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A CONVENIENT APPROACH TO SYNTHESIS OF 1,2,3-TRIAZOLE-4-CARBOTHIOAMIDES

T. V. Glukhareva[1], Yu. Yu. Morzherin[1], V. S. Mokrushin[1], A. V. Tkachev[2], and V. A. Bakulev[1]

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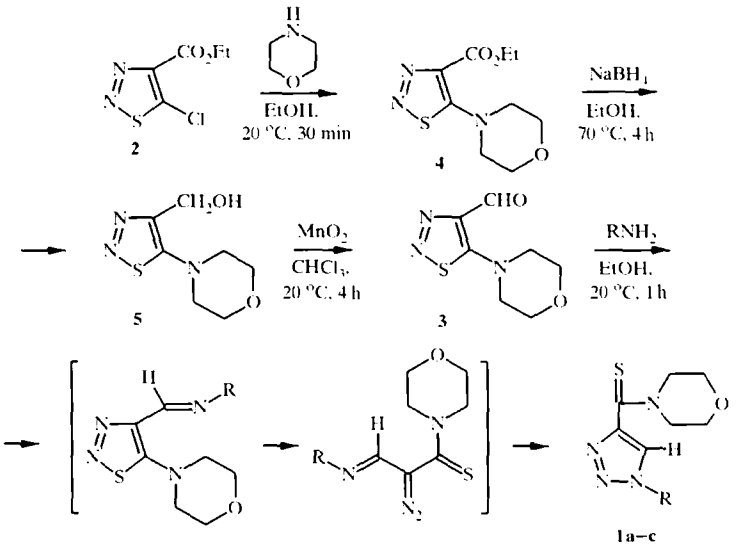
In this paper, we present a method for obtaining 1,2,3-triazole-4-carbothioamides **1** starting from the readily available [1] 5-chloro-1,2,3-thiadiazole-4-carboxylic acid ethyl ester **2**.



1a R = Me, **b** R = C_6H_4-OMe-2, **c** R = NHC_6H_3-$(NO_2)_2$-2,4

The proposed method involves: nucleophilic substitution of the chlorine atom in the 5 position of the thiadiazole ring, reduction of the ester group to a hydroxymethyl group by sodium borohydride, conversion of the alcohol group to an aldehyde group upon oxidation by activated MnO_2. Aldehyde **3** formed then reacts with different amines, which leads to formation of an unstable imine that as a result of the Konfort rearrangement [2] is converted to the 1-substituted 4-morpholinothiocarbonyl-1,2,3-triazole **1**.

1-Methyl-1,2,3-triazole-4-carbothiomorpholide (1a). Yield 50%; mp 114°C (alcohol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.47 (1H, s, $C_{(5)}H$); 4.31 (2H, t, CH_2); 4.10 (2H, t, CH_2); 4.06 (3H, s, CH_3); 3.77 (2H, t, CH_2); 3.67 (2H, t, CH_2). ^{13}C NMR spectrum: 184.42 (C=S), 146.94 ($C_{(4)}$), 130.23 ($C_{(5)}$), 65.38 (CH_2), 64.82 (CH_2), 51.71 (CH_2), 49.12 (CH_2), 35.41 (CH_3). Mass spectrum, *m/z* (I_{rel}, %): 212 [M]$^+$ (25). Found, %: N 26.1; S 14.6. $C_8H_{12}N_4OS$. Calculated, %: N 26.4; S 15.1.

[1] Ural State Technical University, Ekaterinburg 620002, Russia; e-mail: morzherin@htf.ustu.ru.
[2] Novosibirsk Institute of Organic Chemistry, Novosibirsk 630090, Russia; e-mail: atkachev@nioch.nsc.ru.
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1-(2-Methoxyphenyl)-1,2,3-triazole-4-carbothiomorpholide (1b). Yield 53%; mp 160°C (alcohol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.77 (1H, s, $C_{(5)}H$); 7.67 (1H, dd, ArH); 7.55 (1H, ddd, ArH); 7.33 (1H, ddd, ArH); 7.16 (1H, dd, ArH); 4.35 (2H, t, CH_2); 4.12 (2H, t, CH_2); 3.87 (3H, s, OCH_3); 3.79 (2H, t, CH_2); 3.71 (2H, t, CH_2). ^{13}C NMR spectrum: 185.14 (C=S), 151.60 (ArO), 147.66 ($C_{(4)}$), 131.11 (Ar), 130.33 ($C_{(5)}$), 125.70 (ArH), 125.00 (Ar_i), 120.84 (ArH), 113.04 (ArH), 66.37 (CH_2), 65.82 (CH_2), 56.20 (CH_3), 52.79 (CH_2), 50.09 (CH_2). Mass spectrum, *m/z* (I_{rel}, %): 304 $[M]^{+\cdot}$ (12). Found, %: N 18.5; S 10.5. $C_{14}N_{16}N_4O_2S$. Calculated, %: N 18.4; S 10.5.

1-(2,4-Dinitrophenyl)amino-1,2,3-triazole-4-carbothiomorpholide(1c). Yield 63%; mp 182°C (alcohol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 11.8 (1H, s, NH); 8.92 (1H, d, ArH); 8.83 (1H, s, $C_{(5)}H$); 8.35 (1H, dd, ArH); 6.46 (1H, d, ArH); 4.35 (2H, t, CH_2); 4.12 (2H, t, CH_2); 3.81 (2H, t, CH_2); 3.75 (2H, t, CH_2). Found, %: N 25.5; S 8.5. $C_{13}H_{13}N_7O_5S$. Calculated, %: N 25.8; S 8.4.

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