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Synthesis of 2-nitromethyl-5-nitro-1,2,3,4-tetrazole

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One of most interesting objects for studying the ability of polyfunctional nucleophiles is the nitromethyl derivatives series of 1,2,3,4-tetrazole, which also have wide practical application.

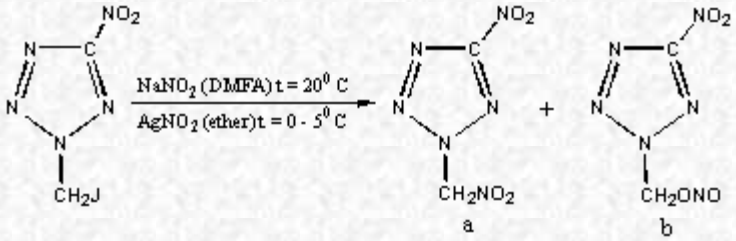
Some derivatives in that series can be used for the synthesis of medicinal preparations, however in the literature there is no information on the synthesis of mononitrometyltetrazoles with nitromethyl's group in position 2.

The aim of this work was to synthesize 2-nitromethyl-5-nitro-1,2,3,4-tetrazole (NMNT) and to investigate its structure.

The synthesis NMNT was performed by several known methods:[1] :

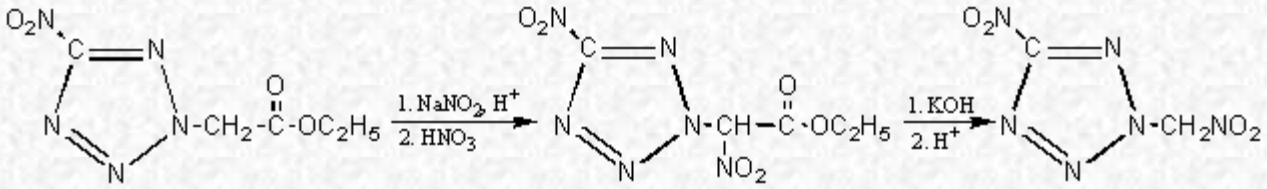
I. by reactions of Kornblume's and Meyer's;
II. by nitrosation of active methylene's compounds with the subsequent oxidation;
III. by nitration of active methylene's compounds with use of the diluted nitric acid and oxides of nitrogen.

The synthesis based on method I which uses 2-iodmethyl-5-nitro-1,2,3,4-tetrazole as starting material is shown in the following scheme:



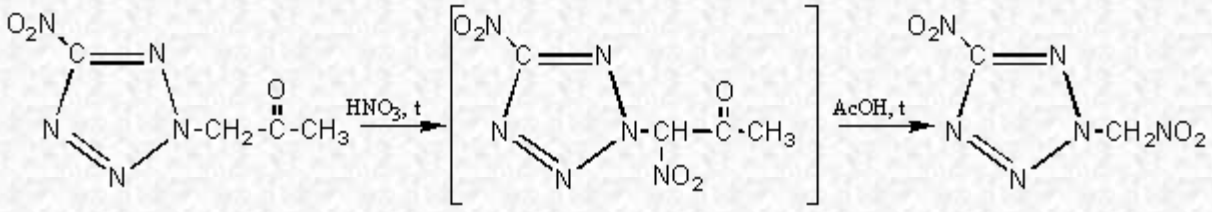
The identification of products from the reaction has not confirmed the presence of NMNT, but has shown that the product of the reaction is 5-nitro-1,2,3,4-tetrazole (NT). The melting point was identical to literature data [2]. It is possible to explain the formation of NT by decomposition of the substance a by joint action of NO_2^- and substance b, parallel formed during reaction.

At use of a method II as an initial product took ethyl 5-nitro-1,2,3,4-tetrazole-2-yl-acetate. Experiments have been done by method, which analogical of described in literature[3], carried out under the following scheme:



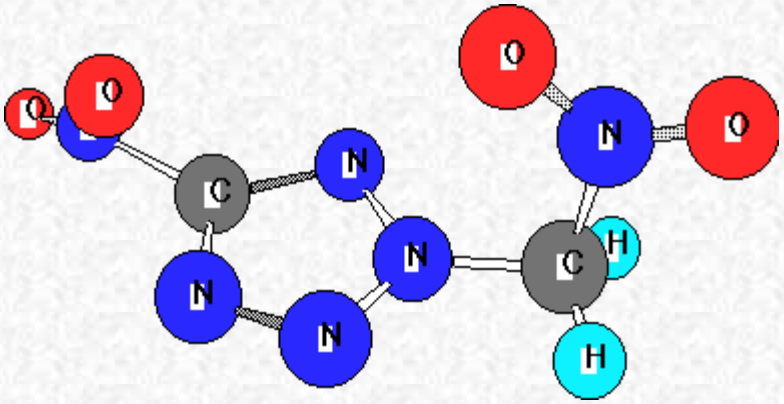
Result of this experiment was received NMNT (yeild 5-10 %). This result drawes conclusion about appling of this method for syntesis of nitromethylene derivates.

On a method III, where as initial took 2-oxopropyl-5-nitro-1,2,3,4-tetrazole (ONT) and acid mixes of structure HNO_3-CH_3COOH-H_2O containing $HNO_3$from 5 up to 30%., the desirable compounds with an yeild 40-45 % under the following sheme was received:



As well as in a method I was allocated NT, that speaks about two possible centres of attack nitrosonium cation of a molecule ONT. First is p-electrons and not divided electronic pairs tetrazolic of a cycle, at which attack there is a break of bond N-CH_2 and is formed NT, and second - activated methylene's the bridge, which at influence nitrosonium cation with oxidation by system HNO_3^- oxides of nitrogen results to NMNT.

The given product was investigated by a method x-ray of the analysis. The result are given below:



Crystal system – monoclinic, Density calculated – 1.800 g/cm^3

Bond	Length	Bond	Length
$N_2 - N_1$	1.323	$N_6 - O_2$	1.217
$N_2 - N_3$	1.330	$N_6 - C_5$	1.441
$N_2 - C_7$	1.430	$C_7 - H_2$	0.955
$C_5 - N_1$	1.310	$C_7 - H_1$	0.974
$C_5 - N_4$	1.338	$C_7 - N_8$	1.503
$N_3 - N_4$	1.302	$N_8 - O_3$	1.203
$N_6 - O_1$	1.216	$N_8 - O_4$	1.220

Experimental:

H^1NMR spectra were obtaned on a Perkin-Elmer R12(60MHz) instruments in acetone D_6 relative HMDS. The IR spectra were recorded on a Nicolet IMPACT-400 with reformative Furye. X-ray research were obtaned on diffractometer Kuma-diffraction KM-4.

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Method II: A solution sodium nitrite 18,4g.(0,27M.) in water (100ml.) was heated for 40 to 50°C, then added ethyl 5-nitro-1,2,3,4-tetrazole-2-yl-acetate. After 2h., the reaction mixture acidity 85% phosphoric acid. The pricipitate was filtered off and dissolved in mixture 57% nitrogen acid(20ml.) and sulphuric acid 93%(40ml.). The reaction mixture was stirred for 1h. at room temperature. Then pricipitate was filtered off, washed with cool water,dried and dissolved in solution of 20% potassium hydrate(30ml.) and stirred for 20h. at room temperature. Cooled to 0 °C and acidify 10% chlorine hydride. Product extracted with either(4 x 30ml.). The solvent was evaporated. The residue crystallized from ethanol. The yield was 1,1g (10%),m.p. 130-132 °C.

Method III: The mixtures of acids(30ml.): acetic acid and nitric acid(68%), m=4:1 was stirred and heated to50-60 °C. Then added 2-oxopropyl-5-nitro-1,2,3,4-tetrazole(2g.,0,012M.). The reaction mixture was stirred for 3h. at 50-60 °C then poured into ice(50g.). The precipitate was filtered off, washed with cool water, dried and crystallized from ethanol.The yield was 0,92g.(45%),m.p. 130-132 °C.

The elementary organic analysis: Found(%): C - 13,63 ; H – 1,18 ; N – 48,39. Calculated(%): C - 13,79 ; H – 1,15 ; N – 48,27. H^1NMR, d: 6,70c(2H,CH_2). IR (cm^{-1}): 1620, 1550, 1320, 1120, 1070, 850.

References

[1] Organic reaction [in Russian], Vol.12: Moscow, 1965, pp. 117-173.

[2] Pat. N562511 (Germany),1932.

[3] A.N.Terpigorev, I.V. Tcelinskii, A.V.Makarevitch, G.M. Frolova, A.A.Melnikov. J.Org.Chem.[in Russian], 1987, XXIII(1), pp. 244-254.
