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UNUSUAL SYNTHESIS OF 2-(2-ARYL-2-OXO-ETHYLIDENE)-3-OXO-1,2,3,4-TETRAHYDRO-QUINOXALIN-1-YL(N-CYANO-O-PHENYL)-CARBOXIMIDATES

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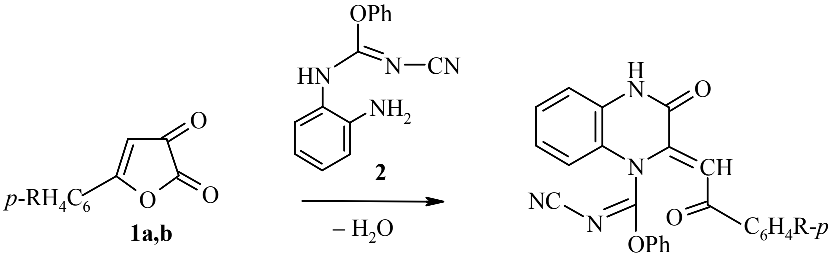
Keywords: N-(2-aminophenyl)-N'-cyano-O-phenylisourea, 5-aryl-2,3-dihydrofuran-2,3-diones, 2-(2-aryl-2-oxoethylidene)-3-oxo-1,2,3,4-tetrahydroquinoxalin-1-yl(N-cyano-O-phenyl)carboximidates, recyclization.

We have previously reported that heating 5-aryl-2,3-dihydrofuran-2,3-diones (**1**) with N-cyano-N'-phenyl-S-methylisothiourea in anhydrous toluene gave 6-aryl-2-[(methylthio)(phenylamino)methylene]amino-4H-1,3-oxazin-4-ones [1]. When this reaction was carried out in the case of the N-(2-aminophenyl)-N'-cyano-O-phenylisourea (**2**) the 2-(2-aryl-2-oxoethylidene)-3-oxo-1,2,3,4-tetrahydroquinoxalin-1-yl(N-cyano-O-phenyl)-carboximidates **3** were unexpectedly separated from the reaction mixture.



1, 3 a R = H, **b** R = Me

Evidently in the first stage of the reaction opening of the furan ring at the O–C(1) bond by the NH_2 group of the isourea **2** occurs with intermediate formation of the N-[[(2-cyanoimino)(phenoxy)-methyl]amino]phenyl-2,4-dioxo-4-arylbutanamide (**4a**) existing in solution in the tautomeric form **4b** [2]. This is confirmed by the initial observation in the ^{1}H NMR spectrum of the reaction mass at room temperature of a methine group proton signal at 6.90, a multiplet for 14 benzene rings protons in the range 7.05-8.10, and signals for the corresponding amino groups protons at 10.48 and 12.28 ppm. In the IR spectra the absorption for the stretching band of the cyano group in the isourea fragment is preserved at 2200 and a characteristic strong absorption band at 1675 cm^{-1} is observed corresponding to the amide carbonyl.

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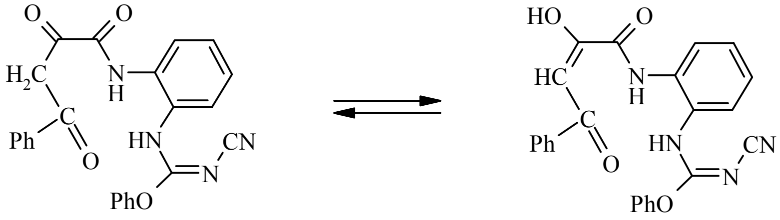
Subsequent raising of the temperature to 50-60ºC leads to a spontaneous intramolecular cyclization involving the enolic hydroxyl and the secondary amino group in the intermediate **4** to form the final compounds **3**.



4a **4b**

IR spectra were recorded on a UR-20 instrument in vaseline oil. ^{1}H NMR spectra were taken on a Mercury Plus 300 instrument (300 MHz) using $CDCl_3$ with TMS as internal standard.

3-Oxo-2-(2-oxo-2-phenylethylidene)-1,2,3,4-tetrahydroquinoxalin-1-yl(N-cyano-O-phenyl)carboximidate (3a). A solution of the N-(2-aminophenyl)-N'-cyano-O-phenylisourea (**2**) (1.26 g, 5 mmol) and 5-phenyl-2,3-dihydrofuran-2,3-dione (**1a**) (0.9 g, 5 mmol) in dioxane (30 ml) was stirred for 40 min at 50-60ºC to give a yellow precipitate of compound **3a** with mp 180-181ºC (2-propanol) in 63% yield. IR spectrum, ν, cm^{-1}: 1675 (C=O), 1665 (C=O), 2200 (C≡N), 3386 (NH). ^{1}H NMR spectrum, δ, ppm: 7.05-8.10 (14H, m, C_6H_5); 6.90 (1H, s, =CH–); 12.28 (1H, s, NH). The spectroscopic data was closely similar to that for previously obtained quinoxalines [3]. Found, %: C 70.9; H 4.0; N 13.6. $C_{24}H_{16}N_4O_3$. Calculated, %: C 70.6; H 3.9; N 13.7.

3-Oxo-2-(2-oxo-2-*p*-tolylethylidene)-1,2,3,4-tetrahydroquinoxalin-1-yl(N-cyano-O-phenyl)carboximidate (3b) was prepared similarly from compounds **1b** and **2**. Yield 75%, mp 195-197ºC (2-propanol). IR spectrum, ν, cm^{-1}: 1670 (C=O), 1660 (C=O), 2195 (C≡N), 3380 (NH). ^{1}H NMR spectrum, δ, ppm: 2.36 (3H, s, CH_3); 7.05-8.10 (13H, m, Ar); 6.90 (1H, s, =CH–); 12.28 (1H, s, NH). Found, %: C 71.2; H 4.1; N 13.4. $C_{25}H_{18}N_4O_3$. Calculated, %: C 71.1; H 4.3; N 13.3.

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