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LETTERS TO THE EDITOR

REVERSIBLE REARRANGEMENT OF 1,2,3-TRIAZOLE-4-CARBOTHIOAMIDE TO 1,2,3-THIADIAZOLE-4-CARBIMINES

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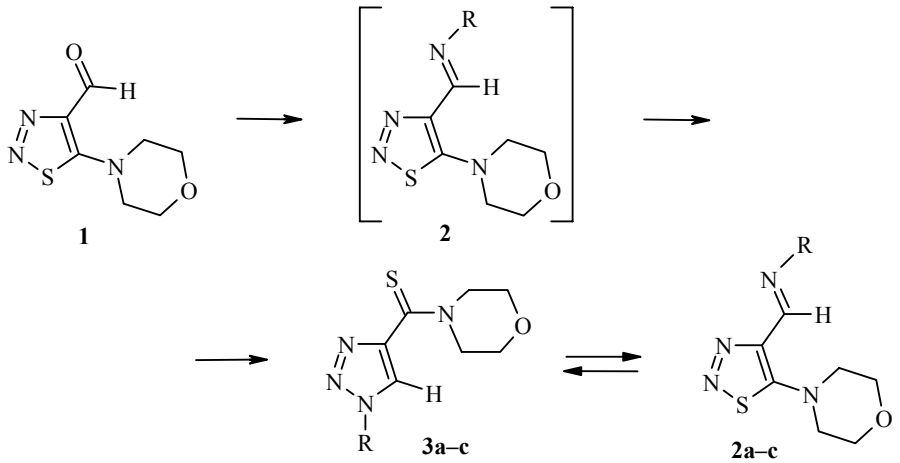
When amines, hydrazides, and hydroxylamines react with 5-dialkylamino-1,2,3-thiadiazole-4-carbaldehydes **1**, the corresponding carbimines **2** are not isolated: under the reaction conditions, they rearrange to 1,2,3-triazole-4-carbothioamides **3** [1, 2]. In this work, we have observed that when compounds **3a-c** (containing the substituents OH, OMe, NHC_6H_3-(2,4-$(NO_2)_2$) on the 1 position of the triazole ring) are held in $CDCl_3$, DMSO-d_6, or pyridine-d_5 solution, we observe the appearance of the corresponding isomeric structures **2**. For 1,2,3-triazole-4-carbothioamides **3** [2] with aryl and alkyl substituents on the 1 position of the ring, the reverse rearrangement has not been observed.



2, **3** **a** R = OH, **b** R = OMe, **c** R = $NHC_6H_3(NO_2)_2$-2,4

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In the ^{1}H NMR spectrum of compounds **2**, the signal from the methine proton in the imino group is detected at 8.65 ppm, i.e., shifted downfield by 0.5 ppm compared with the signal from the H-5 proton of the triazole structure **3**. The singlet from the protons of the methoxy group for compound **2b**, on the other hand, is detected upfield compared with the triazole **3b**, at 3.99 ppm. In the ^{13}C NMR spectrum, the signal from the $C_{(5)}$ carbon atom in the thiadiazole structure **2b** is detected in the 168.1 ppm region, i.e., shifted upfield by 16.7 ppm compared with the triazole isomer (186 ppm), when this atom is found in the thioamide functional group. The carbon atom of the imino group of 1,2,3-thiadiazole ($C_{(5)}$ in triazole **3b**), on the other hand, becomes exocyclic and its signal is observed shifted downfield by 20 ppm. The signal from the $C_{(4)}$ carbon atom of the thiadiazole ring is upfield compared with the triazole isomer (139 ppm compared with 142 ppm).

In the cell of the NMR spectrometer, we studied the effect of temperature and the nature of the solvent on the 1,2,3-triazole:thiadiazole ratio. We established that the amount of the product of reverse rearrangement **2** increases in the solvent series DMSO, pyridine, chloroform. Thus for compound **3b** at room temperature in a $CDCl_3$ solution, in the ^{1}H NMR spectra we detected the presence of triazole **3b** and thiadiazole **2b** structures in 6:1 ratio (calculated from the integrated intensities of the signals from the methine protons). Study of the effect of temperature on the ratio of the isomers **3b** and **2b** in pyridine-d5 solution showed that at 297 K in pyridine solution, 32% is the thiadiazole structure (calculated from the ratio of the integrated intensities of the protons of the methoxy group in the ^{1}H NMR spectrum). When the solution is heated to 333 K, the thiadiazole content increases up to 38%; when it is cooled, we observe the original ratio of the isomers.

Thus we have observed that the Cornforth rearrangement for 1,2,3-triazole-4-carbothioamides is reversible for substituents such as OH, OMe, $NHC_6H_3(2,4\text{-}(NO_2)_2)$.

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