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UNEXPECTED DESTRUCTION OF TRIAZOLE RING BY THE ACTION OF DEHYDROACETIC ACID

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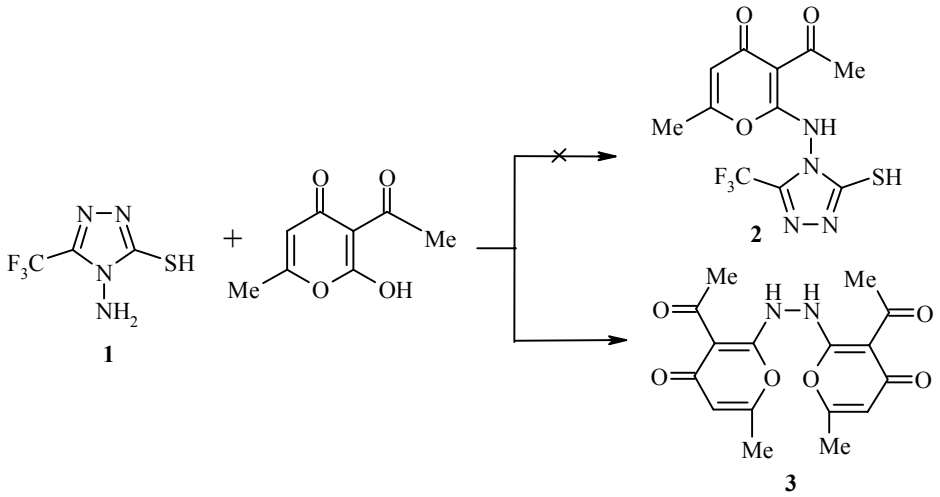
Keywords: 4-amino-5-trifluoromethyl-4H-1,2,4-triazole-3-thiol, dehydroacetic acid, N^1,N^2-di(3-acetyl-6-methyl-4-oxo-4H-2-pyranyl)hydrazine, triazole ring destruction.

Dehydroacetic acid displays properties of a ketone in its reactions with aldehydes and dimethyl acetal of DMF [1, 2], while this acid reacts with different amines to give the corresponding derivatives of 3-acetyl-6-methyl-2-(R-amino)-4-pyranone [3].

We attempted to carry out the condensation of dehydroacetic acid with 4-amino-5-trifluoromethyl-4H-1,2,4-triazole-3-thiol (**1**).

The spectral data showed that N^1,N^2-di(3-acetyl-6-methyl-4-oxo-4H-2-pyranyl)hydrazine (**3**) was obtained instead of the expected 3-acetyl-6-methyl-2-(3-mercapto-5-trifluoromethyl-4H-1,2,4-triazol-4-ylamino)-4H-4-pyranone (**2**).



1 **2** **3**

The mass spectral data support this conclusion. The peaks for the molecular ion *m/z* 332 and ion *m/z* 166, which arises upon decomposition of the molecule at the N–N bond, as well as the ions characteristic for the decomposition of such compounds (*m/z* 15, *m/z* 41 (CH=C=O), and *m/z* 443) provide the most structural information. The ion with *m/z* 191 is of a special interest. It can be considered as a product of intramolecular cyclization **4**.

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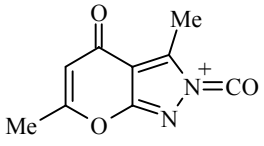

4

However, the reaction does not proceed at all in the attempted condensation of 2-acetyl-4-hydroxy-6-methyl-2H-pyran-2-one and amino thiols with electron-donor substituents such as CH_3, C_2H_5, C_3H_7, and $PhCH_2CH_3$ instead of the trifluoromethyl group.

N^1,N^2-Di[1-(6-methyl-2,4-dioxo-3,4-dihydro-2H-3-pyranyliden)ethyl]hydrazine (3). Mixture of compound **1** (1.84 g, 0.01 mol) and dehydroacetic acid (1.68 g, 0.01 mol) in ethanol (40 ml) was heated at reflux for 3 h and cooled. The colorless precipitate formed was filtered off and dried to give 1.43 g (43%) of compound **3**; mp 110°C (ethanol). ^{1}H NMR spectrum (DMSO-d_6, 500 MHz, TMS as the internal standard), δ, ppm: 2.26 (6H, s, CH_3); 2.57 (6H, s, CH_3); 6.27 (2H, s, CH); 16.52 (2H, s, NH). Mass spectrum, *m/z*: 322 $[M]^+$. Found, %: N 8.27; O 28.7. $C_{16}H_{16}N_2O_6$. Calculated, %: N 8.43; O 28.9.

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ERRATUM

To the article "Imidazo[1,5-*a*]- and Thiazolo[3,4-*a*]quinoxalines Based on 3-(α-Thiocyanobenzyl)-quinoxalin-2(1H)-one" by V. A. Mamedov, A. A. Kalinin, I. Kh. Rizvanov, N. M. Azancheev, Yu. Ya. Efremov, and Ya. A. Levin (Chemistry of Heterocyclic Compounds, Vol. 38, No. 9, pp. 1121-1129, September, 2002).

On page 1128, 1th line of the third paragraph, "3-(α-Chlorobenzyl)-2(1H)-one (**10**)" should read "3-(α-Chlorobenzyl)quinoxaline-2(1H)-one (**10**)".