# Chemistry of acyl(imidoyl)ketenes
## 6.* Synthesis and the molecular structure of ethyl 2-oxo-2,5-dihydrofuro[2,3-*b*]quinoxaline-3-carboxylate

*Z. G. Aliev,[a]★ A. N. Maslivets,[b] O. V. Golovnina,[b] O. P. Krasnykh,[b] and L. O. Atovmyan[a]*

*[a]Institute of Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588. E-mail: aliev@icp.ac.ru
[b]Perm State University,
15 ul. Bukireva, 614600 Perm, Russian Federation.
Fax: +7 (342 2) 33 3983*

Thermal decarbonylation of ethyl 1,2,4-trioxo-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate afforded ethyl 2-oxo-2,5-dihydrofuro[2,3-*b*]quinoxaline-3-carboxylate. The structure of the resulting compound was established by X-ray diffraction analysis.

**Key words:** pyrroledione, intramolecular cyclization, X-ray diffraction analysis.

Acyl(imidoyl)ketenes can be involved into [4+2]-cycloaddition as both dienophiles and dienes. However, stabilization through intramolecular cyclization is more favorable for most of these compounds. Thus cyclization of aroyl(*N*-benzylimidoyl)ketenes affords substituted 2-furanones and furoisoquinolines.[2] Acyl(*N*-arylimidoyl)ketenes undergo cyclization to form substituted 3-acyl-4-quinolones due to intramolecular acylation of the *ortho* position of the *N*-aryl group with the ketene fragment.[3] Thermal decarbonylation of 3-aroyl-2,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]benzooxazine-1,2,4-triones is a convenient procedure for generation of acyl(*N*-arylimidoyl)ketenes[1,4] in which the *N*-aryl group is fixed (as a result of its involvement in the fused system) in such a manner that the above-described cyclization giving rise to 4-quinolones cannot occur, and stabilization is achieved through intermolecular [4+2]-cyclodimerization.[1,4]

As part of our continuing studies, in the present work we investigated thermolysis of ethyl 1,2,4-trioxo-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinoxaline-3-carboxylate (**1**).[5] The reaction would be expected to afford (3-oxo-3,4-dihydroquinoxalin-2-yl)ethoxycarbonylketene (**2**), which cannot undergo intramolecular cyclization to give substituted 4-quinolones. The structural characteristics of ketene **2** do not exclude its stabilization through both intramolecular cyclization (but different from that described above) and the involvement in intermolecular [4+2]-cyclodimerization.

### Results and Discussion

Heating of a solution of compound **1** in Dowtherm A (an eutectic mixture of biphenyl and diphenyl ether) at 166—168 °C for 15—20 min afforded a high-melting crystalline compound, which was identified as ethyl 2-oxo-2,5-dihydrofuro[2,3-*b*]quinoxaline-3-carboxylate (**3**) based on the X-ray diffraction data (Scheme 1).

Apparently, ketene **2** formed upon thermal decarbonylation of pyrroloquinoxalinetrione **1** was stabilized due to conversion of the amide into the hydroxyimine form followed by intramolecular acylation of the OH group with the ketene fragment and 1,3-hydrogen shift to the N atom.

Crystals of compound **3** studied by X-ray diffraction analysis were additionally recrystallized from aqueous ethanol. According to the data from elemental analysis and X-ray diffraction study, compound **3** exists in the crystal as a monohydrate. The overall view of the molecule is shown in Fig. 1. The proton is localized at the N(1) atom at position 4 giving rise to an intramolecular hydrogen bond of the H-chelate type between the NH group and the ester carbonyl group. The N(1)...O(3)

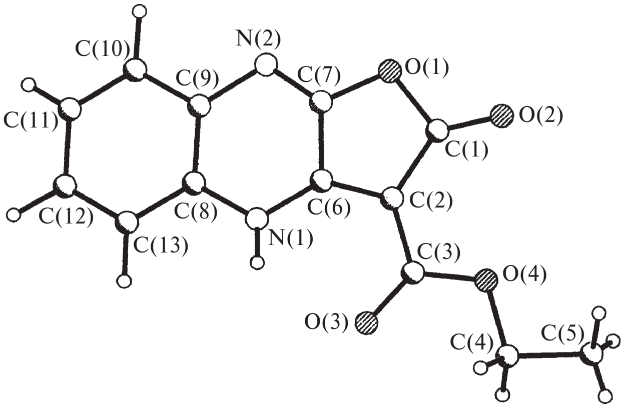

**Fig. 1.** Structure of molecule **3**.

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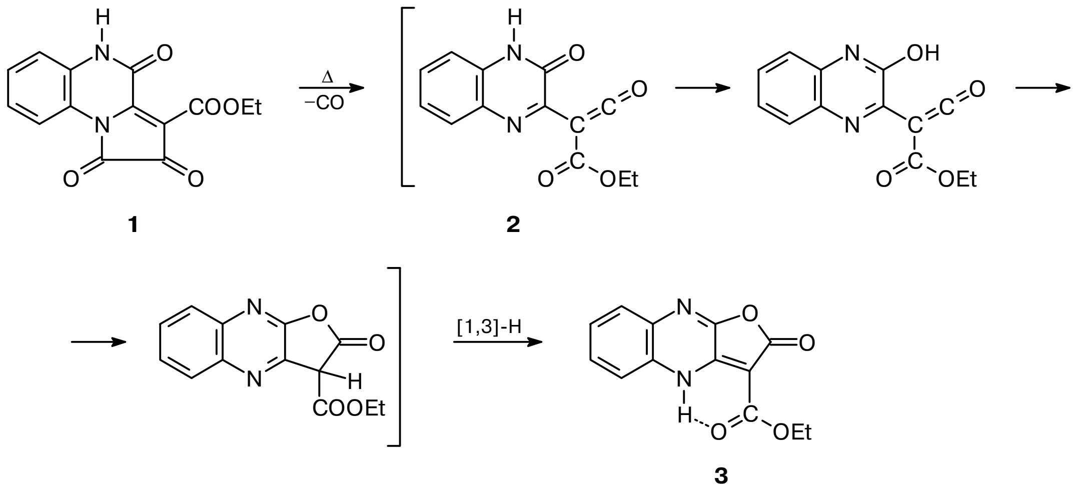
**Scheme 1**



and H(1)...O(3) distances are 2.93 and 2.32 Å, respectively, and the angle at the H(1) atom is 124°. The molecule as a whole, including the ester group, is planar. The average deviation of the atoms from the plane is 0.05 Å. The exocyclic C(2)—C(1)—O(2) and C(1)—C(2)—C(3) bond angles are increased to 134.3° and 129.5°, respectively, due to steric interactions between the carbonyl and ester groups. The N(2)—C(7) bond in the quinoxaline fragment (1.268 Å) has a pronounced double character. The C(2)=C(6) double bond is somewhat elongated (1.363 Å) and the N(1)—C(6) single bond is shortened (1.339 Å) due apparently to the n—π interaction between the lone electron pair of the N atom and the antibonding orbital of the C=C bond. The water molecules of crystallization are linked to molecules **3** through the N(1)—H(1)...Ow (2.91 Å) and N(2)...Hw1—Ow (2.98 Å) hydrogen bonds to form infinite chains along the screw axis.

The observed systematic absences indicated two possible space groups, *viz.*, $P2_1$ and $P2_1/m$. The model of the structure was established within the space group $P2_1$ by the direct statistical method. However, the refinement by the least-squares method reduced the $R$ factor only to 0.18. Analysis of the crystal structure demonstrated that two crystallographically independent molecules **3** in this space group are related by the glide symmetry plane *a* and the true space group of the crystal is $P2_1/a$. The refinement of the structure within the latter group, in which the reflections $h0l$ breaking this symmetry were ignored, converged to $R$ = 0.16. It should be noted that the bond lengths and bond angles in both cases have reasonable values. Based on the analysis of the experimental intensity data, it was suggested that the crystal is twinned with a twin matrix 1 0 0, 0 −1 0, 0 0 −1. The unit cell parameters are such that this twinning leads to overlapping of the reflections $hnl$ with even $l$ from two single crystals giving rise to the reflections $h0l$ with odd $h$ and even $l$, which are "false" in the space group $P2_1/a$. The inclusion and refinement of the twin fraction using the TWIN operation (the fraction was 0.12) led to $R$ = 0.115.

## Experimental

The IR spectrum was recorded on a UR-20 spectrometer in Nujol mulls. The $^1$H NMR spectrum was measured on a Bruker WP-80-SY instrument (80 MHz) in DMSO-$d_6$ with HMDS as the internal standard. The homogeneity of compound **3** was confirmed by TLC on Silufol plates using the 2 : 1 benzene—ethyl acetate system.

**Ethyl 2-oxo-2,5-dihydrofuro[2,3-*b*]quinoxaline-3-carboxylate (3).** A solution of compound **1** (573 mg, 0.002 mol) in Dowtherm A (1.5 mL)[6] was kept at 166—168 °C for 20 min and cooled. The precipitate that formed was filtered off. Compound **3** was obtained in a yield of 60 mg (11%), m.p. 212—214 °C (decomp., from EtOH). Found (%): C, 56.56; H, 4.40; N, 10.19. $C_{13}H_{10}N_2O_4 \cdot H_2O$. Calculated (%): C, 56.52; H, 4.38; N, 10.14. IR, ν/cm$^{-1}$: 3372 (NH); 1786 (C(2)=O); 1660 (COOEt). $^1$H NMR, δ: 1.26 (t, 3 H, $CH_3$, $J$ = 7.0 Hz); 4.27 (q, 2 H, $CH_2$, $J$ = 7.0 Hz); 7.70 (m, 4 H, $C_6H_4$); 13.26 (br.s, 1 H, NH).

**X-ray diffraction study of compound 3.** Well-faceted crystals of a monohydrate of compound **3** were obtained as pale-yellow elongated prisms by slow crystallization from aqueous EtOH. The crystals belong to the monoclinic system, $C_{13}H_{10}N_2O_4 \cdot H_2O$, $M$ = 276.25, $a$ = 11.094(2) Å, $b$ = 16.549(3) Å, $c$ = 7.073(1) Å, β = 108.43(3)°, $V$ = 1232.0(4) Å$^3$, $d_{\text{calc}}$ = 1.489 g cm$^{-3}$, $Z$ = 4, space group $P2_1/a$. The X-ray diffraction data were collected on an automated four-circle KM-4 diffractometer (KUMA DIFFRACTION) using monochromated Cu-Kα radiation (graphite monochromator) in the angle range of 2.7° < θ < 80.3°. A total of 2469 independent nonequivalent reflections were measured.

The hydrogen atoms of molecule **3** were placed in geometrically calculated positions. The positions of the H atoms of the water molecule of crystallization were revealed from the difference electron density synthesis. The final anisotropic refinement by the least-squares method converged to $R$ = 0.088

using 1500 reflections with $I > 2\sigma(I)$. Only the positional parameters of the H atoms were refined. Absorption was ignored ($\mu = 0.988$ mm$^{-1}$). All calculations were carried out on a PC computer using the SHELX86 [7] and SHELXL97 [8] program packages.

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