ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 11, pp. 2366–2373. © Pleiades Publishing, Ltd., 2010.
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Adamantylazoles: XIV.[1] Acid-Catalyzed Alkylation of 5-Aminotetrazoles with Tertiary Alcohols

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Received March 1, 2010

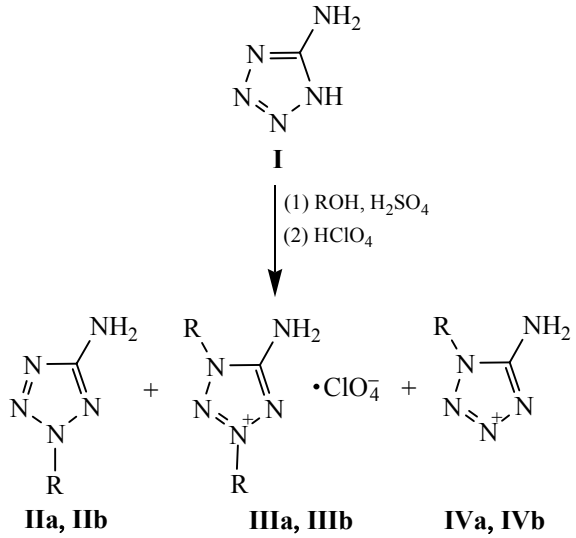
Abstract—Alkylation of 5-aminotetrazole with *tert*-butyl alcohol or adamantan-1-ol in sulfuric acid gave a mixture of isomeric N^1- and N^2-alkyl derivatives, as well as 1,3-dialkyl-5-aminotetrazolium salt. Adamantylation of 1-substituted 5-aminotetrazoles led to the formation of mixtures of 1,3- and 1,4-disubstituted 5-aminotetrazolium salts which can be converted into the corresponding free bases.

DOI: 10.1134/S1070363210110228

Alkylation in strong acids is widely used for the synthesis of various azole derivatives [2]. We previously examined reactions of 1-susbtituted tetrazole-5-thiones and tetrazol-5-ones with adamantan-1-ol or *tert*-butyl alcohol in sulfuric acid [1, 3]. An interesting substrate for further studying acid-catalyzed alkylation of azoles is 5-aminotetrazole (**I**). Like tetrazolethiones and tetrazolones, compound **I** possesses an exocyclic heteroatom with an unshared electron pair. It is known that alkylation of aminotetrazole **I** in alkaline or neutral medium gives mixtures of N^1- and N^2-alkyl derivatives [4, 5]. Voitekhovich et al. [6] reported on the reaction of 5-aminotetrazole (**I**) with *tert*-butyl alcohol in perchloric acid, which produced 5-amino-2-*tert*-butyltetrazole (**IIa**) or 5-amino-1,3-di-*tert*-butyltetrazolium perchlorate (**IIIa**).

In the present work we examined alkylation of 5-aminotetrazole (**I**) with *tert*-butyl alcohol and adamantan-1-ol in 94% sulfuric acid. The reaction of tetrazole **I** with an equimolar amount of *tert*-butyl alcohol, apart from compounds **IIa** and **IIIa**, gave also 1-*tert*-butyltetrazol-5-amine (**IVa**). According to the ^{1}H NMR data, the ratio of isomers **IIa** and **IVa** was 75 : 25. The yield of tetrazolium salt **IIIa** reached 26%. Adamantylation of aminotetrazole **I** in sulfuric acid occurred in a similar way to produce a mixture of isomeric 2-(1-adamantyl)tetrazol-5-amine (**IIb**) and 1-(1-adamantyl)tetrazole-5-amine (**IVb**) at a ratio of 65 : 35 and 1,3-bis(1-adamantyl)-5-aminotetrazolium salt **IIIb** which was isolated as perchlorate in 19% yield (Scheme 1).

Scheme 1.



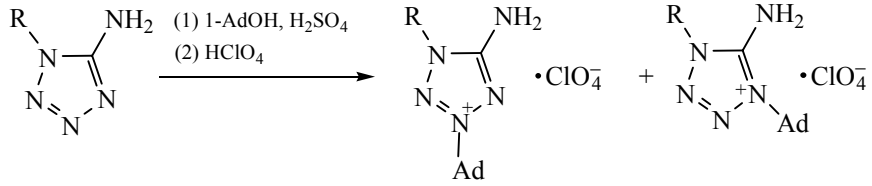
R = *t*-Bu (**a**), 1-Ad (**b**).

Aminotetrazole derivatives having an alkyl or aromatic substituent on N^1, in particular 1-methyltetrazol-5-amine (**Va**), 1-phenyltetrazol-5-amine (**Vb**), and 1-(4-nitrophenyl)tetrazol-5-amine (**Vc**), reacted with an equimolar amount of adamantan-1-ol in sulfuric acid to form mixtures of 1-R-3-(1-adamantyl)-

[1] For communication XIII, see [1].

and 1-R-4-(1-adamantyl)-5-aminotetrazolium salts **VIa**–**VIc** and **VIIa**–**VIIc** which were isolated as perchlorates (Scheme 2). In all cases, 1,3-disubstituted derivatives **VI** were the major products. According the the ^{1}H NMR data, the **VI**-to-**VII** ratio was 76 : 24 (**a**), 60 : 40 (**b**), and 65 : 35 (**c**).

Scheme 2.

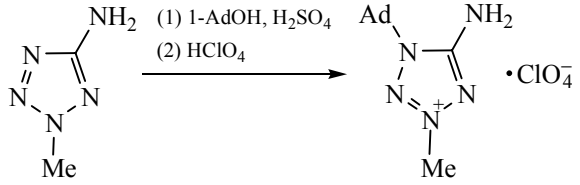


Va–Vc **VIa–VIc** **VIIa–VIIc**

R = Me (**a**), Ph (**b**), 4-$NO_2C_6H_4$ (**c**).

It is known that 1,3-disubstituted products are selectively formed in the alkylation of 2-substituted 5-aminotetrazole derivatives [7, 8]. Likewise, by adamantylation of 2-methyltetrazol-5-amine (**VIII**) in sulfuric acid we obtained only 1-(1-adamantyl)-5-amino-3-methyltetrazolium salt **IX** (Scheme 3).

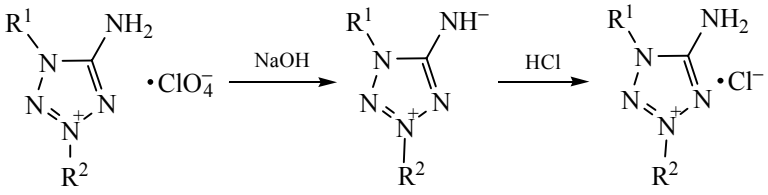
Scheme 3.



VIII **IX**

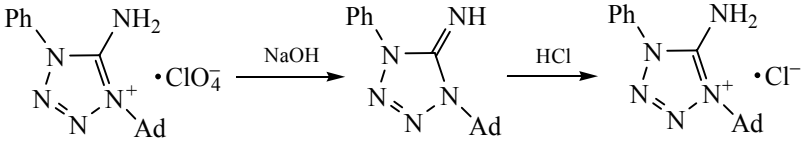
Unlike derivatives of tetrazole-5-thiones and tetrazol-5-ones, tetrazolium salts derived from tetrazol-5-amine can be converted into the corresponding free bases by treatment with alkali [6]. Thus the reaction of 1-R^1-3-R^2-5-aminotetrazolium salts **IIIb**, **VIa**, and **IX** with sodium hydroxide gave mesoionic compounds, 1-R^1-3-R^2-tetrazolium-5-aminides **Xa**–**Xc**. 1-(1-Adamantyl)-5-amino-4-phenyltetrazolium perchlorate (**VIIb**) under analogous conditions was converted into 1-(1-adamantyl)-4-phenyl-4,5-dihydro-1*H*-tetrazol-5-imine (**XII**). By treatment of compounds **Xa**–**Xc** and **XII** with hydrochloric acid we obtained the corresponding tetrazolium chlorides **XIa**–**XIc** and **XIII** (Scheme 4).

Scheme 4.



IIIb, VIa, IX **Xa–Xc** **XIa–XIc**

IIIb, **Xa**, **XIa**, $R^1 = R^2 = $ 1-Ad; **VIa**, **Xb**, **XIb**, R^1 = Me, R^2 = 1-Ad; **IX**, **Xc**, **XIc**, R^1 = 1-Ad, R^2 = Me.



VIIb **XII** **XIII**

It should be noted that our attempts to perform alkylation of monosubstituted 5-aminotetrazoles **Va**–**Vc** and **VIII** with *tert*-butyl alcohol in sulfuric acid were unsuccessful. Presumably, these reactions were accompanied by oxidation processes with participation of sulfuric acid (tarring and evolution of sulfur dioxide were observed).

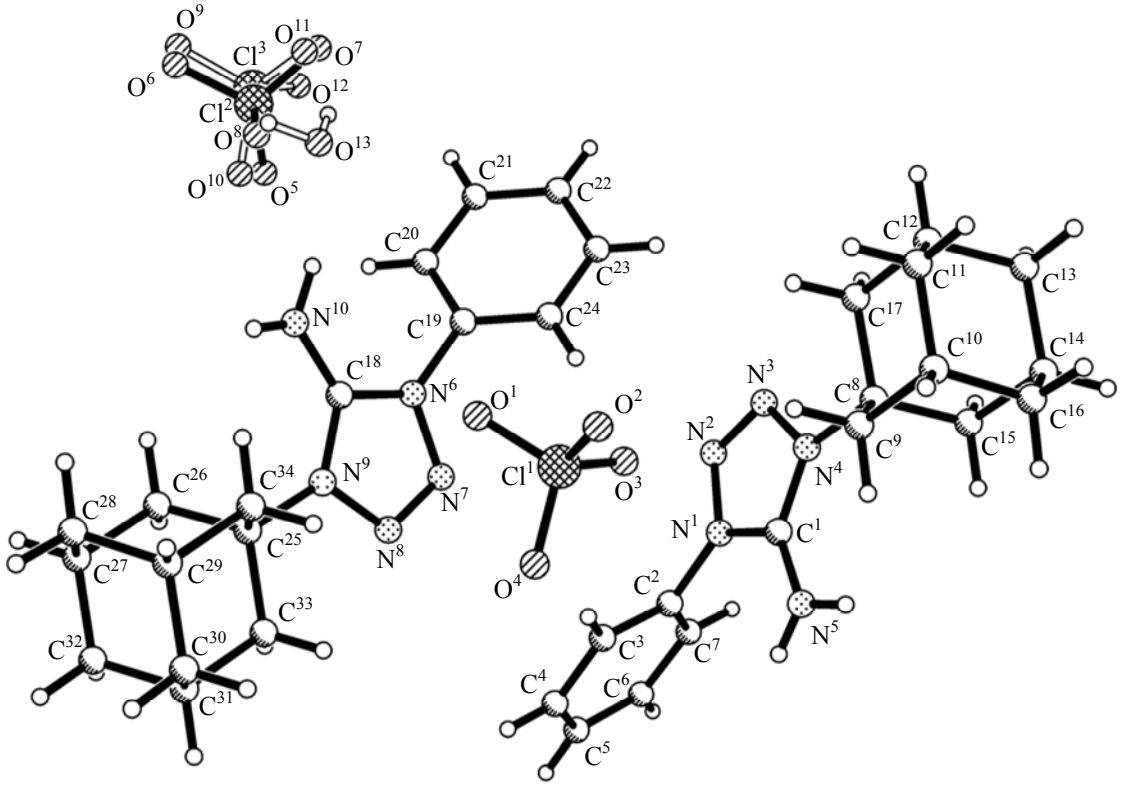
It is important that in almost all cases considered above the major alkylation product was 1,3-disub-

Table 1. ^{13}C NMR spectra of compounds **II–VII**, **IX**, **X**, and **XII** in DMSO-d_6–CCl_4 (4 : 1)

Comp. no.	Chemical shifts δ_C, ppm		Comp. no.	Chemical shifts δ_C, ppm	
	C^5	substituents		C^5	substituents
IIa	167.45	62.63, 29.59 (*t*-Bu)	**VIc**	158.04	149.69, 136.56, 128.15, 126.02 (C_6H_4); 69.96, 41.42, 35.76, 29.67 (Ad)
IIb	167.23	62.55, 42.42, 36.27, 29.64 (Ad)	**VIIa**	147.64	64.06, 39.24, 35.52, 29.78 (Ad); 34.95 (Me)
IIIa	157.04	69.53, 64.57, 28.56, 27.35 (*t*-Bu)	**VIIb**	147.15	132.36, 131.79, 130.85, 127.34 (Ph); 64.63, 39.21, 35.52, 29.83 (Ad)
IIIb	156.78	68.96, 65.22, 41.31, 38.88, 35.76, 35.36, 29.72, 29.61 (Ad)	**VIIc**	147.26	149.74, 136.64, 129.10, 126.08 (C_6H_4); 64.84, 39.24, 35.49, 29.83 (Ad)
IVa	155.21	58.43, 28.70 (*t*-Bu)	**IX**	156.99	65.08, 38.97, 35.36, 29.75 (Ad); 43.55 (Me)
IVb	155.00	59.15, 40.34, 35.97, 29.78 (Ad)	**Xa**	162.30	65.11, 59.77, 41.45, 38.91, 36.38, 36.08, 29.56, 29.56 (Ad)
Vb	155.56	134.54, 130.50, 129.66, 124.38 (Ph)	**Xb**	162.84	65.60, 41.53, 36.08, 29.59 (Ad); 32.04 (Me)
Vc	155.59	147.58, 139.53, 125.86, 124. 84 (C_6H_4)	**Xc**	162.33	59.96, 38.91, 36.33, 29.59 (Ad); 41.93 (Me)
VIa	158.66	68.86, 41.42, 35.71, 29.61 (Ad); 35.17 (Me)	**XII**	146.37	135.38, 130.28, 128.31, 122.33 (Ph); 59.99, 39.45, 36.27, 29.67 (Ad)
VIb	157.93	132.33, 131.79, 130.74, 126.35 (Ph); 69.56, 41.45, 35.81, 29.70 (Ad)			

stituted 5-aminotetrazolium salt in which the cation structure is essentially similar to the structure of protonated mesoionic derivatives of tetrazolethione and tetrazolone [3]. We can conclude that the main direction of the alkylation of 5-aminotetrazoles is the same as in the reactions with 1-R-tetrazol-5-ones and -thiones.

The substitution pattern in the isolated compounds was determined on the basis of their ^{13}C NMR spectra (Table 1) where the position of the C^5 signal was characteristic and was consistent with published data. The following ranges of δ_{C^5} values are typical for known 5-aminotetrazole derivatives: 1-R-5-amino-



Structure of crystallographically independent components of a unit cell of 1-(1-adamantyl)-5-amino-4-phenyltetrazolium perchlorate (**VIIb**) according to the X-ray diffraction data.

Table 2. Some bond lengths and bond angles in cations **A** and **B** of structure **VIIb**

Cation **A**				Cation **B**			
Bond	*d*, Å	Angle	ω, deg	Bond	*d*, Å	Angle	ω, deg
N^1–C^1	1.335(4)	$C^1N^1N^2$	109.4(2)	N^6–C^{18}	1.333(4)	$C^{18}N^6N^7$	109.4(3)
N^1–N^2	1.359(4)	$C^1N^1C^2$	129.0(3)	N^6–N^7	1.365(4)	$C^{18}N^6C^{19}$	129.6(3)
N^1–C^2	1.436(4)	$N^2N^1C^2$	121.5(3)	N^6–C^{19}	1.436(4)	$N^7N^6C^{19}$	120.6(2)
N^2–N^3	1.268(4)	$N^3N^2N^1$	107.4(3)	N^7–N^8	1.270(4)	$N^8N^7N^6$	108.0(2)
N^3–N^4	1.368(4)	$N^2N^3N^4$	109.4(3	N^8–N^9	1.371(4)	$N^7N^8N^9$	108.8(3)
N^4–C^1	1.334(4)	$C^1N^4N^3$	107.9(3)	N^9–C^{18}	1.344(4)	$C^{18}N^9N^8$	108.2(3)
N^4–C^8	1.497(4)	$C^1N^4C^8$	132.0(3)	N^9–C^{25}	1.491(4)	$C^{18}N^9C^{25}$	131.7(3)
N^5–C^1	1.318(4)	$N^3N^4C^8$	120.1(3)	N^{10}–C^{18}	1.315(4)	$N^8N^9C^{25}$	120.0(3)
		$C^1N^5H^{51}$	122(3)			$C^{18}N^{10}H^{101}$	122(3)
		$C^1N^5H^{52}$	115(3)			$C^{18}N^{10}H^{102}$	118(3)
		$H^{51}N^5H^{52}$	120(4)			$H^{101}N^{10}H^{102}$	121(4)
		$N^5C^1N^1$	124.0(3)			$N^{10}C^{18}N^6$	124.7(3)
		$N^5C^1N^4$	130.1(3)			$N^{10}C^{18}N^9$	129.7(3)
		$N^4C^1N^1$	105.8(3)			$N^6C^{18}N^9$	105.6(3)

tetrazoles, δ_C 153.5–156.9 ppm [9, 10]; 2-R-5-aminotetrazoles, δ_C 167.2 ppm [6, 9]; 1-R^1-3-R^2-tetrazolium-5-aminides, δ_C 162.1–162.5 ppm [6, 9, 11]; 1-R^1-3-R^2-5-aminotetrazolium salts, δ_C 156.1–158.7 ppm [6, 8, 9, 11]; 5-amino-1,4-dimethyltetrazolium chloride, δ_C 148.5–148.9 ppm [8, 9].

Taking into account that the formation of 1,4-disubstituted derivatives like **VIIa**–**VIIc** in acid-catalyzed alkylation of 1-R-5-aminotetrazoles was not reported previously [6], it was reasonable to obtain additional proofs for their structure. The structure of compound **VIIb** was unambiguously determined by X-ray analysis.

Independent part of a unit cell of compound **VIIb** in crystal includes two cations, two ClO_4^- anions, and 0.36 water molecule (see figure). Independent organic cations **A** and **B** are characterized by fairly similar geometric parameters (Table 2) which indicate delocalization of electron density over the aminotetrazolium fragment. Analogous geometric structure of aminotetrazolium fragment was found for unsubstituted aminotetrazolium cation (HL^+) in compounds like $(HL)ClO_4 \cdot L$ [12], as well as for some 5-amino-1,4-dimethyltetrazolium salt with different anions, such as I^-, 5-nitrotetrazolate $CN_5O_2^-$ [13], ClO_4^-, NO_3^-, N_3^-, dinitramide $N_3O_4^-$ [14], azotetrazolate $C_2N_{10}^{2-}$ [15], and picrate $C_6H_2N_3O_7^-$ [16]. Nonequivalence of the exocyclic bond angles $N^1C^1N^5/N^4C^1N^5$ and $C^1N^1C^2/C^1N^4C^8$ in anion **A**, as well as of the angles $N^6C^{18}N^{10}/N^9C^{18}N^{10}$ and $C^{18}N^6C^{19}/C^{18}N^9C^{25}$ in anion **B** is likely to be induced by steric repulsion between the bulky adamantyl fragment and NH_2 group. No significant differences were observed between the corresponding exocyclic bond angle couples in symmetrically substituted 5-amino-1,4-dimethyltetrazolium cation. Cations **A** and **B** differ appreciably by relative rotation of the planar aminotetrazole and phenyl fragments; however, in both cases, no conjugation is possible between the tetrazole and phenyl rings: the dihedral angle between the $C^1N^1N^2N^3N^4N^5$ and $C^2C^3C^4C^5C^6C^7$ planes (cation **A**) is 44.56(14)°, and that between the $C^{18}N^6N^7N^8N^9N^{10}$ and $C^{19}C^{20}C^{21}C^{22}C^{23}C^{24}$ planes (cation **B**) is 56.63(10)°.

The relative position of the cations in anions in a unit cell suggests electrostatic attraction between the oxygen atoms in the anions and positively charged fragments of the tetrazole rings. The tetrazole ring planes in cations **A** and **B** are mutually orthogonal (the corresponding dihedral angle is 89.8°). The Cl^1O^1–O^4 anion is arranged between cations **A** and **B** in such a

Table 3. Parameters of hydrogen bonds in the crystalline structure of compound **VIIb**

D–H···A	Symmetry transformation of the A atom	*d*(H···A), Å	*d*(D···A), Å	∠DHA, deg
N^5–H^{51}···O^4	–*x*, –*y* + 2, –*z*	2.25(4)	3.031(5)	159(3)
N^{10}–H^{101}···O^{13}	*x*, *y*, *z*	1.85(4)	2.691(8)	152(4)
N^{10}–H^{101}···O^8	*x*, *y*, *z*	2.57(4)	3.333(8)	142(3)
N^{10}–H^{102}···O^1	–*x*, –*y* + 2, –*z* + 1	2.65(4)	3.242(5)	134(4)
N^{10}–H^{102}···O^2	–*x*, –*y* + 2, –*z* + 1	2.49(4)	3.124(5)	139(4)
O^{13}–H^{131}···O^{11}	*x*, *y*, *z*	2.06	2.88(2)	160
O^{13}–H^{132}···O^4	–*x*, –*y* + 2, –*z* + 1	2.38	3.152(9)	151

way that the O^1 atom is involved in shortened contacts with the C^{18}, N^6, and N^9 atoms [2.981(4), 3.097(4), and 3.142(4) Å, respectively], and the O^3 atom, with C^1, N^1, and N^4 [2.930(4), 3.090(5), and 3.073(4) Å, respectively]. Presumably, just the above interactions fix the position of Cl^1O^1–O^4. Disordered perchlorate anion appears at the other side of the tetrazole ring plane in cation **A** and is involved in the following shortened contacts: O^6···C^1, O^6···N^1, O^6···N^4 (*x*, *y*, 1 + *z*) [2.85(1), 2.90(1), 3.14(1) Å] or O^9···C^1, O^9···N^1, O^9···N^4 (*x*, *y*, 1 + *z*) [3.19(2), 3.06(2), 3.14(2) Å]; among these, any contact does not fix the anion unambiguously.

The amino group, water molecule, and oxygen atoms in the ClO_4^- anions participate in hydrogen bonding (Table 3). The Cl^1O^1–O^4 anion is involved in two weak N–H···O hydrogen bonds one of which is bifurcate. One weak N–H···O hydrogen bond is formed with the disordered perchlorate ion Cl^2O^5–O^8. Water molecule is included into the crystalline structure together with the Cl^3O^9–O^{12} anion through the hydrogen bond O^{13}–H^{131}···O^{11}. The second hydrogen atom in water molecule is oriented toward the ordered anion (O^{13}–H^{132}···O^4), and the oxygen atom in water molecule gives rise to relatively strong N^{10}–H^{101}···O^{13} hydrogen bond.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker WM-400 spectrometer using DMSO-d_6 as solvent. The ^{13}C NMR spectra were recorded on a Bruker AC-200 instrument. The elemental compositions were determined using a Hewlett–Packard 185B analyzer. The purity of the isolated compounds was checked by TLC on Sorbfil or Silufol UV-254 plates using $CHCl_3$, $CHCl_3$–EtOAc (4 : 1), or $CHCl_3$–acetone (1 : 1) as eluent; spots were visualized under UV light or by treatment with iodine vapor. Silica gel Chemapol L 100/160V was used for column chromatography.

The X-ray diffraction data for compound **VIIb** were acquired on a Bruker SMART APEX2 automatic diffractometer (MoK_α irradiation, graphite monochromator) at room temperature from a 0.20 × 0.14 × 0.06-mm colorless prismatic single crystal. Triclinic crystal system; unit cell parameters: a = 10.932(3), b = 13.297(4), c = 13.659(4) Å; α = 92.631(5)°, β = 102.418(5)°, γ = 103.658(5)°; V = 1874.6(9) Å^3; d_{calc} = 1.414 g/cm^3; μ(Mo) = 0.239 mm^{-1}; Z = 4; space group $P\bar{1}$. Total of 21 389 reflection intensities were measured in the range 1.97° < θ < 30.00° and were used to solve the structure by the direct method. The structure was refined using the set of reflections restricted by θ_{max} = 23° since distant reflections were systematically weak [average $I/\sigma(I)$ < 2]. One perchlorate ion (Cl^1O^1–O^4) was ordered, while the other was disordered by two closely located positions (Cl^2O^5–O^8 and Cl^3O^9–O^{12}) with populations of 0.64 and 0.36, respectively. The oxygen atom in the water molecule (O^{13}) was not coupled with the Cl^2O^5–O^8 anion for steric reasons; therefore, the population of the corresponding position was equal to the population of Cl^3O^9–O^{12}. The positions of hydrogen atoms attached to carbon atoms were calculated, and hydrogen atoms in the amino groups were localized by difference syntheses. The H^{131} atom in the water molecule was localized by difference synthesis, and the position of H^{132} was calculated with account taken of hydrogen bond where the O^{13} atom was proton acceptor and of the O^{13}···O^4 contact which may be regarded as weak hydrogen bond. The structure was refined by the least-squares procedure in anisotropic approximation for non-hydrogen atoms, assuming that the geometric parameters of disordered perchlorate anions tend to fit a regular tetrahedral configuration. The positions of NH hydrogen atoms were refined in isotropic approximation with no constraints, and the positions of the other hydrogen atoms were refined according to the riding model (U_{iso} = 1.2U_{equiv} for the corresponding non-hydrogen atom). The final divergence factors were R_1 = 0.0527, wR_2 = 0.1293 for 3845 reflections with $I > 2\sigma(I)$ and R_1 = 0.0738, wR_2 = 0.1415 for all 5194 independent reflections; goodness of fit 1.021. The residual electron density ranged from –0.204 to 0.380 e/Å^3.

The set of reflection intensities $I(hkl)$ was acquired and processed using APEX2, SAINT, and SADABS programs [17], and the calculations were performed using SHELX97 software package [18]. Data from the Cambridge Structural Database (version 5.30) [19] were used. The crystallographic data for compound **VIIb** were deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 761 669).

Initial compounds **Va** and **VIII** were synthesized by methylation of 5-aminotetrazole as described in [4]. 1-Aryl-5-aminotetrazoles **Vb** and **Vc** were prepared in three steps from the corresponding anilines according to the procedure reported in [20, 21].

Reaction of 1*H*-tetrazol-5-amine (I) with *tert*-butyl alcohol. *tert*-Butyl alcohol, 13.0 mmol, was added dropwise to a solution of 11.7 mmol of compound **I** in 10 ml of 94% sulfuric acid. The mixture was stirred for 1 h at room temperature, poured onto ice, neutralized with a 15% solution of sodium hydroxide to pH 4–5, and extracted with chloroform (4 × 25 ml). The extracts were dried over Na_2SO_4 and evaporated on exposure to air, and the residue (a mixture of compounds **IIa** and **IVa**) was analyzed by ^{1}H NMR spectroscopy. Compound **IVa** was isolated by double crystallization, the solvent was distilled off from the mother liquor, and the residue was subjected to column chromatography on silica gel using $CHCl_3$–EtOAc as eluent to isolate compound **IIa**.

The aqueous filtrate was treated with 4 ml of 50% $HClO_4$ and extracted with methylene chloride (3 × 50 ml), and the extracts were dried over Na_2SO_4 and evaporated in air to isolate tetrazolium perchlorate **IIIa**.

2-*tert*-Butyl-2*H*-tetrazol-5-amine (IIa). Yield 20%, mp 111–113°C (from hexane–*i*-PrOH, 4 : 1). ^{1}H NMR spectrum, δ, ppm: 5.73 s (2H, NH_2), 1.59 s (9H, *t*-Bu). Found, %: C 42.41; H 7.53; N 49.57. $C_5H_{11}N_5$. Calculated, %: C 42.55; H 7.80; N 49.65.

5-Amino-1,3-di-*tert*-butyltetrazolium perchlorate (IIIa). Yield 26%, mp 149°C (decomp., from *i*-PrOH). ^{1}H NMR spectrum, δ, ppm: 8.02 s (2H, NH_2), 1.70 s (9H, *t*-Bu), 1.68 s (9H, *t*-Bu). Found, %: C 36.59; H 6.70; N 23.87. $C_9H_{20}N_5 \cdot ClO_4$. Calculated, %: C 36.30; H 6.72; N 23.53.

1-*tert*-Butyl-1*H*-tetrazol-5-amine (IVa). Yield 2%, mp 183–185°C (from hexane–benzene, 1 : 1). ^{1}H NMR spectrum, δ, ppm: 6.30 s (2H, NH_2), 1.58 s (9H, *t*-Bu). Found, %: C 42.39; H 7.99; N 49.47. $C_5H_{11}N_5$. Calculated, %: C 42.55; H 7.80; N 49.65.

Reaction of 1*H*-tetrazol-5-amine (I) with adamantan-1-ol. A solution of 11.7 mmol of compound **I** and 11.8 mmol of adamantan-1-ol in 25 ml of 94% sulfuric acid was stirred for 2 h at room temperature. The mixture was poured onto ice and diluted with water to a volume of 400 ml. The precipitate was filtered off, washed with water (3 × 25 ml) and dried in air. We thus isolated compound **IIb**. The aqueous filtrate was treated with 4 ml of 50% $HClO_4$, and the precipitate (tetrazolium perchlorate **IIIb**) was filtered off, washed with water (3 × 25 ml), and dried in air. The filtrate was extracted with methylene chloride (5 × 30 ml), and the extracts were dried over Na_2SO_4 and evaporated in air to obtain 0.64 g of a mixture of compounds **IIIb** and **IVb**, which was analyzed by ^{1}H NMR. This mixture was then dissolved in methylene chloride, the solution was washed with 25 ml of a 5% solution of sodium hydroxide, the organic phase was dried over, the solvent was removed in air, and the residue was recrystallized to isolate compound **IVb**.

2-(1-Adamantyl)-2*H*-tetrazol-5-amine (IIb). Yield 30%, mp 184–186°C (from hexane–*i*-PrOH, 10 : 1). ^{1}H NMR spectrum, δ, ppm: 5.81 s (2H, NH_2), 2.17 s (9H, Ad), 1.73 s (6H, Ad). Found, %: C 60.13; H 7.50; N 32.21. $C_{11}H_{17}N_5$. Calculated, %: C 60.27; H 7.76; N 31.96.

1,3-Bis(1-adamantyl)-5-aminotetrazolium perchlorate (IIIb). Yield 19%, mp 179–181°C (from benzene–*i*-PrOH, 10 : 1). ^{1}H NMR spectrum, δ, ppm: 8.10 s (2H, NH_2), 2.26 s (9H, Ad), 2.24 s (9H, Ad), 1.79–1.71 m (12H, Ad). Found, %: C 55.30; H 6.15; N 15.42. $C_{21}H_{32}N_5 \cdot ClO_4$. Calculated, %: C 55.56; H 7.05; N 15.43.

1-(1-Adamantyl)-1*H*-tetrazol-5-amine (IVb). Yield 2%, mp 233–234°C (from benzene–*i*-PrOH, 4 : 1). ^{1}H NMR spectrum, δ, ppm: 6.32 s (2H, NH_2), 2.19 s (9H, Ad), 1.80–1.66 m (6H, Ad). Found, %: C 60.68; H 8.07; N 32.28. $C_{11}H_{17}N_5$. Calculated, %: C 60.27; H 7.76; N 31.96.

Reaction of 1-substituted 5-aminotetrazoles Va–Vc with adamantan-1-ol. A solution of 5.1 mmol of compound **Va**–**Vc** and 5.1 mmol of adamantan-1-ol in 10 ml of 94% sulfuric acid was stirred for 2 h at room temperature. The mixture was poured onto ice, diluted with water to a volume of 200 ml, and filtered. The filtrate was treated with 3 ml of 50% $HClO_4$ and extracted with chloroform (3 × 30 ml), the extracts were dried over Na_2SO_4, the solvent was removed in air, and the residue (a mixture of isomers **VI** and **VII**) was analyzed by ^{1}H NMR spectroscopy.

Compound **VIa** was isolated from the product mixture by successive recrystallizations from isopropyl alcohol and water. The mother liquors were evaporated in air, the residue was treated with hot benzene (2 × 20 ml), and the benzene solution was evaporated in air. The residue was compound **VIIa** containing about 30% of isomer **VIa**. We failed to isolate compound **VIIa** with a better purity.

Compound **VIIb** was isolated by successive recrystallizations from isopropyl alcohol and water. The mother liquors were evaporated in air, and the residue was subjected to double recrystallization from benzene–chloroform (2 : 1) to isolate compound **VIb**.

Compound **VIIc** was isolated by recrystallization from ethyl acetate. The mother liquor was evaporated in air, and the residue was recrystallized from benzene–isopropyl alcohol (10 : 1). The product was treated with hexane–*i*-PrOH (1 : 1, 3×15 ml), and the solvent was removed in air. The residue was pure compound **VIc**.

3-(1-Adamantyl)-5-amino-1-methyltetrazolium perchlorate (VIa). Yield 27%, mp 190–192°C (from *i*-PrOH). ^{1}H NMR spectrum, δ, ppm: 8.19 s (2H, NH_2), 3.92 s (3H, Me), 2.27 s (3H, Ad), 2.23 s (6H, Ad), 1.75 s (6H, Ad). Found, %: C 43.10; H 6.16; N 20.80. $C_{12}H_{20}N_5{\cdot}ClO_4$. Calculated, %: C 43.14; H 5.99; N 20.97.

3-(1-Adamantyl)-5-amino-1-phenyltetrazolium perchlorate (VIb). Yield 5%, mp 168°C (decomp.) ^{1}H NMR spectrum, δ, ppm: 8.35 s (2H, NH_2), 7.70 s (5H, Ph), 2.33 s (9H, Ad), 1.80 s (6H, Ad). Found, %: C 51.08; H 5.66; N 17.51. $C_{17}H_{22}N_5{\cdot}ClO_4$. Calculated, %: C 51.58; H 5.56; N 17.70.

3-(1-Adamantyl)-5-amino-1-(4-nitrophenyl)tetrazolium perchlorate (VIc). Yield 14%, mp 159°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 8.55 s (2H, NH_2), 8.53 d (2H, ^3J = 8.9 Hz, C_6H_4), 8.03 d (2H, ^3J = 8.9 Hz, C_6H_4), 2.32 s (9H, Ad), 1.79 s (6H, Ad). Found, %: C 45.68; H 5.40; N 17.72. $C_{17}H_{21}N_6O_2{\cdot}ClO_4$. Calculated, %: C 46.31; H 4.77; N 19.07.

1-(1-Adamantyl)-5-amino-4-methyltetrazolium perchlorate (VIIa). ^{1}H NMR spectrum, δ, ppm: 8.75 s (2H, NH_2), 3.86 s (3H, Me), 2.24 s (9H, Ad), 1.84–1.70 m (6H, Ad). Found, %: C 43.49; H 5.97; N 21.22. $C_{12}H_{20}N_5{\cdot}ClO_4$. Calculated, %: C 43.14; H 5.99; N 20.97.

1-(1-Adamantyl)-5-amino-4-phenyltetrazolium perchlorate (VIIb). Yield 7%, mp 199°C (decomp., from *i*-PrOH). ^{1}H NMR spectrum, δ, ppm: 8.83 s (2H, NH_2), 7.70 s (5H, Ph), 2.34 s (6H, Ad), 2.28 s (3H, Ad), 1.89–1.72 m (6H, Ad). Found, %: C 51.37; H 5.75; N 17.59. $C_{17}H_{22}N_5{\cdot}ClO_4$. Calculated, %: C 51.58; H 5.56; N 17.70.

1-(1-Adamantyl)-5-amino-4-(4-nitrophenyl)tetrazolium perchlorate (VIIc). Yield 12%, mp 193°C (decomp., from EtOAc). ^{1}H NMR spectrum, δ, ppm: 8.97 s (2H, NH_2), 8.54 d (2H, ^3J = 8.9 Hz, C_6H_4), 8.01 d (2H, ^3J = 8.9 Hz, C_6H_4), 2.32 s (6H, Ad), 2.28 s (3H, Ad), 1.88–1.72 m (6H, Ad). Found, %: C 45.92; H 5.20; N 18.68. $C_{17}H_{21}N_6O_2{\cdot}ClO_4$. Calculated, %: C 46.31; H 4.77; N 19.07.

1-(1-Adamantyl)-5-amino-3-methyltetrazolium perchlorate (IX). The reaction of 2-methyl-2*H*-tetrazol-5-amine (**VIII**) with adamantan-1-ol was carried out as described above for the adamantylation of compounds **Va**–**Vc**. After addition of $HClO_4$, the precipitate was filtered off and washed with water (3 × 25 ml). The filtrate was extracted with chloroform (3 × 30 ml), the extracts were dried over Na_2SO_4, and the solvent was removed in air. The residue was combined with the first precipitate and recrystallized. Yield 63%, mp 223°C (decomp., from EtOH). ^{1}H NMR spectrum, δ, ppm: 8.10 s (2H, NH_2), 4.30 s (3H, Me), 2.22 s (9H, Ad), 1.78–1.65 m (6H, Ad). Found, %: C 43.52; H 6.15; N 21.43. $C_{12}H_{20}N_5{\cdot}ClO_4$. Calculated, %: C 43.14; H 5.99; N 20.97.

Transformation of tetrazolium perchlorates IIIb, VIa, VIIb, and IX into the corresponding free bases and chlorides. A solution of 2.0 mmol of compound **IIIb**, **VIa**, **VIIb**, or **IX** in 20 ml of methylene chloride and 20 ml of a 2% solution of sodium hydroxide was stirred for 10 min at room temperature. The organic phase was separated, washed with water (2 × 15 ml), and dried over Na_2SO_4, and the solvent was removed in air to obtain compound **Xa**–**Xc** or **XII**. The product was dissolved in 40 ml of ethyl acetate, the solution was treated with concentrated hydrochloric acid to pH 5 and cooled, and the precipitate of chloride **XIa**–**XIc** or **XIII** was filtered off, washed with ethyl acetate (2 × 20 ml), and dried in air.

1,3-Bis(1-adamantyl)tetrazolium-5-aminide (Xa). Yield 98%, mp 216–218°C (from hexane). ^{1}H NMR spectrum, δ, ppm: 4.09 s (1H, NH), 2.30 s (6H, Ad), 2.21 s (3H, Ad), 2.15 s (3H, Ad), 2.12 s (6H, Ad), 1.71 s (12H, Ad). Found, %: C 71.30; H 8.50; N 20.04. $C_{21}H_{31}N_5$. Calculated, %: C 71.39; H 8.78; N 19.83.

3-(1-Adamantyl)-1-methyltetrazolium-5-aminide (Xb). Yield 52%, mp 82–84°C (from hexane). ^{1}H

NMR spectrum, δ, ppm: 3.51 s (3H, Me), 2.22 s (3H, Ad), 2.15 s (6H, Ad), 1.73 s (6H, Ad). Found, %: C 60.92; H 8.64; N 28.36. $C_{12}H_{19}N_5$. Calculated, %: C 61.80; H 8.15; N 30.04.

1-(1-Adamantyl)-3-methyltetrazolium-5-aminide (Xc). Yield 99%, mp 181–183°C (from hexane–benzene, 1 : 2). ^{1}H NMR spectrum, δ, ppm: 3.92 s (3H, Me), 2.29 s (6H, Ad), 2.16 s (3H, Ad), 1.71 s (6H, Ad). Found, %: C 61.47; H 7.79; N 30.15. $C_{12}H_{19}N_5$. Calculated, %: C 61.80; H 8.15; N 30.04.

1,3-Bis(1-adamantyl)-5-aminotetrazolium chloride (XIa). mp 221°C (decomp., from *i*-PrOH). ^{1}H NMR spectrum, δ, ppm: 8.29 s (2H, NH_2), 2.28 s (9H, Ad), 2.23 s (9H, Ad), 1.85–1.68 m (12H, Ad). Found, %: C 64.68; H 8.35; N 17.85. $C_{21}H_{32}ClN_5$. Calculated, %: C 64.70; H 8.21; N 17.97.

3-(1-Adamantyl)-5-amino-1-methyltetrazolium chloride (XIb). mp 212°C (decomp., from *i*-PrOH). ^{1}H NMR spectrum, δ, ppm: 8.69 s (2H, NH_2), 4.06 s (3H, Me), 2.27 s (3H, Ad), 2.23 s (6H, Ad), 1.75 s (6H, Ad). Found, %: C 52.93; H 7.65; N 25.92. $C_{12}H_{20}ClN_5$. Calculated, %: C 53.43; H 7.42; N 25.97.

1-(1-Adamantyl)-5-amino-3-methyltetrazolium chloride (XIc). mp 201°C (decomp., from *i*-PrOH). ^{1}H NMR spectrum, δ, ppm: 8.34 s (2H, NH_2), 4.31 s (3H, Me), 2.25 s (6H, Ad), 2.22 s (3H, Ad), 1.85–1.67 m (6H, Ad). Found, %: C 52.68; H 7.28; N 25.54. $C_{12}H_{20}ClN_5$. Calculated, %: C 53.43; H 7.42; N 25.97.

1-(1-Adamantyl)-4-phenyl-4,5-dihydro-1*H*-tetrazol-5-imine (XII). Yield 77%, mp 115–116°C (from 50% *i*-PrOH). ^{1}H NMR spectrum, δ, ppm: 7.53–7.40 m (5H, Ph), 5.19 s (1H, NH), 2.33 s (6H, Ad), 2.19 s (3H, Ad), 1.75–1.72 m (6H, Ad). Found, %: C 69.47; H 7.55; N 23.43. $C_{17}H_{21}N_5$. Calculated, %: C 69.15; H 7.12; N 23.73.

1-(1-Adamantyl)-5-amino-4-phenyltetrazolium chloride (XIII). mp 205°C (decomp., from *i*-PrOH). ^{1}H NMR spectrum, δ, ppm: 9.14 s (2H, NH_2), 7.69 s (5H, Ph), 2.37 s (6H, Ad), 2.26 s (3H, Ad), 1.92–1.69 m (6H, Ad). Found, %: C 61.97; H 6.09; N 21.08. $C_{17}H_{22}ClN_5$. Calculated, %: C 61.54; H 6.64; N 21.12.

REFERENCES

1. Logvinov, A.V., Polyakova, I.N., and Golod, E.L., *Russ. J. Gen. Chem*., 2009, vol. 79, no. 10, p. 2230.
2. Golod, E.L., *Panorama sovremennoi khimii Rossii. Uspekhi khimii adamantana* (Survey of Modern Chemistry in Russia. Advances in the Chemistry of Adamantane), Moscow: Khimiya, 2007, p. 89.
3. Logvinov, A.V., Polyakova, I.N., and Golod, E.L., *Russ. J. Gen. Chem*., 2009, vol. 79, no. 10, p. 2220.
4. Henry, R.A. and Finnegan, W.G., *J. Am. Chem. Soc*., 1954, vol. 76, no. 3, p. 923.
5. Spear, R.J., *Aust. J. Chem*., 1984, vol. 37, no. 12, p. 2453.
6. Voitekhovich, S.V., Gaponik, P.N., Lyakhov, A.S., and Ivashkevich, L.S., *Tetrahedron*, 2008, vol. 64, no. 37, p. 8721.
7. Henry, R.A., Finnegan, W.G., and Lieber, E., *J. Am. Chem. Soc*., 1954, vol. 76, no. 11, p. 2894.
8. Moderhack, D. and Holtmann, B., *J. Prakt. Chem*., 2000, vol. 342, no. 6, p. 591.
9. Bocian, W., Jazwinski, J., Kozminski, W., Stefaniak, L., and Webb, G.A., *J. Chem. Soc., Perkin Trans. 2*, 1994, no. 6, p. 1327.
10. Karaghiosoff, K., Klapötke, T.M., Mayer, P., Piotrowski, H., Polborn, K., Willer, R.L., and Weigand, J.J., *J. Org. Chem*., 2006, vol. 71, no. 4, p. 1295.
11. Araki, S., Yamamoto, K., Yagi, M., Inoue, T., Fukagawa, H., Hattori, H., Yamamura, H., Kawai, M., and Butsugan, Y., *Eur. J. Org. Chem*., 1998, vol. 1998, no. 1, p. 121.
12. Klapötke, T.M., Sabaté, C.M., and Stierstorfer, J., *Z. Anorg. Allg. Chem*., 2008, vol. 634, no. 11, p. 1867.
13. Klapötke, T.M., Karaghiosoff, K., Mayer, P., and Welch, J.M., *Propellants, Explos., Pyrotech*., 2006, vol. 31, no. 3, p. 188.
14. Karaghiosoff, K., Klapötke, T.M., Mayer, P., Sabaté, C.M., and Penger, A., *Inorg. Chem*., 2008, vol. 47, no. 3, p. 1007.
15. Klapötke, T.M. and Sabaté, C.M., *Chem. Mater*., 2008, vol. 20, no. 5, p. 1750.
16. Klapötke, T.M. and Sabaté, C.M., *Eur. J. Inorg. Chem*., 2008, no. 34, p. 5350.
17. *APEX2 (Version 2008.6-1), SAINT (Version 7.60A), SADABS-2008/1*, Madison, Wisconsin, USA: Bruker AXS.
18. Sheldrick, G.M., *Acta Crystallogr., Sect. A*, 2008, vol. 64, no. 2, p. 112.
19. Allen, F.H., *Acta Crystallogr., Sect. B*, 2002, vol. 58, no. 3, p. 380.
20. Voitekhovich, S.V., Vorob'ev, A.N., Gaponik, P.N., and Ivashkevich, O.A., *Khim. Geterotsikl. Soedin*., 2005, no. 8, p. 1174.
21. Gaponik, P.N., Karavai, V.P., and Grigor'ev, Yu.V., *Khim. Geterotsikl. Soedin*., 2005, no. 8, p. 1174.