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A NEW DIRECTION IN THE REACTION OF AN ENAMINO KETONE WITH OXALYL CHLORIDE

A. N. Maslivets, N. Yu. Lisovenko, O. V. Golovnina, E. S. Vostrov, and O. P. Tarasova

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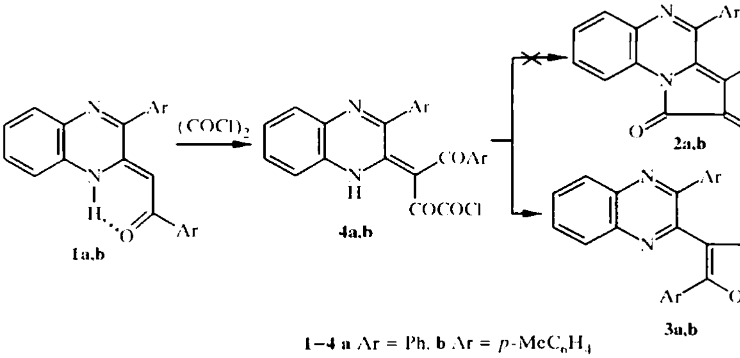
The reaction of primary β-enamino ketones with oxalyl chloride is the most widely used method for the synthesis of substituted 4-acyl-2,3-dihydro-2,3-pyrrolediones [1]. From the heterocyclic enamino ketones – substituted 1-acylmethylene-1,2,3,4-tetrahydroisoquinolines [2], 3-acylmethylene-3,4-dihydro-2H-1,4-benzoxazin-2-ones [3], 2-acylmethylene-3,4-dihydro-2H-1,3-benzoxazin-4-ones [4], 3-acylmethylene-1,2,3,4-tetrahydro-2-quinoxalones [5] – the respective 4-acyl-2,3-dihydro-3,2-pyrrolediones annellated with the azaheterocycles at side [*a*] have been obtained with good yields by this method; there is a single report on isolation as a minor side product [5].

In the reaction of 3-aryl-Z-2-phenacylidene-1,2-dihydroquinoxalines **1a,b** with oxalyl chloride 3-aryl-2-(2-aryl-4,5-dioxo-4,5-dihydro-3-furyl)quinoxalines **3a,b** are formed instead of the expected 4-aryl-3-aroyl-1,2-dihydropyrrolo[1,2-*a*]quinoxaline-1,2-diones **2a,b**.



At the first stage of the reaction the β-CH group of the enamino ketone fragment of compounds **1a,b** is probably acylated by the oxalyl chloride, which is typical of β-enamino ketones. This is followed by the conversion of the acid chlorides **4a,b** from the enamino ketone form to the hydroxyenimine form and intramolecular cyclization to the furandiones **3a,b**. Cyclization of the acid chlorides **4a,b** to the pyrrolediones **2a,b** does not occur as a result, probably, of steric hindrances created by the bulky aryl and aroyl groups. The reaction represents a new direction in the reaction of an enamino ketone with oxalyl chloride and also the first method for the production of substituted 2,3-dihydro-2,3-furandiones containing a heterocyclic fragment at position 4 of the furandione ring.

2,3-Di(4,5-dioxo-2-phenyl-4,5-dihydro-3-furyl)quinoxaline is formed from 2,3-di(phenacylidene)-1,2,3,4-tetrahydroquinoxaline by an analogous scheme. At the same time, however, 3-benzoyl-4-phenyl-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinazoline-1,2,5-trione is formed from 2-phenacylidene-3-phenyl-1,2,3,4-tetrahydroquinazolin-4-one.

Perm State University, Perm 614000, Russia; e-mail: info@psu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 556-558, April, 2000. Original article submitted February 25, 2000.

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 absolute chloroform (40 ml) was boiled for 100 min. The solvent was distilled to a volume of 20 ml, and absolute hexane (50 ml) was added. The mixture was cooled, and the precipitate was filtered off. Yield 3.02 g (80%); mp 142-143°C (dec., from chloroform–hexane, 1:3). IR spectrum, cm^{-1}: 1825 ($C^2{=}O_{furan}$), 1730 ($C^3{=}O_{furan}$). ^1H NMR spectrum (250 MHz, DMSO-d_6), δ, ppm: 7.03 (1H, d, *J* = 7.0 Hz, *o*-CH); 7.15-8.25 (13H, m, C_6H_5 + $2C_6H_4$). Mass spectrum, *m/z* (*I*, %): M^+ 378 (10), 350 (35), 321 (100), 305 (10), 293 (30), 105 (25), 77 (20). 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.

2-(4,5-Dioxo-2-*p*-tolyl-4,5-dihydro-3-furyl)-3-*p*-tolylquinoxaline (3b). Yield 80%; mp 170-171°C (dec., from chloroform–hexane, 1:3). IR spectrum, cm^{-1}: 1830 ($C^2{=}O_{furan}$), 1720 ($C^3{=}O_{furan}$). ^1H NMR spectrum (250 MHz, DMSO-d_6), δ, ppm: 2.30 (3H, s, CH_3); 2.36 (3H, s, CH_3); 6.70-8.10 (12H, m, $3C_6H_4$). Found, %: C 76.68; H 4.45; N 7.02. $C_{26}H_{18}N_2O_3$. Calculated, %: C 76.83; H 4.46; N 6.89.

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