SYNTHESIS OF 5-SUBSTITUTED TETRAZOLES BASED ON THE DISODIUM SALT OF AZOTETRAZOLE. INVESTIGATION OF THE AZOTETRAZOLE-2-(TETRAZOLYL-5)-6-IMINO-1,2,3,4-PENTAZINE MESOION TAUTOMERISM

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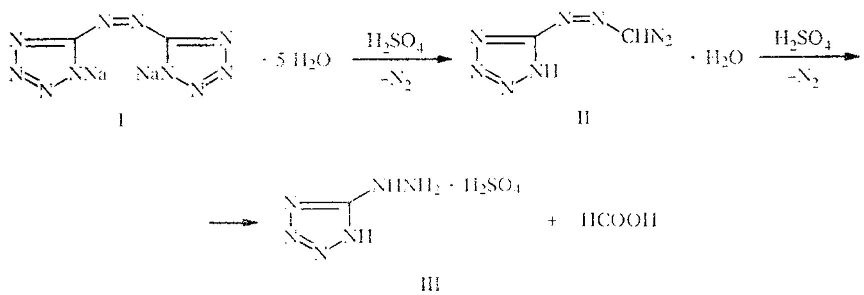
For the example of a salt of azotetrazole, for the first time we have investigated the azotetrazole-1,2,3,4,5-pentazine tautomerism. Upon treatment of an excess of the disodium salt of azotetrazole with dilute sulfuric acid, we isolated 5-substituted tetrazole, which on the basis of analysis data (with introduction of the ^{15}N *isotope into the compound) and study of the chemical properties with sufficiently high probability of assigning the structure of the first representative of the previously unknown class of compounds of the pentazine mesoion: the tetrahydrate of the sodium salt of the 2-(tetrazolyl-5)-6-imino-1,2,3,4,5-pentazine mesoion. We synthesized the dehydrate of the sodium and silver salts of 5-azodiazomethanotetrazole; using derivatography, we have studied the properties of the isolated compounds.*

We know [1] that salts of azotetrazole, in particular the pentahydrate of the disodium salt I, are decomposed in acid medium with formation of 5-azodiazomethanotetrazole II, which under the action of acid is converted to the corresponding 5-salt of hydrazinotetrazole III [1], and upon heating in water gives 5-azohydroxymethyltetrazole [2].



Considering salt I was a prospective synthon for obtaining different 5-substituted tetrazoles (especially for obtaining 5-azo derivatives of tetrazole), we continued research in this direction. We should note that in 5-azo derivatives of tetrazole, the tetrazole ring and the azo group may lie in the same plane and be found in configuration; this should lead to an increase in their stability and in turn should facilitate the possibilities of using them for preparative purposes (the hypothesis that it is possible for the tetrazole ring and the azo group to be coplanar can be made in analogy with data on the coplanarity of the tetrazole ring and the exocyclic N=N bond in the 2-methyl-5-nitroaminotetrazole anion [3]). The results of experiments showed that in dilute acids, salt I rather rapidly decomposes even when cooled down to 1-5°C. These data allow us to assume that evolution of nitrogen is unlikely as a result of decomposition of the tetrazole ring by the intermediate monosodium salt of azotetrazole IV or the tautomeric imidazole V, since the tetrazole–imidazide tautomerism has been studied in a rather detailed fashion and it is known that the tetrazole ring and the imidazides are relatively stable [4-6].

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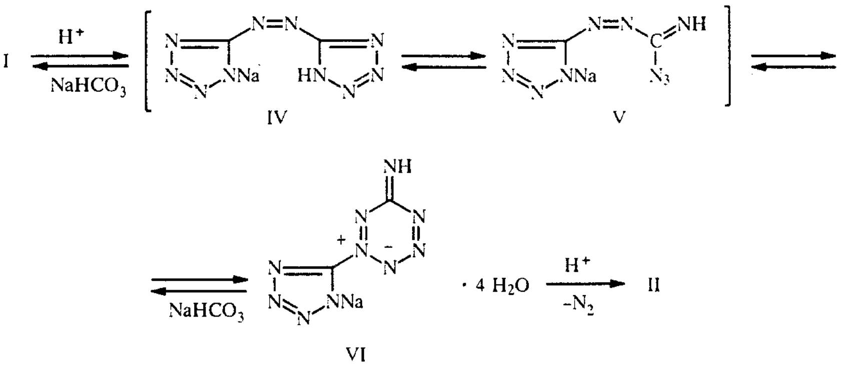
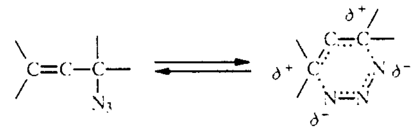
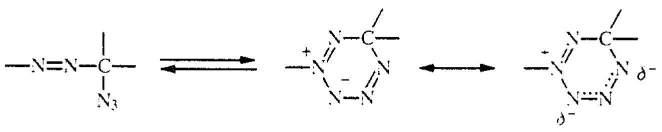


Evolution of nitrogen is more likely in decomposition of another tautomer: the pentazine mesoion VI, since we know that as the number of nitrogen atoms increases in six-membered rings, their stability decreases; and starting with tetrazine (containing four nitrogen atoms one after another), the stability is reduced so much that they are difficult to obtain, although possible in general [7] (however, the stability of these compounds can be increased by introducing certain substituents into the ring [8-10], which made it possible, for example, to isolate stable 1,2,3,4-tetrazine-1,3-dioxide [11]). At the same time, there is no information in the literature about the possibility of obtaining compounds of the pentazine class and examples of azotetrazole–pentazine mesoion tautomerism, although some analogies are known: intramolecular cyclization at the azo group of aromatic azido compounds with abstraction of the nitrogen from the azido group and formation of azapentalene mesoions [5, 12], and also rearrangement of the allylazides which, as assumed, occurs through a cyclic triazine transition state [13, 14].

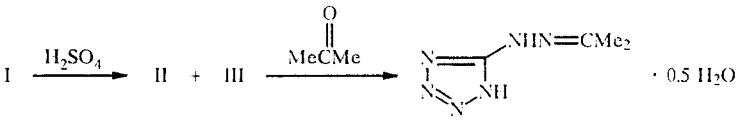


We may assume that such a process also occurs in the case of azoazides



VII

In order to prove the hypothesis of intermediate formation of the pentazine mesoion, we studied the reaction of salt I with sulfuric acid under different conditions. Upon treatment of an excess of compound I with a 3% solution of sulfuric acid (instead of a stoichiometric ratio, as in the technique in [1]), we isolated the sodium salt. On the basis of elemental analysis data, IR spectroscopy (see Table 1), and a study of the chemical properties, we assign the structure of the pentazine mesoion VI to this salt with high probability. The fact that salt VI is a tautomer of the monosodium salt of azotetrazole IV, unambiguously proves that it converts to the starting compound I when treated with an aqueous solution of $NaHCO_3$ (see Table 1). For additional proof of the structure of the isolated salt I, we treated it with a stoichiometric amount of a 3% aqueous solution of sulfuric acid; as a result, the expected compounds II and III were formed (compound III was isolated in the form of its derivative, the hydrazone VIII).

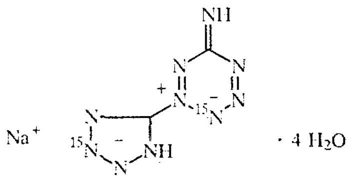


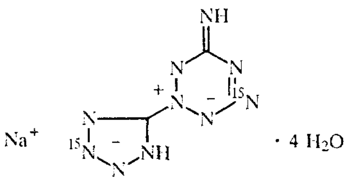
VIII

The IR spectrum of salt VI does not contain absorption bands from the azido group in the 2100-2200 cm^{-1} region; according to literature data [15], for azidotetrazole tautomerism, this excludes existence of imidazides, in particular the tautomeric structure V. A characteristic feature of the IR spectrum of pentazine VI is the presence of relatively rarely encountered absorption bands in the 1938 cm^{-1} region, characteristic for allene structures [16, 17]. We can assume that the indicated absorption band is due to the moiety

$$-\mathrm{N}^{-}-\mathrm{N}=\mathrm{N}- \rightleftarrows -\mathrm{N}^{\delta-}\cdots\mathrm{N}\cdots\mathrm{N}^{\delta-}-$$

of the pentazine ring VII (the indicated moiety has a certain similarity to the allene group $=\mathrm{C}=\mathrm{C}=\mathrm{C}=$). To prove this hypothesis, we compared the IR spectra of pentazine VI, containing only $^{14}\mathrm{N}$ isotopes, and mixtures of the pentazines IX and X, also containing $^{15}\mathrm{N}$ isotopes in the moiety of interest to us.


IX


X

For synthesis of a mixture of pentazines IX and X, we used a method for introducing $^{15}\mathrm{N}$ isotopes into the azide group which is similar to the method of introducing the $^{15}\mathrm{N}$ isotope into the azide group of phenylazide by diazotization of phenylhydrazine using $\mathrm{H}^{15}\mathrm{NO}_2$ [5].

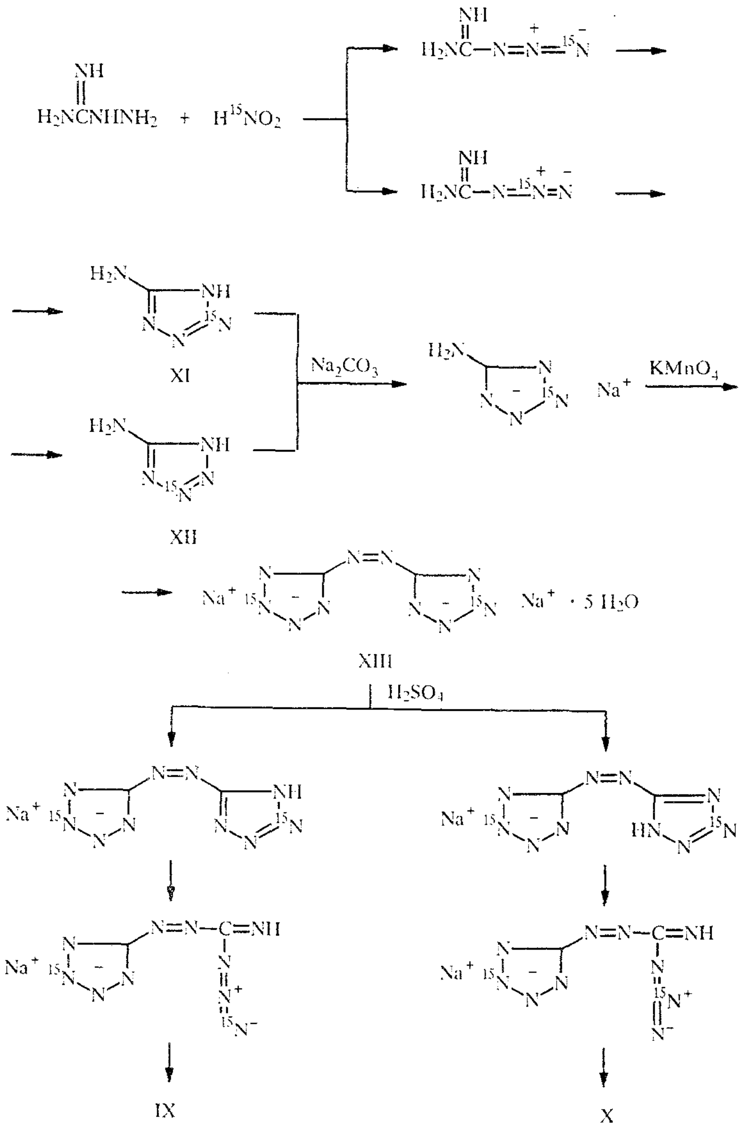


TABLE 1. Spectral Data for 5-Substituted Tetrazoles I, II, VI, VIII, XIX, XX, Mixture of IX and X, Mixture Containing XVII and XVIII

Compound	Empirical formula	IR spectra, ν, cm^{-1}	Yield, %
I	$C_2N_{10}Na_2 \cdot 5\ H_2O$	1050, 1070, 1100, 1170, 1205, 1410 (anion tetrazole ring), 1615[1*] (N=N), 3260...3470 (crystallization water)	81
II	$C_2H_2N_8 \cdot H_2O$	980, 1070, 1129 (tetrazole ring), 1584 (N=N), 2160 (diazo group, br) 3232 (water of crystallization)	42[2*]
VI	$C_2HN_{10}Na \cdot 4\ H_2O$	995, 1050, 1100, 1165, 1200, 1410 (anion tetrazole ring) 1636 (C=N), 1938 (N-N=N pentazine ring) 3410...3470 (water of crystallization) br. 3570 (NH)	41
VIII	$C_4H_8N_6 \cdot 0{,}5\ H_2O$	960, 1010, 1140 (tetrazole ring) 1660 (C=N), br. 3230 (crystallization water) [4*]	66
IX, X	$C_2HN_{10}Na \cdot 4\ H_2O$	928, 1024, 1072, 1144, 1192, 1400 (anion (tetrazole ring) 1632 (C=N), 1920 (N-N=N pentazine ring) 3392...3512 (water of crystallization) br. 3576 (NH)	16
XVII, XVIII	$C_2H_2N_8 \cdot H_2O$	944, 1016, 1068, 1168 tetrazole ring) 1584 (N=N), 2144 (diazo group) br. 3232 (crystallization water)	28
XIX	$C_2HN_8Na \cdot 2\ H_2O$	995, 1070, 1170, 1205, 1400 (anion tetrazole ring) 1585 (N=N), 2154 (diazo group) 3240...3430 (water of crystallization)	76[5*]
XX	$C_2HN_8Ag \cdot 2\ H_2O$	—	97

[1*] IR spectrum identical to IR spectrum of reference salt [18].

[2*] Yield when obtained from salt I; yield when obtained from pentazine VI by treatment with H_2SO_4, 35%; by treatment with water, 9%; yield when obtained from salt XIX, 67%.

[3*] IR spectra identical to IR spectrum of reference compound [1].

[4*] IR spectrum identical to IR spectrum of reference compound [1].

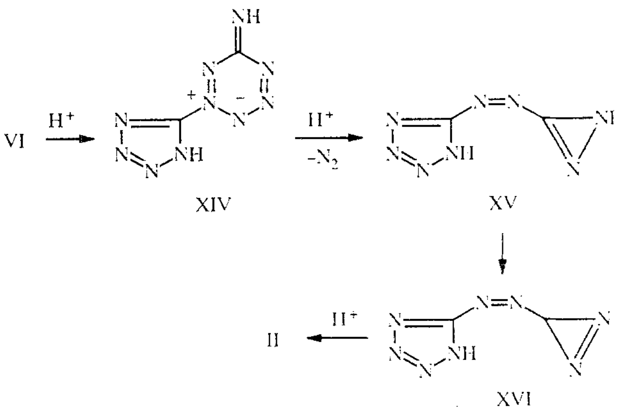
[5*] Yield when carrying out reaction at 20°C; yield when carrying out reaction at 50°C, 66%.

As expected, introducing ^{15}N isotopes into the pentazine ring caused a marked shift of the above-indicated absorption band (from 1938 to 1920 cm^{-1}); this agrees well with the hypothesis that the 1938 cm^{-1} band corresponds to absorption of the $-N^{-}-N=N-$ moiety of the pentazine ring. We should note that introducing the ^{15}N isotope into the tetrazole ring of compound VI (compounds IX and X) also considerably shifts its absorption bands (see Table 1).

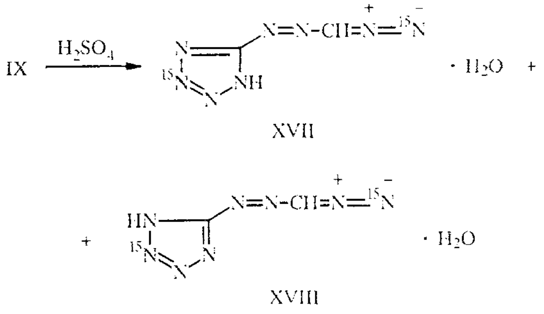
For additional proof of the presence of water of crystallization in pentazine VI, we synthesized it in a mixture of $D_2O-H_2O-D_2SO_4$. As expected, in the IR spectrum of the isolated compound a broad absorption band appeared at 2500 cm^{-1}, characteristic for crystallization of D_2O.

Treatment of pentazine VI with 3% sulfuric acid leads to evolution of nitrogen and formation of the diazo compound II; from this it follows that pentazine VI probably is an intermediate in synthesis of compound II from salt I in an acid medium. In discussion of the mechanism for the formation of the diazo compound II, we can assume that as a result of evolution of nitrogen from pentazine XIV, at first the unstable 1H-diazirine XV is formed [7], which is successively isomerized to the more stable 3H-diazirine XVI [7], and then to the diazo compound II (in the literature, it is indicated that isomeric diazirine–diazo compound conversions are possible [18], including the possibility of isomerization in an acid medium [19]) (see scheme on top of following page).

For decomposition of pentazine XIV, abstraction of the $N_{(4)}$ and $N_{(5)}$ or $N_{(3)}$ and $N_{(4)}$ nitrogen atoms of the pentazine ring is most likely. In order to resolve this question, we treated a mixture of pentazines IX and X with 3% sulfuric acid. We might expect that in the case of abstraction of the $N_{(3)}$ and $N_{(4)}$ atoms, ^{15}N isotopes should not be present in the diazo group

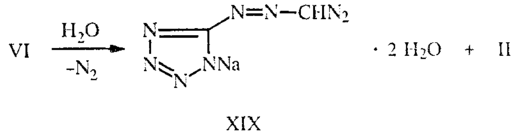


of the compound formed; if the $N_{(4)}$ and $N_{(5)}$ nitrogen atoms are abstracted, then in the case of decomposition of pentazine IX, the diazo group of compounds XVII, XVIII should contain the ^{15}N isotope.

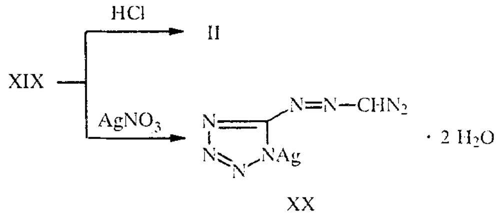


The results of experiments in this direction have shown that the substance formed contains the ^{15}N isotope in the diazo group (shift of the absorption band of the diazo group from 2160 to 2144 cm^{-1}); this is consistent with abstraction of the $N_{(4)}$ and $N_{(5)}$ nitrogen atoms from the pentazine ring.

Pentazine VI also decomposes with evolution of nitrogen when dissolving in water or organic solvents (for example, in DMF, DMSO) even with cooling (for precisely this reason, we could not take its Raman and PMR spectra). Upon heating a solution of pentazine VI in water, we isolated the dihydrate of the sodium salt XIX; upon prolonged holding of the solution of pentazine VI in water without heating, along with the salt XIX, we isolated a small amount of compound II.



The structure of salt XIX has been additionally confirmed by chemical conversions: Upon its treatment with dilute hydrochloric acid or an aqueous solution of silver nitrate, we isolated respectively the diazo compound II or the dihydrate of the silver salt XX.



We should note that for compounds II, VI, XIX, and XX we could not determine the carbon and hydrogen content, since they exploded upon heating during the analysis. The salt XX also exploded upon attempts to determine the nitrogen content; due to the high risk, we also did not carry out IR spectroscopy. When attempting to take the mass spectrum of pentazine VI, we also observed decomposition with explosion. Accordingly, we assessed the thermal stability of the synthesized compounds by derivatography. The results of the experiments showed that upon heating the tetrahydrate of pentazine VI from 50 to 70°C, two water molecules are lost (the first endothermic effect); further heating up to 90°C leads to loss of one more water molecule (the second endothermic effect), and the remaining monohydrate of pentazine decomposes with explosion at 90°C. The sodium salt XIX has higher thermal stability than the corresponding acid II. Upon heating compound II up to 96°C, the water of crystallization is lost (endothermic effect); at 130°C, rapid decomposition of the material begins, ending at 142°C with explosion. The dihydrate of salt XIX loses one water molecule upon heating up to 63°C (first endothermic effect); then we observe a second endothermic effect without a pronounced maximum, corresponding to loss of a second water molecule. The temperature of onset of rapid decomposition of the compound is 137°C; the temperature of rapid decomposition (without explosion) is 164°C.

The dihydrate of the silver salt XX loses one water molecule upon heating up to 80°C (first endothermic effect); then we observe a second endothermic effect without a pronounced maximum, corresponding to loss of the second water molecule. The temperature of onset of rapid decomposition of the material is 117°C; at 125°C, it explodes. The data obtained show that among the synthesized compounds, the most thermally unstable is pentazine VI.

EXPERIMENTAL

The IR spectra were recorded for KBr disks on UR-20 and Specord-M80 spectrometers. The derivatograms were taken on the Derivatograph system of F. Paulik, J. Paulik, and L. Erdey in air with heating rate 5°C/min. A mixture of 5-aminotetrazoles containing ^{15}N isotopes (compounds XI and XII) was synthesized according to the technique in [20] using $Na^{15}NO_2$ and $H^{15}NO_3$. The starting pentahydrate of the disodium salt of azotetrazole containing ^{15}N isotopes (compound XIII) was synthesized according to the technique in [21] using a mixture of 5-aminotetrazoles XI, XII.

The elemental analysis data for compounds I, VI, and XIX and a mixture of products IX and X on N and Na; for compounds II and VIII and a mixture containing the products XVII and XVIII on N; for compound XX on Ag correspond to the calculated values.

Pentahydrate of the Disodium Salt of Azotetrazole (I). Pentazine VI 1.27 g (4.88 mmoles) was added with stirring for 20 min to a solution of 0.44 g (5.24 mmoles) $NaHCO_3$ in 5 ml water, held for 30 min, and heated at 95°C until evolution of carbon dioxide stopped. After cooling the solution, the precipitating crystals of salt I were filtered.

Hydrate of 5-azodiazomethanotetrazole (II) and the Hydrate of 5-(1,2-Aza-3-methyl-2-butene)tetrazole (VIII). A 32-ml sample of 3% sulfuric acid was added dropwise to a suspension of 3 g (10 mmoles) salt I in 50 ml water with stirring, held for 2 h, and allowed to stand for 15-20 h. The precipitate of diazo compound II was filtered, washed with water and ethanol. The filtrate obtained, containing salt III, was neutralized with Na_2CO_3 to pH 5-6. Concentrated HCl (0.5 ml) was added, and acetone was added until the inorganic salts precipitated out. The precipitating salts were filtered, and after removal of the solvent from the filtrate, the remaining residue was washed with acetone (3 × 25 ml). After removal of the acetone and crystallization of the remaining material from acetone, we obtained hydrazone VIII with T_{mp} 175-176°C (according to the data in [1], T_{mp} is 175-176°C).

Hydrate of 5-Azodiazomethanotetrazole (II) and Dihydrate of Sodium Salt of 5-Azodiazomethanotetrazole (XIX). A solution of 0.5 g (1.92 mmoles) pentazine VI in 9.5 ml water were held for 7 days. The precipitate of compound II was filtered, washed with water and ethanol. After removal of the solvent from the filtrate, the remaining salt XIX was washed with ethanol.

Hydrate of 5-Azodiazomethanotetrazole (II). A. Pentazine VI (1.43 g, 5.5 mmoles) was added to 9 ml 3% sulfuric acid with stirring at a rate avoiding vigorous foaming. After holding for two hours, the precipitate II was filtered, and washed with water and ethanol.

B. Hydrochloric acid (0.5 N) was added to a solution of 0.2 g (1.02 mmoles) salt XIX in 50 ml water to a value of pH ≈4.0 and it was allowed to stand for 10 h. The precipitate II was filtered and washed with ethanol.

Tetrahydrate Sodium Salt of 2-(Tetrazolyl-5)-6-imino-1,2,3,4,5-pentazine Mesoion (VI). A 12-ml portion of 3% sulfuric acid was added dropwise with stirring for 5-7 sec to a suspension of 3 g (10 mmoles) salt I in 20 ml water. The suspension was filtered and the precipitate fell out of the filtrate. The precipitated pentazine VI was filtered and washed with 1 ml water and 2.5 ml acetone.

Tetrahydrates of Sodium Salts of 2-(Tetrazolyl-5)-6-imino-1,2,3,4,5-pentazine Mesoion Containing ^{15}N Isotopes (IX, X). The synthesis was carried out according to the above-indicated technique for obtaining compound VI, using XIII as the starting compound.

Hydrates of 5-Azodiazomethanotetrazoles Containing ^{15}N Isotopes (XVII, XVIII). These were synthesized according to the above-indicated technique (A) using a mixture of compounds IX and X as the starting material.

Dihydrate of Sodium Salt of 5-Azodiazomethanotetrazole (XIX). A suspension of 0.5 g (1.92 mmoles) pentazine VI in 3 ml water was heated up to 50°C and held at this temperature until evolution of nitrogen stopped. After cooling the solution down to 10°C, the precipitated salt XIX was filtered and washed with 0.5 ml water and acetone. An additional amount of salt XIX was obtained after removal of water from the filtrate.

Dihydrate of Silver Salt of 5-Azodiazomethanotetrazole (XX). A solution of 0.28 g (1.65 mmoles) silver nitrate in 5 ml water was added with stirring to a solution of 0.2 g (1.02 mmoles) salt XIX in 35 ml water and allowed to stand for 2 days. The precipitated salt XX was filtered and washed with water and ethanol.

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