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NEW PATHWAY FOR STABILIZATION OF ACYL(IMIDOYL)KETENES

A. N. Maslivets, O. V. Golovnina, O. P. Krasnykh, and Z. G. Aliev

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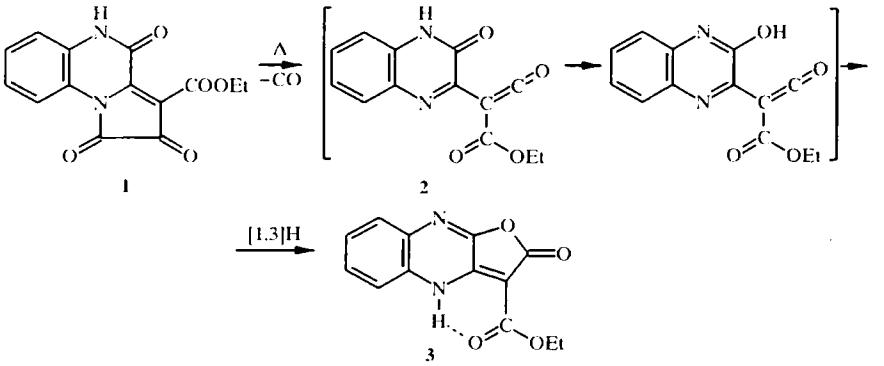
Acyl(imidoyl)ketenes can be stabilized by intermolecular [4+2]-cycloaddition reactions or by intramolecular transformations. The intramolecular cyclization of aroyl(N-benzylimidoyl)ketenes leads to substituted 2-furanones and furoisoquinolinones [1]. N-Arylimidoyl(acyl)ketenes undergo intramolecular cyclization to give substituted 3-acyl-4-quinolones through acylation of the *ortho* position of the aromatic ring at the imidoyl nitrogen atom by the ketene fragment [2]. Cyclization in aroyl(2-oxo-2H-1,4-benzoxazin-3-yl)ketenes [3], which are N-arylimidoyl(acyl)ketenes with an aromatic substituent at the imidoyl nitrogen atom inaccessible for the ketene fragment, is impossible, leading to the stabilization of these compounds by intermolecular [4+2]-cycloaddition (dimerization) to give substituted pyrido[2,1-*c*][1,4]benzoxazinediones [3].

We have studied the thermolysis of 3-ethoxycarbonyl-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinoxaline-1,2,4-trione (**1**), in which might have expected formation of 3-oxo-3,4-dehydroquinoxalin-2-yl-(ethoxycarbonyl)ketene (**2**), an N-arylimidoyl(acyl)ketene incapable of intramolecular cyclization to give substituted 3-acyl-4-quinolones. The structure of ketene **2** does not exclude stabilization through a different type of intramolecular cyclization or participation in [4+2]-cyclodimerization.

Heating of compound **1** at 166-168°C for 20 min led to 3-ethoxycarbonyl-2,4-dihydrofuro[2,3-*b*]-quinoxalin-2-one (**3**) identified by X-ray diffraction analysis.



Ketene **2**, which is likely formed upon the thermal decarbonylation of **1**, is stabilized by conversion of the quinoxalone fragment from the amide to hydroxyimino form with subsequent intramolecular acylation of the hydroxyimino OH group by the ketene fragment.

3-Ethoxycarbonyl-2,4-dihydrofuro[2,3-*b*]quinoxalin-2-one (3). A solution of compound **1** (0.57 g, 2.0 mmol) in Dowtherm A (1.5 ml) was maintained at 166-168°C for 20 min and cooled. The precipitate was filtered off to give 0.060 g (11%) of compound **3**; mp 212-214 (dec., from ethanol). IR spectrum: 3372 ($N_{(4)}$–H),

Perm State University, 614000 Perm, Russia; e-mail: info@psu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 418-419, March, 2000. Original article submitted December 24, 1999.

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1786 ($C_{(2)}$=O), 1660 cm^{-1} ($CO_2C_2H_5$). ^1H NMR spectrum (DMSO-d_6): 1.26 (3H, t, J = 7.0 Hz, CH_3); 4.27 (2H, q, J = 7.0 Hz, CH_2); 7.70 (4H, m, C_6H_4); 13.26 ppm (1H, s, $N_{(4)}$–H). Mass spectrum, m/z: 258 [M^+]. Found, %: C 60.44; H 3.88; N 10.82. $C_{13}H_{10}N_2O_4$. Calculated, %: C 60.47; H 3.90; N 10.85.

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