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STUDIES IN THE FIELD OF CHEMISTRY OF NITRO COMPOUNDS (TO 100TH BIRTHDAY ANNIVERSARY OF S. S. NOVIKOV)

Synthesis of 5-Dinitromethyltetrazole

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Abstract—A convenient method of synthesizing 5-dinitromethyltetrazole on the basis of 1,1-diamino-2,2-dinitroehtilene was developed.

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Several methods of synthesizing 5-dinitromethyltetrazole (**I**) have been published [1–4]. The first method is the synthesis from dinitroacetonitrile ammonium salts (**II**), which, however, results in a low yield (8.8%) of the target tetrazole and is complicated by a necessity of removing bitetrazole (**III**) formed simultaneously [1] (Scheme 1).

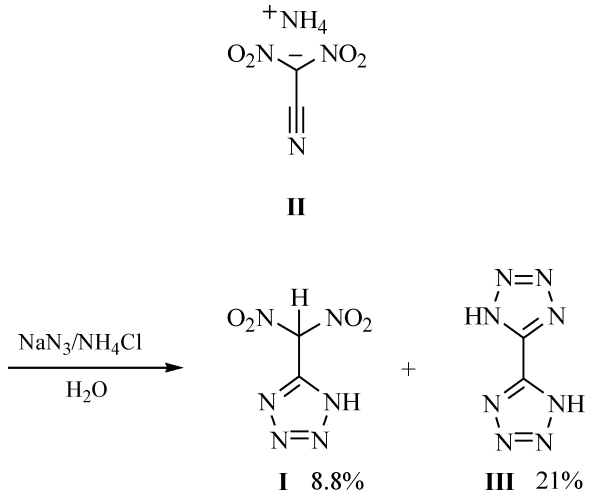
In [2] the reducing denitration of explosive 5-trinitromethyltetrazole (**IV**) is used (Scheme 2).

The method of obtaining monosodium tetrazole salt (**VI**) from amidrazone of dinitroacetic acid (**V**) was described [3] (Scheme 3).

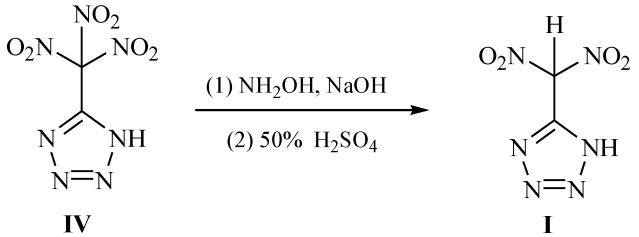
However it is hardly possible to consider this method as comprehensible because of unpredictable behavior of amidrazone (**V**): an occasion of spontaneous explosive decomposition of this compound was described [5]. Recently the two-stage method [4] of obtaining tetrazole (**I**) from ethyl ether of tetrazole-5-ylacetic acid (**VII**) was proposed, and it is highly probable that the intermediately separated product, ethyl ether of dinitrotetrazolylacetic acid (**VIII**), is fairly sensitive (Scheme 4).

A convenient method of the synthesis of 5-dinitromethyltetrazole (DMT) from 1,1-diamino-2,2-dinitroethylene (**IX**) through salt (**X**) without the intermediate isolation of explosive amidrazone (**V**) was developed, which allows obtaining target tetrazole with a high yield (Scheme 5). To carry out the reaction, it is necessary to use three equivalents of sodium nitrite, and in this case formed azide ions are decomposed up to

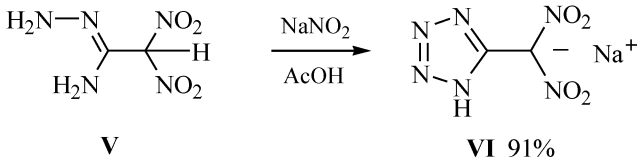
Scheme 1.



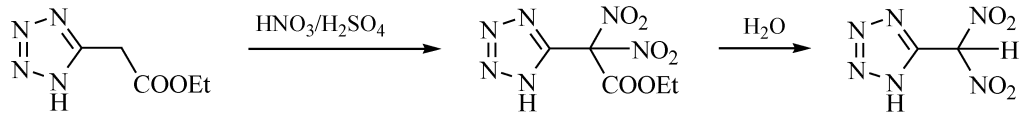
Scheme 2.



Scheme 3.

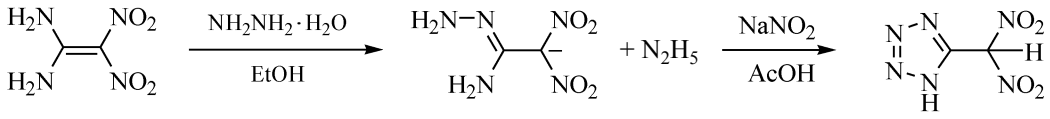


Scheme 4.



VII **VIII** 96% **I** 82%

Scheme 5.



IX **X** 88–94% **I** 87%

a mixture of nitrogen and nitrous oxide (Scheme 5).

A study of the behavior of the synthesized tetrazole has shown that this substance has a sufficiently low thermal resistance: it starts to decompose with a gas evolution at 104–106°C, the second decomposition stage is observed at temperatures higher than 150°C (the crystal phase disappears completely). The observed behavior of compound **I** best agrees with the data [2] [mp 110–112°C (decomposition)]. We note that the literature contains contradicting data not only about the physicochemical characteristics of tetrazole (**I**), but also about properties of salt (**X**). It was synthesized with an essentially smaller yield (about 60% for two stages) in the work [6]. According to the authors of [6], this compound is completely transformed to initial amidrazone (**V**) when stored in an open vessel within 3 days. In none of the works [6–8], in which salt (**X**) is mentioned, the procedure of its obtaining and its characteristics are given in an explicit form. In the present work we have shown that the use of alcohol as a reaction medium allows us to obtain compound **X** with a high yield and without any problems with its storage both in an open and in a closed vessel (the exposure in air within a week has not led to changes in color, aggregate state, decomposition point, and spectral characteristics of this compound). The results of the work of the Korean authors also raise some doubt upon the melting point of 5-dinitromethyltetrazole. Generally the decomposition point given in [4] [mp 122–123°C (decomposition)] drops out of other data on the decomposition points of this substance: according to [1], near 100°C an evolution of nitrogen oxide is observed, according to [2], mp is 110–112°C (with decomposition) and, at last, according to the present work, mp is 104–106°C (with decomposition). Spectral characteristics of the prepared tetrazole in general coincide with the data of [4]. The chemical shift (12.45 ppm) points to the fact that tetrazole (**I**) in DMSO exists entirely in the form of 5-(dinitromethylene)-4,5-dihydro-1*H*-tetrazole, and in less polar deuteroacetone two signals are observed at 8.85 and 6.50 ppm, which most likely points to the presence of a tautomeric equilibrium between the tetrazole and dihydrotetrazole forms. Chemical shifts of NH-protons in the region of 12–14 ppm were observed earlier for hexahydro-1,3,5-triazine derivatives containing a heme-diaminoethylene fragment [9] in their structure, and the chemical shifts of NH-protons for *N,N*'-disubstituted 1,1-diamino-2,2-dinitroethylenes are 8–11 ppm (in DMSO-d_6) [10].

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM300 instrument with TMS as the interior standard, and the IR spectra, on a Specord M82 spectrometer; the melting points were determined on a Boetius table with a heating rate of 4 deg min^{-1}.

1,1-Diamino-2,2-dinitroethylene (IX) was obtained by the procedure described earlier [11] from 2-methyl-4,6-dihydroxypyrimidine, yield 75%, decomposition point >220°C.

Hydrazinium salt of 1,1-diamino-2,2-dinitroethylene (X) was obtained as follows. To a suspension of 1.48 g (10 mmol) of 1,1-diamino-2,2-dinitroethylene in 75 ml of absolute ethanol in a flask equipped with a reflux condenser with a calcium chloride tube filled by a solid alkali, 2 ml of 100% hydrazine hydrate (40 mmol) was added at intensive stirring and heating, brought to boiling, and stirred within 1 h. After cooling precipitated salt

(**X**) was filtered off, washed out with ethanol (3 times, 5 ml each), and dried in air up to a constant weight. Yield 1.73–1.84 g (88–94%), red-orange crystals, mp (decomposition) 120–122°C (at this temperature the crystals lose color and become opaque, and after heating above 160°C they lose the shape). Found (%): C 12.35, H 4.07, N 50.53. $C_2H_9N_7O_4$. Calculated (%): C 12.31, H 4.65, N 50.25.

IR spectrum (KBr), ν, cm^{-1}: 3448, 3371, 3346, 3303, 3260, 3183, 2550, 1665 (NH_2, NH_2NH_3); 1243, 1214, 1109, 1091 (C–N); 1490, 1348, 757 (NO_2). ^1H NMR spectrum, ppm, DMSO-d_6: 5.85 s. ^{13}C NMR spectrum, ppm, DMSO-d_6: 151.25 (N–C=N), 132.50 [$\underline{C}(NO_2)_2$].

To prepare 5-dinitromethyltetrazole (I), to a suspension of 205 mg of salt (**X**) (1.05 mmol) in 5 ml of distilled water we added 205 mg (3.15 mmol) of sodium nitrite with stirring and cooling on a bath with ice, and then within 5 min a solution of 0.5 ml of acetic acid in 1 ml of water (1.5 ml altogether, cautiously, strong gas evolution). The mixture was stirred up to homogenization (30 min–1 h, a transparent yellow solution is formed). Then with strong stirring and cooling we added cautiously 3 ml of concentrated sulfuric acid (slowly in order to prevent heating the mixture above 20°C), extracted with ether (3 times, 20 ml each), passed through a thin layer of calcined sodium sulfate, dried above calcined sodium sulfate, and evaporated. Yield 160 mg of (**I**) (87%): mp 104–106°C (decomposition). Found (%):C 13.86, H 0.91. $C_2H_2N_6O_4$. Calculated (%): C 13.80, H 1.16.

IR spectrum (KBr), ν, cm^{-1}: 3236 (NH); 1583, 1210, 1070, 1045, 1017 (tetrazole), 1523, 1332, 755 (NO_2). ^1H NMR spectrum, ppm, DMSO-d_6: 12.45 br. s. ^{13}C NMR spectrum, ppm, DMSO-d_6: 149.68 (N–C=N), 121.75 [$\underline{C}(NO_2)_2$].

CONCLUSION

A new convenient method of the 5-dinitromethyltetrazole synthesis was developed. On the basis of spectral data it was shown that this compound in DMSO exists in the form of 5-(dinitromethylene)-4,5-dihydro-1*H*-tetrazole, a structural analog of 1,1-diamino-2,2-dinitroethylene.

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