from a 1 : 3 chloroform—hexane mixture). Found (%): C, 77.56; H, 5.10; N, 6.47. $C_{28}H_{22}N_2O_3$. Calculated (%): C, 77.40; H, 5.10; N, 6.45. IR, ν/cm^{-1}: 1820 (C(2)=O_{furan}); 1720 (C(3)=O_{furan}).

4-Benzoyl-3-benzoyloxy-5-phenyl-2-(3-phenylquinoxalin-2-yl)-1*H*-pyrido[1,2-*a*]quinoxalin-1-one (5a). A solution of furandione **3a** (0.38 g, 1 mmol) in anhydrous *p*-xylene (5 mL) was kept for 20 min at 138—140 °C, the solvent was distilled off to 3 mL, and the remaining solution was cooled. The precipitate that formed was filtered off, and compound **5a** was obtained in 85% yield (0.30 g), m.p. 270—271 °C (from MeCN). Found (%): C, 78.83; H, 4.00; N, 7.99. $C_{46}H_{28}N_4O_4$. Calculated (%): C, 78.84; H, 4.03; N, 8.00. IR, ν/cm^{-1}: 1745 (COO); 1662 (CO). ^{1}H NMR, δ: 7.00—7.94 (m, 27 H); 8.12 (d, 1 H, C(10)H, J = 8.4 Hz).

5-(4-Tolyl)-2-[3-(4-tolyl)quinoxalin-2-yl)-4-(4-toluoyl)-3-(4-toluoyloxy)-1*H*-pyrido[1,2-*a*]quinoxalin-1-one (5b) was obtained similarly in 80% yield, m.p. 310—311 °C (from MeCN). Found (%): C, 79.34; H, 4.79; N, 7.41. $C_{50}H_{36}N_4O_4$. Calcu-

lated (%): C, 79.35; H, 4.79; N, 7.40. IR, ν/cm^{-1}: 1750 (COO); 1665 (CO). ^{1}H NMR, δ: 2.15, 2.23, 2.33, 2.39 (all s, 3 H, Me); 7.04—7.86 (m, 23 H); 8.10 (d, 1 H, C(10)H, J = 8.4 Hz).

4-(2,5-Dimethylbenzoyl)-3-(2,5-dimethylbenzoyloxy)-5-(2,5-dimethylphenyl)-2-[3-(2,5-dimethylphenyl)quinoxalin-2-yl]-1*H*-pyrido[1,2-*a*]quinoxalin-1-one (5c) was obtained similarly in 70% yield, m.p. 230—231 °C (from MeCN). Found (%): C, 79.55; H, 5.44; N, 6.90. $C_{54}H_{44}N_4O_4$. Calculated (%): C, 79.78; H, 5.46; N, 6.89. IR, ν/cm^{-1}: 1750 (COO); 1680 (CO). ^{1}H NMR, δ: 1.68, 1.69, 1.95, 2.00, 2.02, 2.07, 2.26, 2.35 (all s, 3 H, Me); 6.88—7.89 (m, 19 H); 8.10 (d, 1 H, C(10)H, J = 8.1 Hz).

X-ray study of compound 5a. For the X-ray study, a sample of compound **5a** was additionally recrystallized from *p*-xylene to give well faced yellow crystals in the form of tetrahedral prisms. The crystals $C_{46}H_{28}N_4O_4 \cdot 0.5(p\text{-}MeC_6H_4Me)$ are monoclinic, space group $P2_1/n$, a = 20.812(4), b = 16.202(3), c = 11.857 Å, β = 98.03(3)°, V = 3958.9(12) Å^3, M = 753.80, d_{calc} = 1.265 g cm^{-3}, Z = 4. The unit cell parameters and set of experimental reflections were measured on a KM-4 automated four-circle diffractometer (KUMA DIFFRACTION) with χ-geometry using the ω—2θ scan mode and monochromated Cu-Kα radiation in the angle interval 3.47° < 2θ < 80.24°. On the whole, 7723 independent reflections were measured, 3099 of them had $I \geq 2\sigma(I)$. No correction for absorption was applied (μ = 0.649 mm^{-1}). The structure was solved by the direct statistical method followed by a series of calculations of the electron density maps.

Hydrogen atoms were specified geometrically after the R factor achieved 0.065 by the least-squares refinement in the anisotropic approximation. The final refinement gave R_1 = 0.039. The *GOOF* parameter was 0.902. All calculations were performed on a PC/AT using the SHELX-97 program complex.[16] The atomic coordinates were deposited with the Cambridge Structure Data Bank.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 01-03-32641 and 02-03-96411).

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Received September 3, 2001;
in revised form December 28, 2001