Chemistry of Heterocyclic Compounds, Vol. 40, No. 4, 2004

NOVEL SYNTHESIS ROUTE FOR PYRROLO[1,2-*a*]QUINAZOLINES

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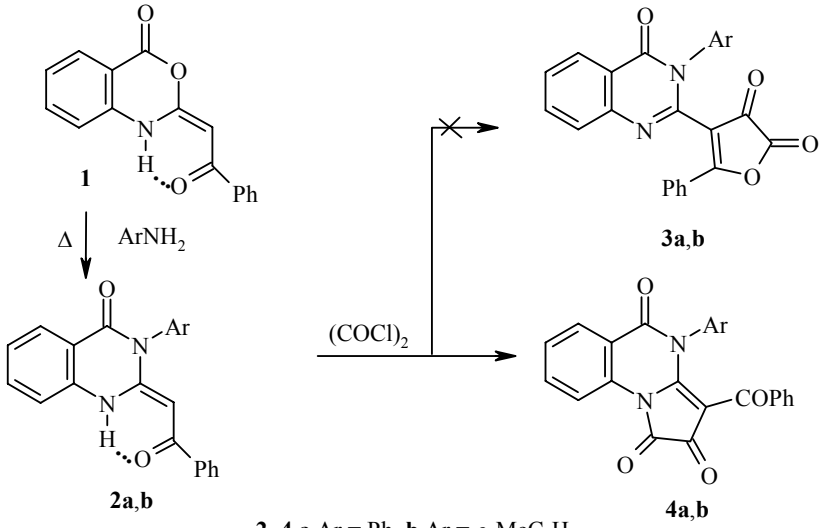
Keywords: 2-aroylmethylene-3-aryl-4-quinazolones, hetereno[*a*]-2,3-dihydro-2,3-pyrrolediones.

3-Phenacylidene-1,2,3,4-tetrahydro-2-quinoxalones react with oxalyl chloride to form substituted 3-aroyl-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinoxaline-1,2,4-triones [1], while 2-phenacylidene-1,2-dihydroquinoxalines react to form 5-aryl-4-quinoxalinyl-2,3-dihydro-2,3-furandiones [2]. With the aim of extending the data so we can predict which of the two directions indicated above will occur, we undertook the synthesis of 2-phenacylidene-3-aryl-1,2,3,4-tetrahydro-4-quinazolones **2a,b** and studied their reaction with oxalyl chloride. The structure of the substituted quinazolones **2a,b** is the limiting factor for realization of one of the alternative directions for reaction of a heterocyclic enaminoketone with oxalyl chloride.

Usually 2-acylmethylene-3-aryl-4-quinazolones are obtained by reaction of 2-(methyl lithium)-3-aryl-4-quinazolones with esters [3] or ester condensation of 2-(methyl lithium)-3-aryl-4-quinazolones in the presence of sodium hydride [4]. We propose a novel and simple method for obtaining substituted quinazolones **2a,b** by reaction of 2-phenacylidene-3,4-dihydro-1H-3,1-benzoxazin-4-one (**1**) with aromatic amines. When substituted quinazolones **2a,b** react with oxalyl chloride under conventional conditions for synthesis of five-membered 2,3-dioxo heterocycles [1, 2], instead of the expected 3-aryl-2-(4,5-dioxo-2-phenyl-4,5-dihydro-3-furyl)-3,4-dihydro-4-quinazolones (**3a,b**), we get 4-aryl-3-benzoyl-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinazoline-1,2,5-triones (**4a,b**).



2–**4** **a** Ar = Ph, **b** Ar = *o*-MeC_6H_4

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 0009-3122/04/4004-0532

In the indicated reaction, probably closure of the pyrroledione ring occurs due to its greater thermodynamic stability compared with the alternative furandione ring, while in our case steric hindrances leading to closure of the furandione ring are not as important as in the case described in [2]. The described reaction is a novel route to constructing a heterocyclic system of a substituted pyrrolo[1,2-*a*]quinazoline.

***E*-2-Phenacylidene-3-phenyl-1,2,3,4-tetrahydro-4-quinazolone (2a).** A solution of benzoxazinone **1** (0.50 g, 1.88 mmol) and aniline (0.17 ml, 1.88 mmol) in decane (1 ml) was boiled for 1 h and then cooled down. The precipitate was filtered out. Yield 0.60 g (93%); mp 212-214°C (2-propanol). IR spectrum (vaseline oil), ν, cm^{-1}: 3040 broad (NH in the intramolecular hydrogen bond), 1685 ($C_{(4)}$=O), 1610 broad (COPh in the intramolecular hydrogen bond). ^{1}H NMR spectrum (250 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 5.04 (1H, s, $C_{(2)}$=CH); 7.30-7.85 (13H, m, ArH); 8.07 (1H, d, *J* = 8.0, $C_{(5)}$H); 15.60 (1H, s, NH). Found, %: C 77.67; H 4.73; N 8.25. $C_{22}H_{16}N_2O_2$. Calculated, %: C 77.63; H 4.74; N 8.23.

***E*-2-Phenacylidene-3-*o*-tolyl-1,2,3,4-tetrahydro-4-quinazolone (2b)** was synthesized similarly. Yield 0.60 g (90%); mp 218-219°C (2-propanol). IR spectrum (vaseline oil), ν, cm^{-1}: 3060 broad (NH in the intramolecular hydrogen bond), 1683 ($C_{(4)}$=O), 1615 broad (COPh in the intramolecular hydrogen bond). ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 2.12 (3H, s, Me); 4.96 (1H, s, $C_{(2)}$=CH); 7.30-7.90 (12H, m, ArH); 8.05 (1H, d, *J* = 7.9, $C_{(5)}$H); 15.38 (1H, s, NH). Found, %: C 77.95; H 5.05; N 7.94. $C_{23}H_{18}N_2O_2$. Calculated, %: C 77.97; H 5.08; N 7.91.

3-Benzoyl-4-phenyl-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinazoline-1,2,5-trione (4a). A solution of quinazolone **1a** (0.10 g, 0.29 mmol) and oxalyl chloride (0.03 ml, 0.29 mmol) in absolute chloroform (3 ml) was boiled for 30 min under reflux and then cooled down. The precipitate was filtered out. Yield 0.10 g (95%); mp 255-256°C (with decomposition, from chloroform). IR spectrum (vaseline oil), ν, cm^{-1}: 1790 ($C_{(1)}$=O), 1728 ($C_{(2)}$=O), 1716 ($C_{(5)}$=O) 1648 (COPh). ^{1}H NMR spectrum (500 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 7.03-7.95 (12H, m, ArH); 8.11 (1H, d, *J* = 7.9, $C_{(6)}$H); 8.68 (1H, d, *J* = 8.0, $C_{(9)}$H). Found, %: C 73.07; H 3.52; N 7.10. $C_{24}H_{14}N_2O_4$. Calculated, %: C 73.10; H 3.55; N 7.11.

3-Benzoyl-4-*o*-tolyl-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinazoline-1,2,5-trione (4b) was synthesized similarly. Yield 0.11 g (93%); mp 230-232°C (with decomposition, from chloroform). IR spectrum (vaseline oil), ν, cm^{-1}: 1783 ($C_{(1)}$=O), 1725 ($C_{(2)}$=O), 1712 ($C_{(5)}$=O), 1650 (COPh). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 2.23 (3H, s, Me); 7.11-7.85 (11H, m, ArH); 8.23 (1H, d, *J* = 7.9, $C_{(6)}$H); 8.82 (1H, d, *J* = 8.0, $C_{(9)}$H). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 17.79 (Me); 114.32 ($C_{(9)}$); 126.25-137.21 (Ar); 156.78 ($C_{(1)}$); 157.49 ($C_{(5)}$); 161.71 ($C_{(3a)}$); 173.49 ($C_{(2)}$), 186.50 (COPh). Found, %: C 73.50; H 3.95; N 6.88. $C_{25}H_{16}N_2O_4$. Calculated, %: C 73.53; H 3.92; N 6.86.

This work was carried out with the financial support of the Russian Foundation for Basic Research (grants Nos. 01-03-32641, 02-03-96411, 03-03-06634). The NMR spectra were taken at the Ural Regional NMR Spectroscopy Center, URAL-NMR (Russian Foundation for Basic Research grant No. 00-03-40139).

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