mole) of 4-chlorobenzaldehyde, and 0.1 g of NH_4Cl in 30 ml of dry methanol for 1 h. Aziridinyl ketone was dissolved, and sediment of the product of the reaction immediately began to precipitate. The flask was sealed and left at room temperature overnight and then placed in the refrigerator for 2-3 days. The precipitated sediment was filtered off and washed with water, aqueous methanol (1:1), and alcohol. Then 3.7 g (96%) of a mixture of *endo*- and *exo*-isomers of XIa, b was obtained. Fractional crystallization from dioxane—isopentyl acetate mixture, 2:1, produced 1.06 g of prismatic crystals of IXa and 0.3 g of needle-shaped crystals of IXb.

Compounds VIIa, VIIIa, and **X-XII** were obtained analogously.

LITERATURE CITED

1. Z. Kaluski, E. Gzhesyak-Figac, N. P. Vorob'eva, A. I. Bakumenko, F. G. Yaremenko, and V. D. Orlov, Khim. Geterosikl. Soedin., No. 8, 1064 (1989).
2. J. Do Minh and A. M. Trozzolo, J. Am Chem. Soc., **92**, 6997 (1970).
3. J. Do Minh and A. M. Trozzolo, J. Am. Chem. Soc., **94**, 4046 (1972).
4. A. Padwa, S. Clough, and E. Glazer, J. Am. Chem. Soc., **92**, 1778 (1970).
5. A. Padwa and E. Glazer, J. Am. Chem. Soc., **94**, 7788 (1972).
6. H. W. Heine, A. B. Smith, and J. D. Bower, J. Org. Chem., **33**, 1097 (1968).
7. H. W. Heine, R. H. Weese, and R. A. Cooper, J. Org. Chem., **32**, 2708 (1967).
8. Organic Electronic Spectral Data, Vol. 6, Interscience, New York (1962-1963), pp. 111, 116, 164, 178.
9. Organic Electronic Spectral Data, Vol. 12, Interscience, New York (1970), p. 64.
10. V. D. Orlov, F. G. Yaremenko, and V. F. Lavrushin, Khim. Geterosikl. Soedin., No. 11, 1489 (1980).

N-NITRATION OF 1(2)-SUBSTITUTED 5-AMINOTETRAZOLES WITH TETRANITROMETHANE

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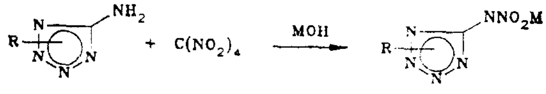
1(2)-Methyl-5-aminotetrazoles and 2-(β-cyanoethyl)-5-aminotetrazole are nitrated by tetranitromethane in the presence of bases with the formation of salts of the corresponding 5-nitroaminotetrazole derivatives. In contrast to this, decyanoethylation takes place in nitration of 1-(β-cyanoethyl)-5-aminotetrazole by tetranitromethane with the formation of 5-nitroaminotetrazole salt. The structure of the 2-methyl-5-nitroaminotetrazole salts (using the 2-methyl-5-nitroaminotetrazole potassium salt) was confirmed by x-ray structural analysis.

Weakly basic aromatic amines are known [1, 2] to react with tetranitromethane in basic medium, forming N-nitroamines. Only anilines containing substituents in the *meta*- or *para*-positions are nitrated. There are published data on N-nitration of unsubstituted 5-aminotetrazole by tetranitromethane [3] and obtaining N-nitroamines from compounds I and II by treatment of the corresponding nitrate salts with sulfuric acid is described [4, 5]. The possibility of N-nitration of 5-aminotetrazole derivatives containing substituents in positions 1 or 2 with tetranitromethane has not yet been studied. We investigated the possibility of N-nitration of 1(2)-substituted 5-aminotetrazoles I-IV, which are weak bases ($pK_{BH^+} = 1.75$ for I and $pK_{BH^+} = 1.81$ for II [6]), with tetranitromethane.

The results of the experiments showed that only compounds I-III are smoothly nitrated into the corresponding 5-nitroaminotetrazole salts (see Table 1).



I-III V-XIV

I R=CH_3-2; II R=CH_3-1; III R=CH_2CH_2CN-2

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TABLE 1. Characteristics of 1(2)-Substituted 5-Nitroaminotetrazoles V-XIV and 5-Nitroaminotetrazole XV

Compound	Empirical formula	R	M	T, °C*	Yield, %
V	$C_2H_7N_7O_2$	2-CH_3	NH_4	211	80
VI	$C_2H_3LiN_6O_2$	2-CH_3	Li	286	60
VII	$C_2H_3N_6NaO_2$	2-CH_3	Na	325	80
VIII	$C_2H_3KN_6O_2$	2-CH_3	K	282	80
IX	$C_2H_3N_6O_2Rb$	2-CH_3	Rb	270	85
X	$C_2H_3CsN_6O_2$	2-CH_3	Cs	—	74
XI	$C_4H_4N_7NaO_2$	2-CH_2CH_2CN	Na	—	68
XII	$C_2H_7N_7O_2$	1-CH_3	NH_4	195	70
XIII	$C_2H_3N_6NaO_2$	1-CH_3	Na	248	65
XIV	$C_2H_3KN_6O_2$	1-CH_3	K	—	67
XV	$C_1N_6Na_2O_2$	—	Na	337	70

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*T: temperature of intense decomposition.

TABLE 2. Polarographic Characteristics of Compounds VII, XIII, XV (in the H form) and Standard Samples of N-Nitroaminotetrazoles XVI-XVIII*

pH	Compound XVI				Compound XVII				Compound XVIII			
	i^{I}, μA	$-E^{\mathrm{I}}_{1/2}$, V	i^{II}, μA	$-E^{\mathrm{II}}_{1/2}$, V	i^{I}, μA	$-E^{\mathrm{I}}_{1/2}$, V	i^{II}, μA	$-E^{\mathrm{II}}_{1/2}$, V	i^{I}, μA	$-E^{\mathrm{I}}_{1/2}$, V	i^{II}, μA	$-E^{\mathrm{II}}_{1/2}$, V
−1,21	2,368	0,536	—	—	1,092	0,487	—	—	2,464	0,499	—	—
−0,64	2,880	0,524	—	—	1,344	0,489	—	—	3,232	0,516	—	—
−0,30	3,072	0,540	—	—	1,440	0,506	—	—	3,216	0,529	—	—
0,01	—**	—**	—**	—**	1,488	0,538	—	—	3,264	0,563	—	—
0,40	3,088	0,614	—	—	1,560	0,585	—	—	3,312	0,607	—	—
0,78	2,608	0,642	1,200	1,051	1,242	0,650	—	—	2,992	0,649	1,712	1,037
1,14	2,352	0,653	1,664	1,052	1,092	0,702	0,882	1,026	2,816	0,710	2,016	1,058
1,40	2,102	0,673	1,856	1,053	0,990	0,745	0,948	1,038	2,272	0,732	2,560	1,045
1,61	1,856	0,683	2,080	1,061	0,828	0,758	1.128	1,033	1,840	0,745	2,960	1,038
2,04	1,712	0,724	2,384	1,079	—	—	1,302	1,035	—	—	3,184	1,047
2,32	—**	—**	—**	—**	—	—	1,818	0,995	—	—	4,384	1,015
2,63	—**	—**	—**	—**	—	—	1,932	1,036	—	—	4.480	1,045
3,06	—	—	2,528	1,135	—	—	1,800	1,104	—	—	4,638	1,131
3,55	—	—	3,910	1,097	—	—	1,680	1,178	—	—	3,952	1,186
3,94	—	—	3,632	1,159	—	—	1,158	1,222	—	—	2,720	1,249

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*Due to the practical coincidence of the values of i and $E_{1/2}$ for the synthesized and standard samples of the N-nitroaminotetrazoles, only the values for standard samples XVI-XVIII are reported for brevity: $4.573 \cdot 10^{-4}$ (XVI); $2.029 \cdot 10^{-4}$ (XVII); $4.734 \cdot 10^{-4}$ M (XVIII). [i^{I}, $E^{\mathrm{I}}_{1/2}$: limiting currents and half-wave potentials of the first wave; i^{II} and $E^{\mathrm{II}}_{1/2}$: limiting currents and half-wave potentials of the second wave.]

**The values were not determined.

Decyanoethylation occurs in nitration of amine IV with the formation of the 5-nitroaminotetrazole salt (see Table 1).

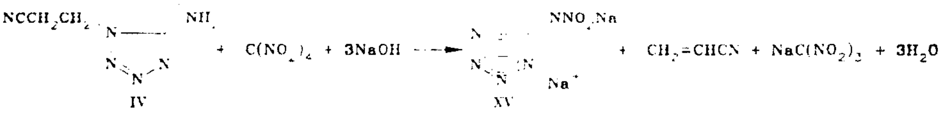

TABLE 3. Coordination Environment of Potassium Cation in Crystals of Salt VIII

K*	Distance l, Å	K*	Distance l, Å	K*	Distance l, Å
$K\cdots O_{(62)}$	2,780	$K\cdots O_{(61)}$**	2,822	$K\cdots N_{(3)}$	2,949
$K\cdots O_{(62)}$	2,863	$K\cdots N_{(5)}$**	3,095	$K\cdots N_{(1)}$	2,932
$K\cdots O_{(61)}$	2,797	$K\cdots N_{(4)}$	2,869		

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*K: coordination of the potassium cation with neighbors.

**Atoms in the molecule of salt VIII to which the potassium anion is related.

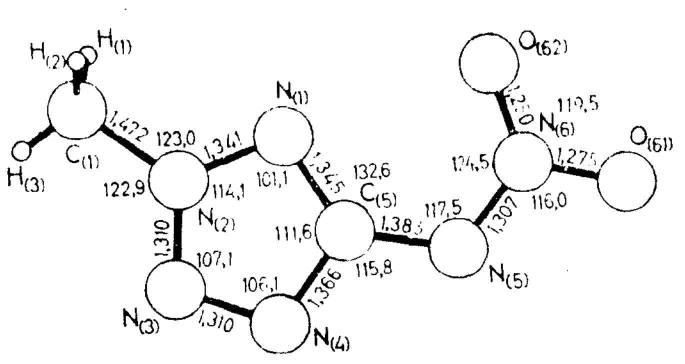


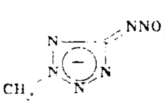
Fig. 1. Structure of the anion of salt VIII: bond lengths, Å; angles, degrees.

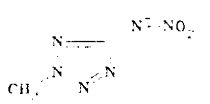
The IR spectra of sodium (VII, XI, XIII) and ammonium (XII) salts contain absorption bands corresponding to the NO_2^- group (at 1570 and 1280 cm^{-1}). The structure of the N-nitroaminotetrazoles obtained is additionally confirmed by the agreement of the polarographic characteristics (limiting currents (i) and half-wave potentials ($E_{1/2}$) as a function of the pH of the medium) for products VII, XIII, XV [in the H form, respectively, 2 methyl-5-nitroaminotetrazole (XVI), 1-methyl-5-nitroaminotetrazole (XVII), 5-nitroaminotetrazole (XVIII)], and standard samples of these N-nitroaminotetrazoles [4, 5, 7] (see Table 2).

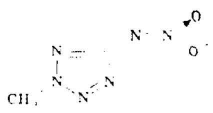
In contrast to aromatic N-nitroamines [8], not one, but two reduction waves were observed in polarography of N-nitroaminotetrazoles for different pH of the medium. This is perhaps due to protonation of N-nitroaminotetrazoles in acid media [5], resulting in reduction of the protonated form (first wave) in more acid medium (pH 1.21-1.61) and of the unprotonated form (second wave) in less acid medium (pH 0.78-3.94).

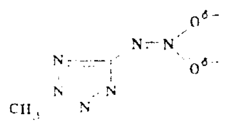
The structure of salt VIII was confirmed by x-ray structural analysis (the salt was prepared for analysis by crystallization from 60% aqueous ethanol).

The following saturated structures of the anion of salt VIII are theoretically possible


XIX


XX


XXI


XXII

The NO bonds are equivalent in the anions of salts of aliphatic N-nitroamines, and alkali metal cations are coordinated with the negatively charged oxygen atoms in the nitro group [9-13]. In contrast to this, the NO bonds in the anion of salt VIII are not equivalent ($N_{(6)}$—$O_{(61)}$ bond 1.275, $N_{(6)}$—$O_{(62)}$ bond 1.250 Å, see Fig. 1), and the potassium cation is coordinated with eight negatively charged atoms of five anion molecules, namely: wtih four oxygen atoms of three anion molecules, with three nitrogen atoms of three tetrazole fragments, and with the amine nitrogen atom (see Table 3).

The $N_{(5)}—N_{(6)}$ bond is unsaturated (1.307 Å), while the $N_{(2)}—N_{(3)}$ and $N_{(3)}—N_{(4)}$ bonds are equal (1.310 Å), which indicates their delocalization. The structure of the anion of salt VIII can thus be considered as intermediate between the structures of the boundary structures of XIX-XXII with a larger contribution of structure XXI (nonequivalence of NO bonds).

It is also possible that the cation can basically be coordinated with either nitrogen atoms or with oxygen atoms as a function of the nature. The formation of the N-isomer exclusively in alkylation of the silver salt of compound XVI with methyl iodide (in contrast to alkylation of the silver salts of other N-nitroamines, where O-isomers are basically formed) can be attributed to coordination of the silver cation by nitrogen atoms (structures XIX, XX), for example [14].

It should be noted that since the anion of salt VIII is planar (except for the methyl group), this should cause effective conjugation of the tetrazole ring and the unsaturated $N_{(5)}—N_{(6)}$ bond (structures XXI, XXII). For this reason, it is not possible to reject the hypothesis that the H form of the anion (compound XVI) could be found in the tautomeric isonitroamine form.

A comparison of the results of N-nitration of 1(2)-substituted 5-aminotetrazoles and N-nitration of 5-aminotetrazole with tetranitromethane [3], and 3-amino-1,2,4-triazole and its derivatives [15] shows that aminotriazoles are not nitrated in the presence of ammonium hydroxide, while aminotetrazoles yield ammonium salts of the corresponding N-nitroamines in these conditions. With respect to the previously proposed radical anion mechanism of N-nitration in [15], it is probably due to the fact that deprotonation of weakly basic aminotetrazoles at an amine group with formation of the corresponding N-anions takes place at pH ~ 11.5 (ammonium hydroxide solution) and deprotonation of more basic aminotriazoles does not take place. The decrease in the basicity of the heterocycle in substitution of a carbon atom by a nitrogen atom can be estimated by comparing the pK_a of the N-nitroamine group bound with these heterocycles: pK_a for 3-methyl-5-nitroamino-1,2,4-triazole is 4.75 [16], 4.80 [17]; 4.30 for 3-nitroamino-5-methyl-1,2,4-triazole [16]; 1.48 for compound XVI [5] (such a comparison is acceptable if the N-nitroamines examined are in the same tautomeric forms).

EXPERIMENTAL

The IR spectra were made on an IKS-29 spectrophotometer in a thin layer (petrolatum) and in KBr pellets. The X-ray structural analysis was conducted in a Syntex four-disk automatic diffractometer (λ_{Mo} radiation, graphite monochromator). A total of 942 nonzero reflections was experimentally measured. The structure was interpreted and the coordinates of the K, C, N, O atoms were more precisely defined in the anisotropic approximation on PC—XT with the SHELX software package. The final value of the R factor was 0.044. The precision of the determination was ± 0.005-0.008 Å, $\omega \pm 0.5°$. The crystals of salt VIII are rhombic and the unit cell parameters are: $a = 7.593(6)$, $b = 10.795(8)$, $c = 8.163(6)$ Å, $V = 669.1(8)$ Å^3; $d_{calc} = 1.809$ g/cm^3; $Z = 4$. Fedorov group P at 2_1.

The temperature of intense decomposition was determined on a DTA-5 thermal analyzer; the samples were heated in an atmosphere of nitrogen with a 10°C/min temperature elevation rate. An ON-102 polarograph was used for studying the i and $E_{1/2}$ as a function of the pH of the medium. The polarograms were made in a thermostated cell at 25±0.1°C. The characteristics of the dropping mercury electrode with induced drop separation were: $m = 1.547$ mg/sec, $\tau = 0.25$ sec. The potential was measured relative to a saturated Calomel electrode. The pH of the solutions were determined on a pH-340 pH-meter. Aqueous solutions of H_2SO_4 and acetate, citrate—phosphate, and borate buffer solutions brought to an ionic strength of 1.0 with Na_2SO_4 were used as the background. The data from elementary analysis of compounds V-XV for N and metal (Li, Na, K, Rb, Cs) corresponded to the calculated data. The data from the analysis of compounds V and XII for the concentration of NH_4 groups corresponded to the calculated data.

2-Methyl-5-nitroaminotetrazole Ammonium, Lithium, Sodium, Potassium, Rubidium, and Cesium Salts (V-X). 1-Methyl-5-nitroaminotetrazole Ammonium, Sodium, and Potassium Salts (XII-XIV). Here 24.2 ml (202 mmole) of tetranitromethane was poured into a solution of 1 g (101 mmole) of amine I (or II) in aqueous hydroxide. For amines I and II, respectively, the amounts were 140 ml and 780 ml of 25% ammonium hydroxide. The amount of the other hydroxides and water were: 350 ml H_2O for 21.2 g (505 mmole) of $LiOH \cdot H_2O$; 360 ml H_2O for 20.2 g (505 mmole) NaOH; 360 ml H_2O for 28.3 g (505 mmole) KOH; 360 ml H_2O for 51.7 g (505 mmole) RbOH; 360 ml H_2O for 75.7 g (505 mmole) CsOH. The reaction mass was stirred for 6 h at 20°C, 6 h at 30°C, and 6 h at 35°C until the tetranitromethane disappeared, evaporated at 50°C to ~100 ml, cooled, and transferred to 600 ml of acetone. The precipitated salts V-X and XII-XIV were filtered, washed with acetone, and crystallized from aqueous ethanol.

2-(β-Cyanoethyl)-5-nitroaminotetrazole Sodium Salt (XI). Here 4 g (29 mmole) of amine III was added to a solution of 5.8 g (145 mmole) of sodium hydroxide in 52 ml of water and after the amine had dissolved, 6.9 ml (58 mmole) of tetranitromethane was added. The reaction mass was stirred for 3 h at 20°C, 20 h at 45°C, 12.2 g (145 mmole) of sodium bicarbonate was added, and the mass was again stirred for 6 h at 45°C. After evaporation of the reaction mass at 45°C, the precipitated sediment was washed with acetone (4 × 100 ml) and extracted with ethanol (4 × 85 ml). The alcohol extracts were combined and salt XI was obtained after elimination of the alcohol; it was purified by reprecipitation from alcohol solution with acetone.

5-Nitroaminotetrazole Disodium Salt (XV). Here 5.2 ml (43 mmole) of tetranitromethane was poured in a solution of 3 g (21.5 mmole) of amine IV and 4.3 g (107 mmole) of sodium hydroxide in 40 ml of water. The reaction mass was stirred for 5 h at 20°C and 10 h at 50°C until the tetranitromethane had disappeared, cooled, poured in 400 ml of acetone, and the precipitated product XV was washed with DMF and crystallized from aqueous ethanol.

LITERATURE CITED

1. A. G. Mayants, K. G. Pyreseva, and S. S. Gordeichuk, Zh. Org. Khim., **22**, 2120 (1986).
2. A. G. Mayants, K. G. Pyreseva, S. S. Gordeichuk, and T. V. Gordeichuk, Zh. Org. Khim., **22**, 2124 (1986).
3. A. G. Mayants, K. G. Pyreseva, and S. S. Gordeichuk, Zh. Org. Khim., **24**, 884 (1988).
4. J. A. Garrison and R. M. Herbst, J. Org. Chem., **22**, 278 (1957).
5. A. G. Mayants, S. S. Gordeichuk, V. A. Shlyapochnikov, T. V. Gordeichuk, and V. P. Gorelik, Khim. Geterosikl. Soedin., No. 11, 1569 (1984).
6. P. Rochlin, D. B. Murphy, and S. Hell, J. Am. Chem. Soc., **76**, 1451 (1954).
7. A. G. Mayants, N. A. Klinova, and S. S. Gordeichuk, Khim. Geterosikl. Soedin., No. 7, 945 (1987).
8. E. Laviron, P. Fournazi, and J. Greusard, Bull. Soc. Chim., No. 4, 1255 (1967).
9. N. Jonathan, J. Mol. Spectrosc., **5**, 101 (1960).
10. V. G. Avakyan, V. A. Chekrygin, and A. N. Kislinskii, Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2687 (1969).
11. V. G. Avakyan, V. A. Shlyapochnikov, and V. A. Chekrygin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 948 (1972).
12. V. A. Shlyapochnikov, N. O. Cherskaya, N. S. Morozova, T. N. Ivshina, V. P. Ivshin, and K. I. Bakhtin, Zh. Obshch. Khim., **53**, 2334 (1983).
13. N. O. Cherskaya, V. A. Shlyapochnikov, V. P. Ivshin, and T. N. Ivshina, Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1533 (1986).
14. A. G. Mayants, V. V. Erina, and S. S. Gordeichuk, Zh. Org. Khim., **25**, 419 (1989).
15. A. G. Mayants and K. G. Pyreseva, Zh. Org. Khim., **23**, 2236 (1987).
16. E. De Vries and E. S. Gantz, J. Am. Chem. Soc., **76**, 1008 (1954).
17. E. Lieber, S. Patinkin, and H. H. Tao, J. Am. Chem. Soc., **73**, 1792 (1951).