Chemistry of Heterocyclic Compounds, Vol. 44, No. 2, 2008

SYNTHESIS OF 5,6-DIHYDRO-[1,2,3]THIADIAZOLO[5,4-*e*]-[1,4]OXAZEPIN-8(4)-ONE

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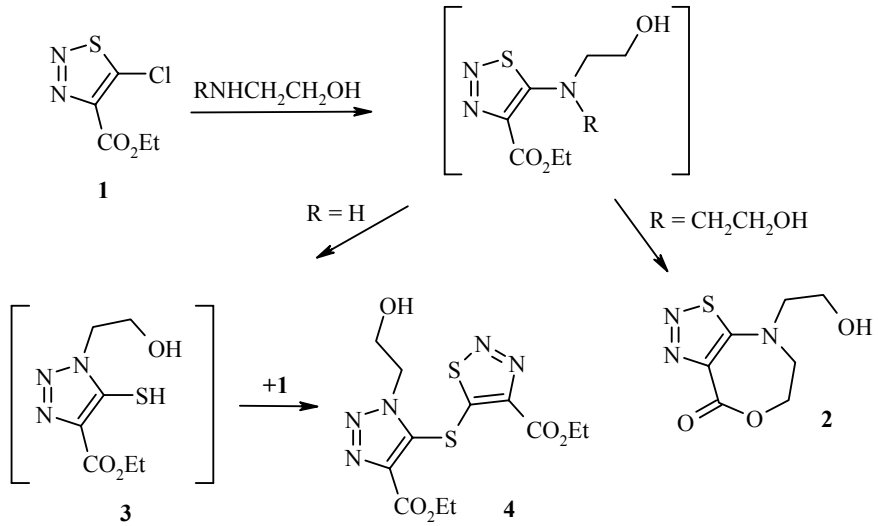
Keywords: 2- oxazepine, 1,2,3-triazole, Dimroth rearrangement.

Nucleophilic substitution in 5-halo-1,2,3-thiadiazoles is a convenient method for the synthesis of various heterocycles [1, 2]. We have previously shown that such reactions may be accompanied by rearrangement of the thiadiazole ring and reactions at C(4) of the ring [3, 4]. In a continuation of our studies, we have developed a simple preparative method for the synthesis of a previously unreported heterocyclic system, namely, [1,2,3]thiadiazolo[5,4-*e*][1,4]oxazepine by the reaction of the ethyl ester of 5-chloro-1,2,3-thiadiazole-5-carboxylic acid (**1**) [5] with diethanolamine. This reaction involves nucleophilic substitution of the chlorine atom followed by intramolecular transesterification to give heterocycle **2**. In contrast to the reaction indicated above, the reaction of thiadiazole **1** with monoethanolamine leads to the Dimroth rearrangement product [6], 5-mercapto-1,2,3-triazole **3**, which reacts with starting 5-chloro-1,2,3-triazole **1** under the reaction conditions to give sulfide **4**.



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The ^{1}H and ^{13}C NMR spectra were taken on a Bruker DRX-400 spectrometer at 400 and 100 MHz, respectively in DMSO-d_6 with TMS as the internal standard.

4-(2-Hydroxyethyl)-5,6-dihydro[1,2,3]thiadiazolo[5,4-*e*][1,4]oxazepin-8(4)-one (2). Freshly distilled diethanolamine (0.42 g, 4 mmol) was added to a solution of compound **1** (0.385 g, 2 mmol) in 96% ethanol (25 ml) and stirred for 4 h at room temperature. The solvent was evaporated off in vacuum and the residue was crystallized from ethanol to give compound **2** (0.38 g, 87%), mp 152-153°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.05 (1H, t, *J* = 6.0, OH); 4.54-4.56 (2H, m, OCH_2); 3.84-3.86 (2H, m, NCH_2); 3.66 (2H, dt, *J* = 6.0, *J* = 5.2) C$\underline{H_2}$OH); 3.46 (2H, t, *J* = 5.2, NCH_2). ^{13}C NMR spectrum: 167.3, 162.4, 132.5, 64.7, 64.3, 57.2, 54.5. Mass spectrum, *m/z* (I_{rel}, %): 215 (100). Found, %: C 38.89; H 4.37; N 19.20; S 14.72. $C_7H_9N_3O_3S$. Calculated, %: C 39.06; H 4.21; N 19.52; S 14.90.

Ethyl Ester of 4-(Ethoxycarbonyl)-5-(1-(2-hydroxyethyl)-1H-1,2,3-triazol-5-ylthio)-1,2,3-thiadiazole-4-carboxylic acid (4) was obtained in 38% yield (0.28 g) as an oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.62 (1H, br. s, OH); 4.42 (2H, q, *J* = 7.1, OCH_2); 4.36 (2H, q, *J* = 7.0, OCH_2); 4.25 (2H, dt, *J* = 6.0, *J* = 6.0, C$\underline{H_2}$OH); 4.16 (2H, t, *J* = 6.0, NC$\underline{H_2}$); 1.38 (3H, t, *J* = 7.1, CH_3); 1.18 (3H, t, *J* = 7.0, CH_3). Found, %: C 38.55; H 4.07; N 19.00; S 17.11. $C_{12}H_{15}N_5O_5O_2$. Calculated, %: C 38.60; H 4.05; N 18.76; S 17.17.

This work was carried out with the financial support of the Russian Basic Research Fund (Grant No. r2004_04-03-96104-p2004ural_a).

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