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SELECTIVE SYNTHESIS OF 1,4-DIMETHYL-1,2,4-TRIAZOL-5-ONE FROM 1-METHYL-5-NITRO-1,2,4-TRIAZOLE AND DIMETHYL SULFATE*

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The alkylation of unsubstituted 3-nitro-1,2,4-triazole with dimethyl sulfate takes place nonselectively with the formation of a complex mixture of products from N-monosubstitution (1-, 2-, and 4-methyl-3-nitro-1,2,4-triazoles) and N,N-disubstitution (nitrotriazolium salts) and 1,4-dimethyl-1,2,4-triazol-5-one (**1**) [2]. The latter is formed here in a very small amount. If the process is conducted with a deficiency of the alkylating agent the yield of **1** does not exceed 3%, and with an excess it is 7%.

During the quaternization of N-monosubstituted nitrotriazoles there is the question of the selectivity of the reaction, which determines to a significant degree its path and products. The main products from the quaternization of N-monosubstituted nitrotriazoles are the N,N-disubstituted salts and the N,N-dialkylnitrotriazolones formed as a result of transformation of the nitrotriazolium ring.

Investigation of the exhaustive alkylation of N-monomethyl-substituted nitrotriazoles with dimethyl sulfate demonstrated the possibility of selective quaternization of the 2-methyl-substituted nitrotriazole with the formation of the triazolone **1**. During the alkylation of 1-methyl-5-nitro-1,2,4-triazole (**2**) with dimethyl sulfate the two $N_{(1)}$ and $N_{(4)}$ nonequivalent atoms of the heterocycle are accessible to attack by the electrophilic agent. Probably, the nitrotriazoles with substituted nitrogen atoms and $N_{(2)}$-substituted nitrotriazoles, in particular, cannot be quaternized at the α-position to the substituent on account of steric hindrances and reduced nucleophilicity. This agrees well with data on the protonation of 1-methyl-5-nitro-1,2,4-triazole, which takes place at the $N_{(4)}$ atom [3]. The process then most probably takes place in the following way. At the first stage attack by the electrophilic agent on the azole heterocycle takes place at the unshared electron pair of the $N_{(4)}$ atom available for coordination or at the π bond with subsequent localization of the substituent at the $N_{(4)}$ atom. Delocalization of the positive charge on the carbon atom at the nitro group leads to the formation of the unstable reactive 1,4-dimethyl-5-nitro-1,2,4-triazolium salt **3**, which is sensitive to the action of nucleophilic reagents. Under the influence of the water the salt **3** changes into the triazolone **1**.

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* Communication 4 of the series "Reactions of derivatives of 3-nitro-1,2,4-triazole with alkylating agents." For Communication 3, see [1].

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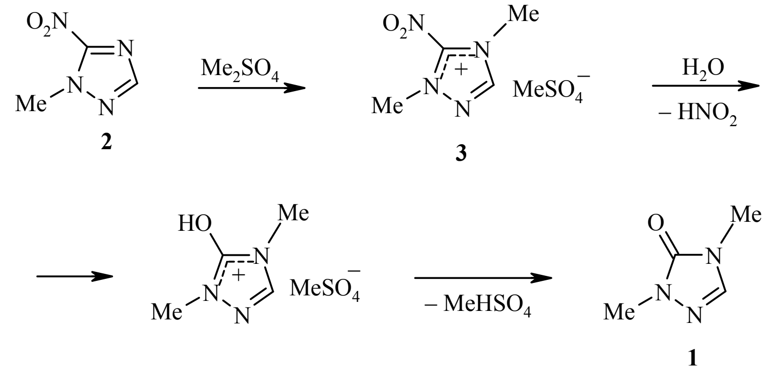
The process goes smoothly at 36-40°C. On heating to 55-60°C there is an uncontrollable exothermic reaction, accompanied by the release of brown gases and ejection of the reaction mass.



Analysis of the reaction mass by GLC showed that the yield of the triazolone **1** after reaction for 14 h amounts to 20.4%, and if the reaction time is increased to 34 h the yield reaches 38.3%.

The synthesized triazolone **1** was characterized by the NMR and IR spectra. The IR spectrum contains a strong band for C=O at 1725 cm^{-1}, characteristic of the carbonyl oxygen atom of N,N-dialkyl-1,2,4-triazol-5-ones [4], and the bands for the out-of-phase and in-phase vibrations of the NO_2 group at 1555 and 1320 cm^{-1}, characteristic of the initial triazole **1**, are absent [1]. In the ^1H NMR spectrum there are two singlets of equal intensity for the protons of the methyl groups at 3.55 and 3.58 ppm.

1,4-Dimethyl-1,2,4-triazol-5-one (3). A suspension of 1-methyl-5-nitro-1,2,4-triazole (9.6 g, 0.075 mol) and dimethyl sulfate (18.9 g, 0.15 mol) was stirred at 36-40°C for 34 h, cooled to 22°C, and separated by one of the following methods: a) 14.5 ml of water and 7.6 g of sodium carbonate were added to the reaction mass with stirring; b) 4.7 ml of water was added to the reaction mass with stirring. The precipitated product was filtered off in a Schott funnel; mp 130-131°C (water). IR spectrum (tablet with potassium bromide), ν, cm^{-1}: 1725 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.55 (3H, s, N–$\underline{CH_3}$); 3.58 (3H, s, N–$\underline{CH_3}$).

REFERENCES

1. G. T. Sukhanov, A. G. Sukhanova, and Yu. V. Il'yasova, *Khim. Geterotsikl. Soedin.*, 1378 (2006). [*Chem. Heterocycl. Comp.*, **42**, 1197 (2006)].
2. G. T. Sukhanov, G. V. Sakovich, A. G. Sukhanova, and A. Yu. Lukin, *Khim. Geterotsikl. Soedin.*, 1168 (2005). [*Chem. Heterocycl. Comp.*, **41**, 994 (2005)].
3. L. I. Bagal and M. S. Pevzner, *Khim. Geterotsikl. Soedin.*, 558 (1970). [*Chem. Heterocycl. Comp.*, **6**, 517 (1970)].
4. A. Bernadini, P. Viallefont, J. Daunis, and M.-L. Roumestant, *Bull. Soc. Chim. France*, 1191 (1975).