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Regioisomeric oximes and thiosemicarbazones derived from 6-substituted pyridoxines

Nikita V. Shtyrlin, Olga A. Lodochnikova and Yurii G. Shtyrlin[*]

Experimental

Melting points were determined using a Stanford Research Systems MPA-100 OptiMelt melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AVANCE 400 spectrometer at operating frequency 400 MHz. Chemical shifts were measured with reference to the residual protons of the solvents (DMSO-*d*$_6$, ^{1}H, 2.50 ppm; $CDCl_3$, ^{1}H, 7.26 ppm). The elemental compositions were determined on a Perkin–Elmer 2400 Series II analyzer.

*9-Hydroxy-3,3,8-trimethyl-1,5-dihydro[1,3]dioxepino[5,6-*c*]pyridine-6-carboxaldehyde* **2**. Activated MnO_2 (10 g, 115 mmol) was added to a stirred solution of compound **1** [10](2 g, 8.44 mmol) in 20 ml of ethanol and 10 ml of water. The mixture was stirred at 40 °C for 5 h, then filtered and the filtrate was evaporated under reduced pressure. The obtained product was purified by column chromatography (chloroform as the eluent). Yield 1.3 g (65%), light-brown crystals, mp 161−162 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.51 (s, 6H, $2CH_3$), 2.56 (s, 3H, CH_3), 4.95 (s, 2H, CH_2), 5.30 (s, 2H, CH_2), 9.98 (s, 1H, C(O)H). Found (%): C, 60.71; H, 6.72; N, 5.90. Calc. for $C_{12}H_{15}NO_4$ (%): C, 60.75; H, 6.37; N, 5.90.

3-Hydroxy-5,6-bis(hydroxymethyl)-2-methylpyridine-4-carboxaldehyde oxime **5a** *monohydrate.* Concentrated H_2SO_4 (0.46 g, 4.70 mmol) was added to a solution of compound **1** (1 g, 4.18 mmol) in 50 ml of water. The mixture was stirred at room temperature for 5 h, then activated MnO_2 (7.5 g, 86.2 mmol) was added and the stirring was continued for 4 min. The mixture was filtered and the filtrate was concentrated to about 5 ml. To the obtained solution AcONa (4 g, 48.8 mmol) and $NH_2OH*HCl$ (0.5 g, 7.19 mmol) were added and the mixture was refluxed for 5 min. Then a solution was cooled to 5 °C and left at this temperature for about 24 h. The precipitate formed was filtered off and washed with water. Yield of **5a** monohydrate was 0.74 g (77%), light-green crystals, mp 162 °C (decomp.).

3-Hydroxy-5,6-bis(hydroxymethyl)-2-methylpyridine-4-carboxaldehyde thiosemicarbazone **5b** *monohydrate*. Concentrated H_2SO_4 (0.46 g, 4.70 mmol) was added to a solution of compound **1** (0.3 g, 1.26 mmol) in 50 ml of water. The mixture was stirred at room temperature for 5 h, then activated MnO_2 (2.5 g, 28.7 mmol) was added and the stirring was proceeded for 10 min. The mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was dissolved in 20 ml of anhydrous ethanol, thiosemicarbazide (0.14 g, 1.54 mmol) was added and the mixture was refluxed for 4 h. The precipitate was filtered off and washed with water and ethanol. Yield of **5b** monohydrate was 0.18 g (50%), yellow crystals, mp 217−218 ^{o}C (decomp.).