Chemistry of Heterocyclic Compounds, Vol. 39, No. 1, 2003

REACTION OF 5-HYDRAZONO-1,2,3-THIADIAZOLES WITH TOLUENE AND XYLENE IN THE PRESENCE OF PCl_5

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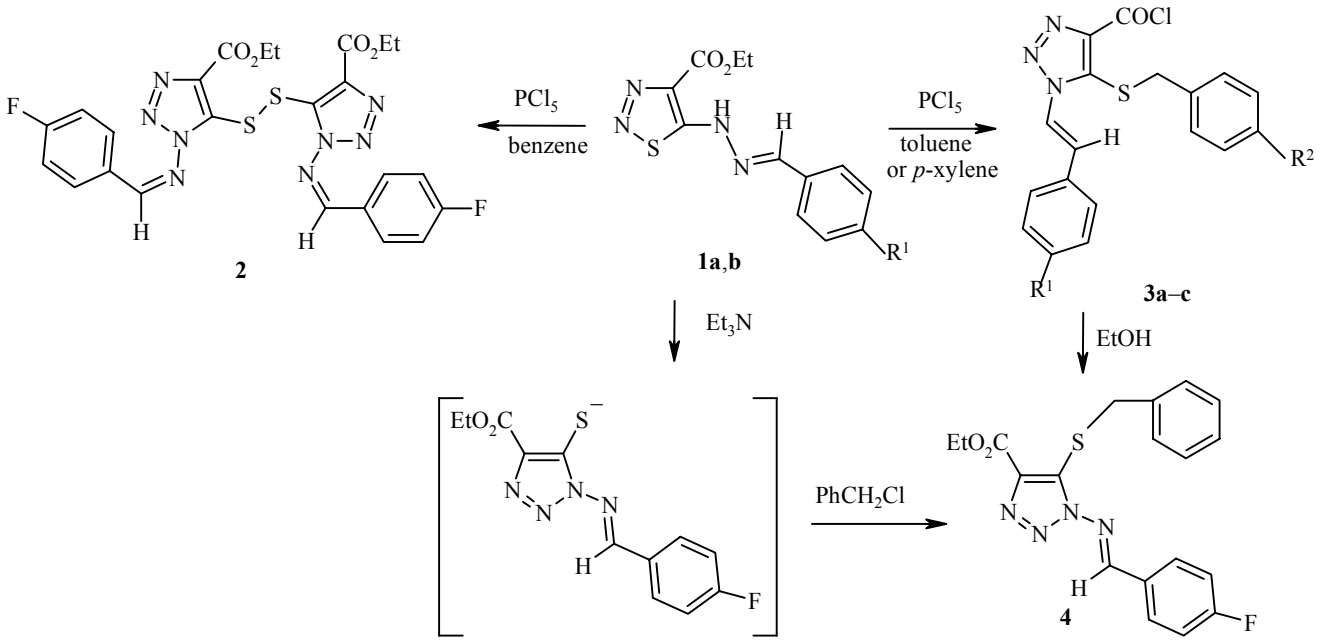
The treatment of 5-hydrazono-1,2,3-thiadiazoles by phosphorus pentachloride in toluene or xylene leads to an anomalous Dimroth rearrangement and the reaction of the mercapto function formed with the methyl group of the solvent to give 5-benzylmercapto-1,2,3-triazole.

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

The Dimroth rearrangement [1] of 5-amino-1,2,3-thiazoles to give 5-mercapto-1,2,3-triazoles proceeds in alkaline media [2]. Only one example of an anomalous course for this transformation in acid medium has been described [3]. The treatment of 5-amino-1,2,3-thiadiazole with sulfuryl chloride gives bis(1,2,3-triazolyl) disulfide. We have shown that an analogous rearrangement also occurs upon the treatment of thiadiazolylhydrazone **1b** with phosphorus pentachloride in benzene to give bistriazolyl disulfide **2**. However, heating **1a** or **1b** in toluene or *p*-xylene at reflux in the presence of PCl_5 gave only acid chloride derivatives of 5-benzylmercapto-1,2,3-triazole-4-carboxylic acids **3a-c**.



1 a R^1 = OMe, **b** R^1 = F; **3 a** R^1 = OMe, R^2 = H; **b** R^1 = F, R^2 = H; **c** R^1 = OMe, R^2 = Me

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 134-136, January, 2003. Original article submitted March 19, 2002.

 0009-3122/03/3901-0126$25.00

Heating acyl chloride **3b** in ethanol for 30 min gave the corresponding ester **4**. We should note that the reaction of **3** with ethanol at room temperature does not proceed. Acyl chlorides **3** may have low activity due to steric hindrance. Ester **4** was also obtained by convergent synthesis by rearrangement of hydrazone **1b** by the action of triethylamine with subsequent alkylation at the sulfur atom by benzyl chloride.

EXPERIMENTAL

Bis(1-(4-ethoxycarbonyl)-(4-fluorobenzylidenamino)-1,2,3-triazol-5-yl) Disulfide (2) was obtained in 33% yield (0.33 g); mp 118-120°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 9.42 (1H, s, CH); 7.35-7.48 (2H, m, ArH); 7.13 (2H, d, *J* = 9.1, ArH); 4.35 (2H, q, *J* = 7.0, CH_2); 1.33 (3H, t, *J* = 7.0, CH_3). Found, %: N 19.02; S 10.76. $C_{24}H_{20}F_2N_8O_4S_2$. Calculated, %: N 19.10; S 10.94.

5-Benzylthio-1-(3-methoxybenzylidenamino)-1,2,3-triazole-4-carboxylic Acid Chloride (3a) was obtained in 60% yield; mp 110°C. IR spectrum, ν, cm^{-1}: 1720 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.20 (1H, s, CH); 7.87 and 7.03 (4H, dd, *J* = 8.8, ArH); 7.24-7.26 (5H, m, Ph); 4.44 (2H, s, CH_2); 3.92 (3H, s, OCH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 141.02 (s, $C_{(4)}$), 135.03 (s, $C_{(5)}$), 38.30 (t, SCH_2), 127.86 (d, $C_{(p)}$), 128.55 (d, $C_{(o)}$), 128.73 (d, $C_{(m)}$), 135.26 (s, $C_{(i)}$), 55.44 (q, OCH_3), 141.65 (d, $C_{(m)}$), 123.91 (s, $C_{(i)}$), 131.45 (d, $C_{(o)}$), 163.80 (s, $C_{(p)}$), 160.04 (s, COCl). Mass spectrum, *m/z* (I_{rel}, %): 386 $[M]^{+\cdot}$ (3). Found, %: C 56.08; H 3.82; Cl 9.4; S 8.33. $C_{18}H_{15}ClN_4O_2S$. Calculated, %: C 55.89; H 3.90; Cl 9.16; S 8.29.

5-Benzylthio-1-(4-fluorobenzylidenamino)-1,2,3-triazole-4-carboxylic Acid Chloride (3b) was obtained in 65% yield; mp 112°C. IR spectrum, ν, cm^{-1}: 1740 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.38 (1H, s, CH); 8.10 (2H, dd, *J* = 8.8, *J* = 5.4, ArH); 7.44 (2H, d, *J* = 8.8, ArH); 7.16-7.48 (5H, m, Ph); 4.46 (2H, s, CH_2). Mass spectrum, *m/z* (I_{rel}, %): 374 $[M]^{+\cdot}$ (2). Found, %: N 19.55; S 8.86. $C_{17}H_{12}ClFN_4OS$. Calculated, %: N 19.95; S 8.56.

1-(4-Methoxybenzylidenamino)-5-(4-methylbenzylthio)-1,2,3-triazole-4-carboxylic Acid Chloride (3c) was obtained in 65% yield (0.73 g); mp 114-116°C. IR spectrum, ν, cm^{-1}: 1700 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.18 (1H, s, CH); 7.87 and 7.11 (4H, dd, *J* = 7.0, ArH); 7.03 and 7.07 (4H, dd, *J* = 7.0, ArH); 4.40 (2H, s, CH_2); 3.91 (3H, s, OCH_3); 2.25 (3H, s, CH_3). Found, %: C 56.08; H 3.82; Cl 9.4; S 8.33. $C_{18}H_{15}ClN_4O_2S$. Calculated, %: C 55.89; H 3.90; Cl 9.16; S 8.29.

Ethyl Ester of 5-Benzylthio-1-(4-fluorobenzylidenamino)-1,2,3-triazole-4-carboxylic Acid (4) was obtained in 39% yield (0.28 g); mp 114-116°C. Method 1. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 9.40 (1H, s, CH); 7.43 and 7.45 (2H, dd, *J* = 8.2, ArH); 7.10-7.30 (5H, m, Ph); 4.44 (2H, s, CH_2); 4.34 (2H, q, *J* = 7.0, CH_2); 1.31 (3H, t, *J* = 7.0, CH_3). Found, %: S 8.85. $C_{19}H_{17}FN_4O_2S_2$. Calculated, %: S 8.70.

This work was carried out with the financial support of the Russian Basic Research Fund (Grant 02-03-96421 Ural) and CDRF Project Grant No. RC-1-2393-EK-02.

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