SYNTHESIS OF 1-CHLORO-4H-1,2,3-THIADIAZOLINE

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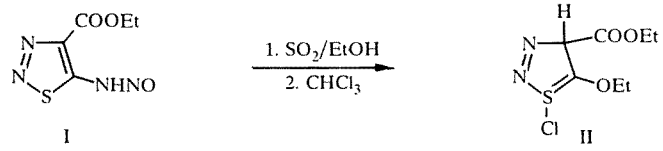
It is known that either amines or hydrazines may be formed when N-nitrosoamines are reduced [1]. However N-nitrosoamines are in equilibrium with the corresponding diazonium salts in acid media and may undergo nucleophilic substitution [2].

We have established that reduction of 4-carbethoxy-5-N-nitrosoamino-1,2,3-thiadiazole (I) with sulfurous acid gave a mixture of the reduction products, 4-carbethoxy-5-amino- and -5-hydrazino-1,2,3-thiadiazole, and also the product of nucleophilic substitution, 5-hydroxy-1,2,3-thiadiazole. However 1-chloro-4-carbethoxy−5-ethoxy-4H-1,2,3-thiadiazoline (II) was formed in 49% yield on reduction of I with sulfur dioxide in absolute ethanol with subsequent isolation of the product by column chromatography with chloroform as eluent. An aqueous solution of this compound reduced silver nitrate to amorphous metallic silver.



I II

Compound II ($C_7H_{11}ClN_2O_2S$). ^1H NMR spectrum: 1.35 (3H), 1.36 (3H), 4.23 (2H), 4.66 (2H), 5.07 ppm (1H) – signal characteristic of the chemical shifts of protons of partially hydrogenated heterocycles [3]. ^{13}C NMR Spectrum: 13.3 (Me), 13.9 (Me), 63.5 (CH_2), 65.0 (CH_2), 63.1 (C_4, d, J = 157.5 Hz), 164.8 (C=O), and 208.3 ppm (C_5). The C_4 (165 ppm) and C_5 (135 ppm) signals characteristic of 1,2,3-thiadiazoles are absent [4]. The spectrum is characteristic of thiophene ions protonated at position 4 [5]. Mass spectrum: the quasimolecular ion, *m/z* 210 (100%) ($[M^{+\cdot}-N_2]$) contains isotopic signals characteristic of a compound containing a chlorine atom; *m/z* 175 ($[M^{+\cdot}-N_2-Cl]$).

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