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FORMATION OF 5-METHYLTHIO-1,3,4-OXADIAZOLES IN THE CONDITIONS OF THE HOGGARTH REACTION

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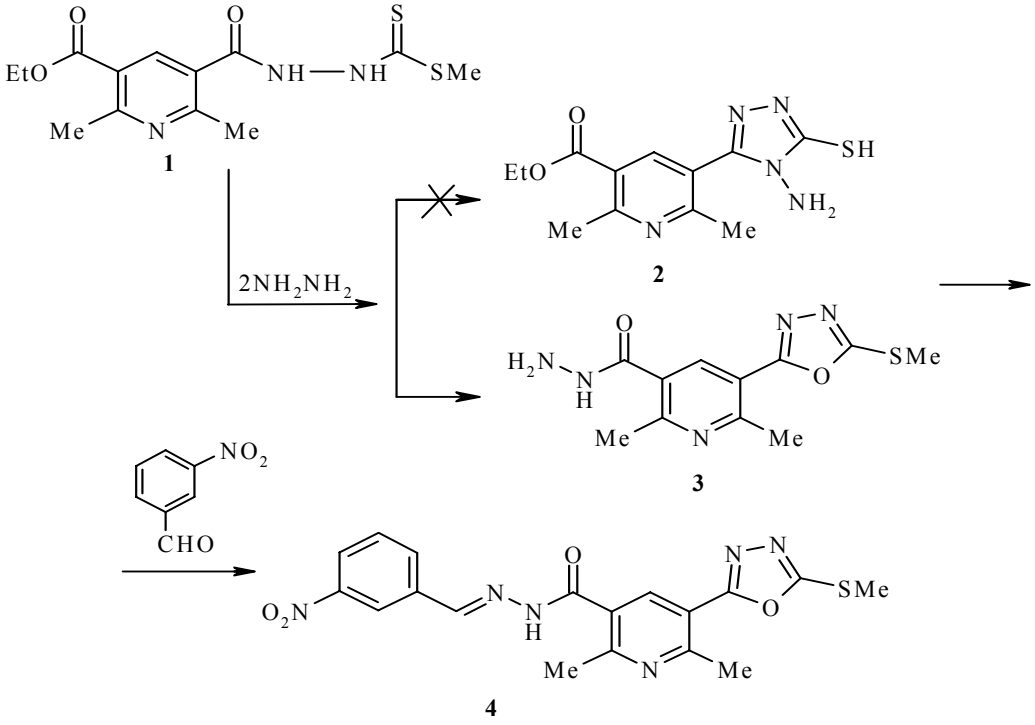
Thioesters of aroyldithiocarbazic acids react with hydrazine hydrate to form 4-amino-3-aryl-5-mercapto-1,2,4-triazoles [1]. We have established that boiling ethyl 2,6-dimethyl-5-(N-methylsulfanylthiocarbohydrazinocarbonyl)nicotinate (**1**) with a twofold excess of hydrazine hydrate in 2-propanol for 6 h did not lead to the formation of the expected N-aminotriazole **2**, but to the formation of the hydrazide of 2,6-dimethyl-5-(5-methyl-



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sulfanyl[1,3,4]oxadiazol-2-yl)nicotinic acid (**3**), the structure of which was confirmed by the formation of the hydrazone **4** on heating with an alcoholic solution of *m*-nitrobenzaldehyde.

It may be suggested that formation of the 1,3,4-oxadiazole ring occurs *via* cyclization of the acylthiocarbazine unit under alkaline conditions, but hydrazinolysis takes place at the ester group.

^{1}H NMR spectra of DMSO-d_6 solutions with TMS as internal standard were recorded with a Varian VXR-300 (300 MHz) instrument.

Hydrazide of 2,6-Dimethyl-5-(5-methylsulfanyl[1,3,4]oxadiazol-2-yl)nicotinic acid (3). Hydrazine hydrate (0.5 ml, 64%) was added to a solution of compound **1** (0.29 g, 1 mmol) in 2-propanol (10 ml) and the mixture was boiled for 6 h. The precipitate was filtered off, and crystallized from 1:1 hexane–ethanol. Yield 0.24 g (85%); mp 221-222°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 2.57 (3H, s, SCH_3); 2.78 (3H, s, 2,6-CH_3); 2.80 (3H, s, 2,6-CH_3); 4.58 (2H, s, NH_2); 8.11 (1H, s, Py); 9.68 (1H, s, NH). Found, %: C 47.32; H 4.67; N 25.11. $C_{11}H_{13}N_5O_2S$. Calculated, %: C 47.27; H 4.70; N 25.07.

3-Nitrobenzalhydrazide of 2,6-Dimethyl-5-(5-methylsulfanyl[1,3,4]oxadiazol-2-yl)nicotinic acid (4). *m*-Nitrobenzaldehyde (0.27 g, 1.79 mmol) was added to a solution of compound **3** (0.5 g, 1.79 mmol) in ethanol (25 ml). The reaction mixture was boiled for 30 min, the precipitate was filtered off and crystallized from DMF. Yield 0.66 g (90%); mp 196-197°C. ^{1}H NMR spectrum, δ, ppm: 2.64 (3H, s, SCH_3); 2.85 (6H, s, 2,6-CH_3); 7.50-8.45 (5H, m, C_6H_4CH); 8.62 (1H, s, Py); 12.25 (1H, s, NH). Found, %: C 52.23; H 4.43; N 20.29. $C_{18}H_{16}N_6O_4S$. Calculated, %: C 52.39; H 3.92; N 20.38.

REFERENCE

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