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UNUSUAL REACTION OF A HETEROCYCLIC ENAMINE WITH OXALYL CHLORIDE

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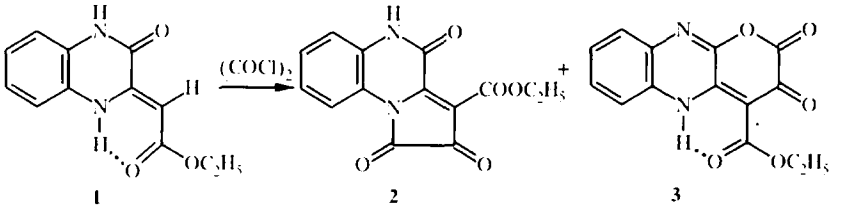
The reaction of primary enamines with oxalyl chloride is the most common method for synthesis of substituted 2,3-dihydro-2,3-pyrrolediones [1]. The corresponding substituted 2,3-dihydro-2,3-pyrrolediones, annelated with the azaheterocycles by side [*a*], have been obtained by this method in practically quantitative yield from heterocyclic enamines such as substituted 1-methylene-1,2,3,4-tetrahydroisoquinolines [2], 3-methylene-3,4-dihydro-2H-1,4-benzoxazin-2-ones [3], and 2-methylene-3,4-dihydro-2H-1,3-benzoxazin-4-ones [4]. The isolation and identification of other products was not reported.

Reaction of (*Z*)-3-ethoxycarbonylmethylene-1,2,3,4-tetrahydro-2-quinoxalone (**1**) with oxalyl chloride formed the expected 3-ethoxycarbonyl-1,2,4,5-tetrahydro-pyrrolo[1,2-*a*]quinoxaline-1,2,4-trione (**2**) and in addition the unexpected 4-ethoxycarbonyl-3,5-dihydro-2H-pyrano[2,3-*b*]quinoxaline-2,3-dione (**3**) was formed as a minor product. Compound **3** was identified by X-ray structural analysis.



1 **2** **3**

Probably a small quantity (not identifiable from ^{1}H NMR spectral data) of the tautomeric hydroxyimine form of **1**, *viz.* 2-ethoxycarbonylmethylene-3-hydroxy-1,2-dihydroquinoxaline, is present in the solution of the initial quinoxalone **1**. This affords the possibility for acylation of the vinyl CH group and the hydroxy imine OH group. An alternative route of forming compound **3** is amide–hydroxy imine isomerization in the course of the reaction. Analogs of quinoxaline **1**, *viz.* (*Z*)-3-phenacylidene-1,2,3,4-tetrahydro-2-quinoxalones, under analogous conditions readily form 3-aroyl-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinoxaline-1,2,4-triones [1], but the possibility of the alternative acylation described above does not occur. The given reaction is a new method for construction of the poorly available condensed pyrano[2,3-*b*]quinoxaline system.

EXPERIMENTAL

3-Ethoxycarbonyl-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinoxaline-1,2,4-trione (2) and 4-Ethoxycarbonyl-3,5-dihydro-2H-pyrano[2,3-*b*]quinoxaline-2,3-dione (3). A solution of oxalyl chloride (1.37 ml, 16.1 mmol) in absolute chloroform (2 ml) was poured into a solution of quinoxalone **1** (3.60 g, 15.5 mmol) in absolute chloroform

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(50 ml). The mixture was boiled for 55 min, cooled, and the precipitated solid compound **3** was filtered off. Yield 0.67 g (15%); mp 194-196°C (MeCN). IR spectrum: 3060 (N–H), 1795 ($C_{(2)}$=O), 1661 cm^{-1} ($C_{(4)}$=O, $COOC_2H_5$). ^1H NMR spectrum (MeCN-d_3): 1.32 (3H, t, J = 7.0 Hz, CH_3); 4.37 (2H, q, J = 7.0 Hz, CH_2O); 7.72 (4H, m, C_6H_4); 13.90 ppm (1H, s, NH). Mass spectrum, *m/z*: 286 $[M]^+$.

The solvent (40 ml) was distilled from the mother liquor, and the precipitated solid compound **2** was filtered off. Yield 2.70 g (60%); mp 179-181°C (decomp., from MeCN). IR spectrum: 3122 (N–H), 178 ($C_{(1)}$=O), 1740 (COO), 1720 ($C_{(2)}$=O), 1672 cm^{-1} ($C_{(4)}$=O). ^1H NMR spectrum (MeCN-d_3): 1.34 (3H, t, J = 7.0 Hz, CH_3); 4.37 (2H, q, J = 7.0 Hz, CH_2O); 7.43 (4H, m, C_6H_4); 10.60 ppm (1H, s, NH).

The data of elemental analysis corresponded to the calculated values.

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