Chemistry of Heterocyclic Compounds, Vol. 37, No. 5, 2001

UNUSUAL REACTION OF HETERENO[*a*]-2,3-DIHYDRO-2,3-PYRROLEDIONES WITH *o*-AMINOTHIOPHENOL

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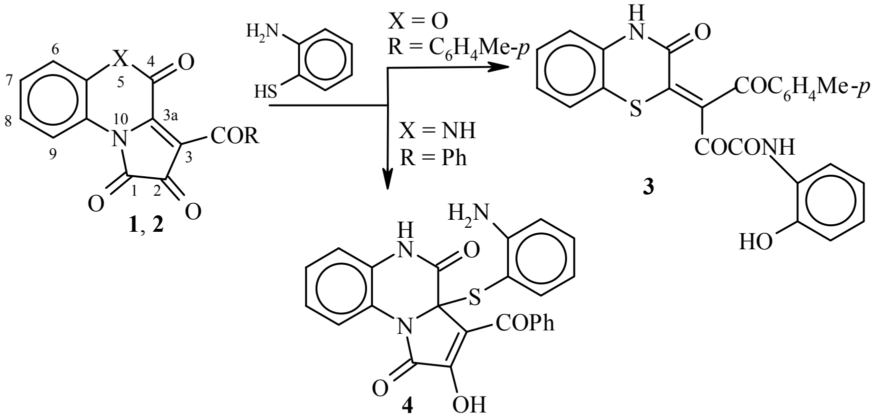
Keywords: *o*-aminothiophenol, 1,4-benzothiazin-3-one, hetereno[*a*]-2,3-dihydro-2,3-pyrrolediones, pyrrolo[1,2-*a*]quinoxaline-1,4-dione.

The reaction of hetereno[*a*]-2,3-dihydro-2,3-pyrrolediones with *o*-aminothiophenol, containing two nonequivalent nucleophilic centers, has not been previously studied. When monocyclic 2,3-dihydro-2,3-pyrrolediones react with *o*-aminothiophenol, pyrrolo[2,3-*b*][1,5]benzothiazepines are formed [1].

Different products are formed when 3-*p*-toluoyl-1,2-dihydro-4H-pyrrolo[5,1-*c*][1,4]benzoxazine-1,2,4-trione (**1**) and 3-benzoyl-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinoxaline-1,2,4-trione (**2**) react with *o*-aminothiophenol under analogous [1] conditions, and even when the conditions are more severe (boiling in MeCN for 5-10 min).



Compound **3** is probably formed as a result of initial nucleophilic attack by the mercapto group of the *o*-aminothiophenol on the $C_{(3a)}$ atom of compound **1**, followed by attack by the free amino group of the reagent on the lactone carbonyl group and opening of the oxazine ring at the $C_{(4)}$–$O_{(5)}$ and $C_{(3a)}$–$N_{(10)}$ bonds, similar to the reactions of these pyrrolobenzoxazinetriones [2] with *o*-phenylenediamine [3].

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By reacting compound **2** with *o*-aminothiophenol, for the first time we were able to isolate the product of initial addition of *o*-aminothiophenol at the $C_{(3a)}$ atom of the starting heterocycle, which had not been previously observed for such binucleophilic reagents as *o*-phenylenediamine and *o*-aminophenol [1, 3, 4]. Attempts to carry out further cyclization of compound **4**, with the goal of obtaining a benzothiazepine ring, were unsuccessful. Furthermore, quantum chemical calculations of the geometrical characteristics of the products of addition of *o*-aminothiophenol to compounds **1** and **2** suggest that the relative arrangement of the moieties in molecule **4** sterically hinder its cyclization with participation of the amino group.

N-*o*-Hydroxyphenylamide of *Z*-2,4-Dioxo-3-(2-oxo-3,4-dihydro-1,4-benzothiazine-3-ylidene)-4-phenylbutanoic Acid (3). A solution of *o*-aminothiophenol (1.25 g, 10 mmol) in MeCN (10 ml) was added to a solution of compound **1** (3.19 g, 10 mmol) [2] in MeCN (50 ml) at room temperature. The white precipitate that fell out of solution after 24 hours was filtered off. Yield 3.12 g (81%); mp 220-222°C (MeCN). IR spectrum (vaseline oil), ν, cm^{-1}: 3280 (CONH), 3150 broad (OH), 1710 $(C_{(2)}=O)_{thiazine}$, 1690 $(C_{(1)}=O)$, 1650 $(C_{(4)}=O)$, 1620 broad $(C_{(2)}=O)$, 1520 (amide II). ^1H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 2.42 (3H, s, CH_3); 6.55-7.67 (12H, $3C_6H_4$); 9.45 (1H, s, $C_{(1)}ONH$); 9.50 (1H, br. s, OH); 10.85 (1H, s, $C_{(2)}ONH$). Found, %: C 65.42; H 4.03; N 5.97; S 6.89. $C_{25}H_{18}N_2O_5S$. Calculated, %: C 65.68; H 3.94; N 6.08; S 6.94.

3a-*o*-Aminophenylmercapto-3-benzoyl-2-hydroxy-1,2,3,4-tetrahydropyrrolo[1,2-*a*]quinoxaline-1,4-dione (4). *o*-Aminothiophenol (1.25 g, 10 mmol) was added dropwise to a solution of compound **2** (3.18 g, 10 mmol) [4] in absolute MeCN (50 ml); the light yellow precipitate was filtered off. Yield 2.55 g (62%); mp 182-184°C (decomp., from MeCN). IR spectrum (vaseline oil), ν, cm^{-1}: 3450 (NH_{2as}), 3345 (NH_{2s}), 3245 (CONH), 3190 broad (OH), 1720 $(C_{(1)}=O)$, 1670 $(C_{(4)}=O)$, 1650 $(CO)_{benzoyl}$. ^1H NMR spectrum (80 MHz, DMSO-d_6), δ, ppm: 5.65 (2H, s, NH_2); 7.19-8.25 (13H, $2C_6H_4+C_6H_5$); 9.67 (1H, br. s, OH); 10.61 (1H, s, $N_{(5)}H$). Found, %: C 69.89; H 3.78; N 9.40; S 7.03. $C_{24}H_{17}N_3O_4S$. Calculated, %: C 65.19; H 3.85; N 9.42; S 7.18.

This research was done with the financial support of the Russian Foundation for Basic Research (grant 01-03-32641).

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