ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 6, pp. 874–881. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © T.P. Kofman, A.E. Trubitsin, I.V. Dmitrienko, E.Yu. Glazkova, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 6, pp. 883–889.

Dedicated to Prof. G.I. Koldobskii on his 75th anniversary

Synthesis and Properties of 5-Substituted 1-Dinitromethyl-3-nitro-1*H*-1,2,4-triazoles

T. P. Kofman, A. E. Trubitsin, I. V. Dmitrienko, and E. Yu. Glazkova

St. Petersburg State Institute of Technology, Moskovskii pr. 26, St. Petersburg, 190013 Russia
fax: +7(812)112 7791

Received December 21, 2007

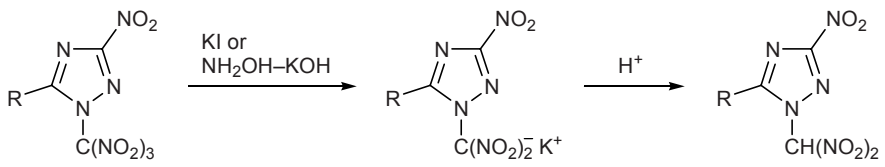
Abstract—Denitration of 5-R-substituted 3-nitro-1-trinitromethyl-1*H*-1,2,4-triazoles (R = CH_3, Cl, Br, N_3, NH_2) by the action of potassium iodide or hydroxylamine, followed by treatment with sulfuric acid, gave the corresponding 1-dinitromethyl derivatives which were shown to be very strong CH acids (pK_a –0.55 to –1.62).

DOI: 10.1134/S1070428008060171

5-Substituted 3-nitro-1-trinitromethyl-1*H*-1,2,4-triazoles **I**–**VI** (R = Me, NH_2, N_3, Cl, Br, NO_2) synthesized by us previously [1, 2] undergo denitration by the action of potassium iodide or hydroxylamine in alkaline medium according to the procedure commonly used for the conversion of trinitromethyl derivatives into dinitromethyl [3, 4]. As a result, the corresponding salts **VII**–**XI** were obtained [5]. If the substituent in the 5-position of the triazole ring in trinitromethyl derivatives is inactive toward nucleophilic reagents or reducing agents (compounds **I** and **II**), both potassium iodide and hydroxylamine can be used. The latter is more advantageous, for it ensures higher yield of salts **VII** and **VIII** (65–75 and 80–90%, respectively). Potassium salts of 5-halo- and 5-azidotriazoles **IX**–**XI** were obtained only using KI to avoid undesirable transformations with participation of the 5-substituent. Specific care was necessary in the synthesis of 5-azido-1-dinitromethyl-3-nitro-1*H*-1,2,4-triazole potassium salt (**IX**): the reaction was carried out by adding potassium iodide to a solution of azide **III** on cooling to 0–5°C, followed by quick separation of the resulting salt from the mother liquor (10–15 min). However, we failed to obtain potassium salt of 1-dinitromethyl-3,5-dinitro-1*H*-1,2,4-triazole using the above technique. Careful treatment of salts **VII**–**XI** with 30% sulfuric acid according to the procedure reported in [5] gave CH acids **XII**–**XVI** (Scheme 1).

The denitration of 3,5-dinitro-1-trinitromethyl-1*H*-1,2,4-triazole (**VI**) was accompanied by side processes leading to a mixture of salts which we failed to separate. Undoubtedly, the product mixture contained salts of dinitromethyl derivatives: the UV spectra of the mixture displayed strong absorption in the region λ 340–350 nm, which is typical of 1-dinitromethyl-1,2,4-triazoles [5]. However, in the IR spectrum we observed absorption bands in the region 1660–1670 cm^{-1}; such absorption is untypical of both dinitromethyl fragment in triazole salts [6] and 1-dinitromethyl-1,2,4-triazole salts [5]. The IR spectra of compounds isolated by treatment of the salt mixture with sulfuric acid and extraction with diethyl ether contained (as might be expected) a strong absorption band in the region 1620–1660 cm^{-1}, which is typical of

Scheme 1.



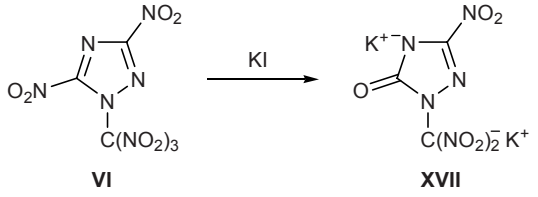
I–V **VII–XI** **XII–XVI**

I, **VII**, **XII**, R = Me; **II**, **VIII**, **XIII**, R = NH_2; **III**, **IX**, **XIV**, R = N_3; **IV**, **X**, **XV**, R = Cl; **V**, **XI**, **XVI**, R = Br.

N-dinitromethyl fragment [5], and a strong band at 1790 cm^{-1} was present. The latter, as well as the absorption at 1620–1660 cm^{-1} in the spectra of salts, can be assigned to stretching vibrations of a carbonyl group. The band at 1550–1570 cm^{-1} in the IR spectra of both potassium salts and CH acids belongs to stretching vibrations of the nitro group in position *3* of the triazole ring.

The above findings suggest that reactions of compound **VI** involve both trinitromethyl group and nitro group in position *5* and that the transformation products are most likely to contain 3-nitro-1,2,4-triazol-5-one derivatives. As a rule, the latter are formed as by-products in reactions of N-substituted 3,5-dinitro-1,2,4-triazoles with various nucleophiles [7]. By treatment of the salt mixture with an acid and subsequent extraction with diethyl ether and neutralization of the extract with an alcoholic solution of potassium acetate we succeeded in isolating a substance whose elemental composition corresponded to 1-dinitromethyl-3-nitro-2,4-dihydro-5*H*-1,2,4-triazol-5-one dipotassium salt (**XVII**) (Scheme 2). Crystallization from water gave the corresponding crystal hydrate; its structure was confirmed by thermogravimetric analysis which showed an endothermic peak at about 100°C with a weight loss corresponding to one water molecule. However, the amount of isolated salt **XVII** was very small, and we failed to obtain and identify the corresponding CH acid.

Scheme 2.



VI **XVII**

As we already noted [5], in the treatment of 1-dinitromethyl-1,2,4-triazole salts with sulfuric acid it is necessary to quickly remove the products from acid medium in order to avoid hydrolysis of the dinitromethyl group to carboxy and subsequent decarboxylation [8] with formation of 3-nitro-1,2,4-triazoles. For this purpose, the product was extracted into diethyl ether *in situ* (diethyl ether was added to sulfuric acid before addition of the salt). The yields of 1-dinitromethyl-1,2,4-triazoles ranged from 60 to 70%.

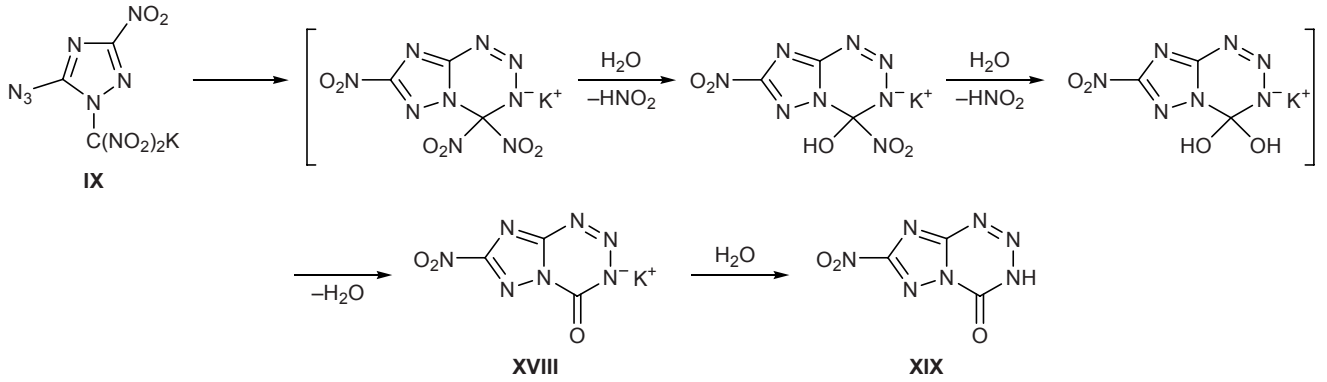
Special precautions should be taken while handling with 5-azido-1-dinitromethyl-3-nitro-1*H*-1,2,4-triazole (**XIV**) and its potassium salt **IX**. The isolation of CH acid **XIV** by extraction must be carried out on cooling. When salt **IX** was kept in sulfuric acid without removal of CH acid **XIV** by extraction, they were converted into new substances **XVIII** and **XIX**; the latter are also formed on careless heating of **IX** and **XIV**. The spectral and analytical data of **XVIII** and **XIX** conform to neither 5-azido-3-nitro-1,2,4-triazole nor its potassium salt, whose formation might be expected as a result of hydrolysis of the dinitromethyl group.

Recrystallization of salt **IX** (mp 113°C) from ethanol gave salt **XVIII** (mp 192°C) which was also obtained as the only product on treatment of **XIX** with alkali. Compounds **XVIII** and **XIX** contained neither azide nor dinitromethyl group. Moreover, in the IR spectrum of **XIX** we observed a strong carbonyl absorption band at 1710 cm^{-1}; the corresponding band in the spectrum of salt **XVIII** was displaced toward lower frequencies (1615, 1620 cm^{-1}). The ^1H NMR spectrum of **XIX** lacked signal assignable to the $CH(NO_2)_2$ proton, but a signal at δ 11.2 ppm was present; the latter disappeared upon addition of D_2O, which is typical of an endocyclic NH group. Compound **XIX** is a weaker acid (pK_a = 3.53; determined by potentiometric titration) than 1-dinitromethyl-1,2,4-triazoles described previously (pK_a = 1.37–0.12) [5].

Products **XVIII** and **XIX**, as well as their azido-substituted precursors, are polynitrogen compounds (the concentration of nitrogen exceeds 50%) that are highly sensitive to thermal and mechanical impacts; this suggests that the azide fragment resides in their structure in a latent form. According to the elemental composition and molecular weight (determined by ebullioscopy; see Experimental), compound **XIX** has the formula $C_3HN_7O_3$. Therefore, it was assigned the structure of 7-nitro[1,2,4]triazolo[5,1-*d*][1,2,3,5]tetrazin-4(3*H*)-one formed via annulation of the azide group to the triazole ring (Scheme 3). Presumably, the mechanism of this transformation involves attack by the terminal nitrogen atom of the azide group on the carbanionic center with proton transfer, stepwise hydrolysis of both nitro groups (which depart as HNO_2), and stabilization of the geminal diol thus formed via elimination of water molecule to give carbonyl group.

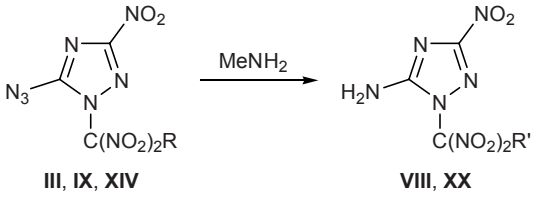
The azide group in the examined triazole derivatives is highly reactive: it is readily reduced to amino group in both 1-trinitromethyl- and 1-dinitromethyl-5-azido-3-nitro-1*H*-1,2,4-triazoles **III** and **XIV** and potassium salt **IX**. Compounds **III**, **XIV**, and **IX** react with nitrogen-centered nucleophiles to give the corresponding amines. For example, treatment of 5-azido-1-

Scheme 3.



trinitromethyl- and 5-azido-1-dinitromethyl-3-nitro-1*H*-1,2,4-triazoles **III** and **XIV** with methylamine gave 5-amino-1-dinitromethyl-3-nitro-1*H*-1,2,4-triazole methylammonium salt (**XX**), while salt **IX** reacted with the same nucleophile to afford potassium salt **VIII** (Scheme 4).

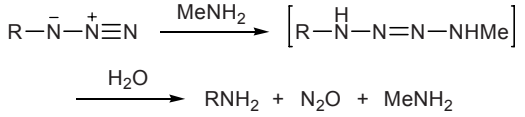
Scheme 4.



III, R = NO_2; **IX**, R = K; **XIV**, R = H; **VIII**, R′ = K; **XX**, R′ = $MeNH_3^+$.

The transformation of azide group into amino rather than the expected replacement by methylamino group, may be interpreted assuming preferential attack by the nucleophile on the terminal nitrogen atom in the azido group rather than on C^5; i.e., the process is likely to follow the addition–elimination pattern (Scheme 5). An analogous transformation was observed by us previously in reactions of other 5-azido-3-nitro-1*H*-1,2,4-triazole derivatives with strong organic bases [9].

Scheme 5.

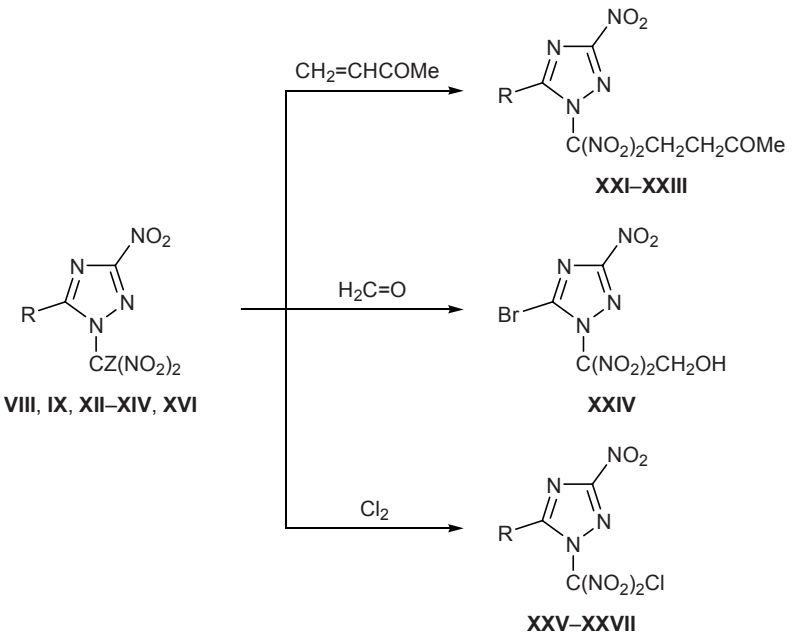


In the IR spectra of 5-substituted 1-dinitromethyl-3-nitro-1*H*-1,2,4-triazoles, as well as in the spectra of 3-substituted 1-dinitromethyl-1*H*-1,2,4-triazoles [5], antisymmetric stretching vibrations of nitro groups in the dinitromethyl fragment are characterized by a higher frequency (ν_{as} 1610–1660 cm^{-1}) as compared to aliphatic dinitromethyl compounds; most frequently, they appear as two high-intensity bands. The IR spectra of the corresponding potassium salts lack absorption in that region, which is typical of salts derived from alkyl- and aryldinitromethanes [6]. Symmetric stretching vibrations of nitro groups in the dinitromethyl fragment have a frequency of 1310–1325 cm^{-1}, and the band belonging to stretching vibrations of the 3-nitro group is also displaced toward higher frequencies (ν_{as} 1575–1590 cm^{-1}) relative to analogous absorption band of N-substituted 3-nitro-5-R-1,2,4-triazoles; this pattern might be expected, taking into account the presence of such a strong electron-withdrawing group in position *1* of the triazole ring.

The CH proton in the dinitromethyl fragment appears in the ^1H NMR spectra in a weak field (δ 9.0–9.5 ppm; cf. [5]), and its signal disappears upon addition of D_2O. The long-wave absorption maximum in the UV spectra of 5-substituted 1-dinitromethyl-3-nitro-1*H*-1,2,4-triazoles **XII**–**XVI** is located at λ 340 nm ($\log\varepsilon$ = 4.1–4.2, see table), and its position almost does not depend on the nature of substituent in the 5-position. Only in the spectrum of triazolone **XVII**, the long-wave absorption maximum appears at λ 350 nm due to reduced aromaticity and hence acceptor power of the triazole ring.

Acid dissociation of the obtained 1-dinitromethyltriazoles was studied by spectrophotometry [10]. All 5-substituted 1-dinitromethyl-3-nitro-1*H*-1,2,4-triazoles (R = H [5], Me, NH_2, N_3, Cl, Br) were found to be very strong CH acids; introduction of any substituent into the 5-position increases the acidity relative to 1-dinitromethyl-3-nitro-1*H*-1,2,4-triazole (see table). Increased acidity of derivatives having electron-withdrawing substituents in position *5* might be expected, whereas electron-donating substituents could raise the acidity as a result of *ortho* effect, i.e., increased steric

Scheme 6.



VIII, **XIII**, **XXII**, **XXV**, R = NH_2; **IX**, **XIV**, **XXVI**, R = N_3; **XI**, **XVI**, **XXIII**, **XXIV**, **XXVII**, R = Br; **XII**, **XXI**, R = Me.

hindrances in going from sp^2- to sp^3-hybridized carbon atom upon proton addition. An analogous pattern was observed previously for *ortho*-substituted aryldinitromethanes [4, 11]. The pK_a values of 5-substituted 1-dinitromethyl-3-nitro-1*H*-1,2,4-triazoles showed no correlation with Hammett substituent constants σ.

5-Substituted 1-dinitromethyl-3-nitro-1*H*-1,2,4-triazoles react with compounds having an activated double bond (Michael addition) and formaldehyde (Henry reaction), while their salts readily undergo chlorination. By reaction of triazoles **XII**, **XIII**, and **XVI** with methyl vinyl ketone in aprotic medium (acetone, diethyl ether) at room temperature in the absence of a catalyst we obtained 5,5-dinitro-5-(5-R-3-nitro-1*H*-1,2,4-triazol-1-yl)pentan-2-ones **XXI**–**XXIII**. CH Acid **XVI** reacted with formaldehyde in acetone to give 2-(5-bromo-3-nitro-1*H*-1,2,4-triazol-1-yl)-2,2-dinitroethanol (**XXIV**). Chlorination of potassium salts **VIII**, **IX**, **XI** in diethyl ether at room temperature gave the corresponding 5-substituted 1-chlorodinitromethyl-3-nitro-1*H*-1,2,4-triazoles **XXV**–**XXVII** (Scheme 6).

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Perkin–Elmer R-12 spectrometer at 60 MHz using acetone-d_6 as solvent and hexamethyldisiloxane as internal reference. The IR spectra were obtained from samples prepared as films on a Specord 75IR instrument. The CH acidities of dinitromethyltriazoles were determined by spectrophotometry in aqueous buffers according to the standard procedure [10] using an SF-16 spectrophotometer and a pH-262 pH-meter. Elemental analysis was performed on a Hewlett–Packard 185B CHN analyzer. The molecular weights were determined by ebullioscopy in dichloroethane. Thermal gravimetric analysis was performed on a Paulik–Paulik–Erdey instrument.

5-Substituted 1-dinitromethyl-3-nitro-1*H*-1,2,4-triazole potassium salts VII, VIII, X, and XI (*general procedure***).** *a*. 5-Substituted 3-nitro-1-trinitromethyl-1*H*-1,2,4-triazole **I**, **II**, **IV**, or **V**, 2.5 mmol,

Absorption maxima in the UV spectra and pK_a values of 5-substituted 1-dinitromethyl-3-nitro-1*H*-1,2,4-triazoles **XII**–**XVII**

Compound no.	λ_{max}, nm	ε_{max}, l mol^{-1} cm^{-1}	pK_a, 20°C
R = H[a]	340	17000	0.12±0.05
XII	340	17300	–0.82±0.05
XIII	340	18000	–0.55±0.03
XIV	340	14500	–0.55±0.03
XV	340	16500	–1.62±0.03
XVI	340	16700	–1.62±0.05
XVII	350	19800	1.24±0.03

[a] Data of [5].

was added in portions to a solution of 0.87 g (5 mmol) of potassium iodide in 7 ml of methanol under stirring at room temperature. The mixture was stirred for 1 h and was left overnight in a refrigerator. The precipitate was filtered off using a Teflon nutsch filter, washed with cold methanol, dried in air, and recrystallized from appropriate solvent.

b. A solution of 0.78 g (14 mmol) of potassium hydroxide in 10 ml of methanol was added to a solution of 0.25 g (3.7 mmol) of hydroxylamine hydrochloride in 8 ml of methanol, the mixture was cooled to 0°C, the precipitate of potassium chloride was filtered off and washed on a filter with cold methanol, and the filtrate was added in portions to a solution of 3.6 mmol of trinitromethyltriazole **I**, **II**, **IV**, or **V** under stirring at 0°C. The mixture was kept for 1 h at 0°C, allowed to warm up to room temperature, and left to stand in a hood to allow the solvent to partially evaporate (to 1/4 of the initial volume). The residue was diluted with 50 ml of diethyl ether, and the mixture was left overnight in a refrigerator. The precipitate was filtered off through a Teflon nutsch filter, washed with diethyl ether, dried in air, and recrystallized if necessary.

Potassium (5-methyl-3-nitro-1*H*-1,2,4-triazol-1-yl)dinitromethanide (VII). Yield 70% (*a*), 90% (*b*); mp 149–150°C (from EtOH–H_2O, 1:1). IR spectrum, ν, cm^{-1}: 870 s, 1050, 1065, 1170 s, 1240 s, 1325, 1380, 1400 s, 1495 s, 1530 (ring), 1550, 1570. ^1H NMR spectrum, δ: 2.45 ppm, s (3H, CH_3). Found, %: C 18.03; H 0.95; N 31.42. $C_4H_3KN_6O_6$. Calculated, %: C 17.78; H 1.12; N 31.10.

Potassium (5-amino-3-nitro-1*H*-1,2,4-triazol-1-yl)dinitromethanide (VIII). Yield 75% (*a*), 90% (*b*); mp 231–232°C (from EtOH–H_2O, 1:1). IR spectrum, ν, cm^{-1}: 870, 1030, 1080, 1100, 1160 s, 1230 s, 1325 s, 1345, 1445, 1525 (ring), 1565, 1590 (NO_2), 1675 s (NH_2), 3440 (NH_2). ^1H NMR spectrum: δ 7.00 ppm, s (2H, NH_2), exchangeable with D_2O. Found, %: C 13.53; H 0.95; N 35.62. $C_3H_2KN_7O_6$. Calculated, %: C 13.28; H 0.74; N 36.16.

Potassium (5-chloro-3-nitro-1*H*-1,2,4-triazol-1-yl)dinitromethanide (X). Yield 60% (*a*), 80% (*b*); mp 158–159°C (from EtOH–H_2O, 1:1). IR spectrum, ν, cm^{-1}: 860, 1020, 1040, 1170 s, 1240 s, 1320 s, 1380, 1400 s, 1470, 1495 s, 1520 (ring), 1580 s (NO_2). Found, %: C 12.46; Cl 12.82; N 28.36. $C_3ClKN_6O_6$. Calculated, %: C 12.40; Cl 12.20; N 28.92.

Potassium (5-bromo-3-nitro-1*H*-1,2,4-triazol-1-yl)dinitromethanide (XI). Yield 65% (*a*), 80% (*b*); mp 195–196°C (from EtOH–H_2O, 1:2). IR spectrum, ν, cm^{-1}: 860, 1020, 1040, 1140 s, 1170 s, 1240 s, 1260 s, 1320 s, 1370, 1400 s, 1460, 1490 s, 1530 (ring), 1580 s (NO_2). Found, %: C 10.46; Br 24.13; N 25.33. $C_3BrKN_6O_6$. Calculated, %: C 10.75; Br 23.85; N 25.08.

Potassium (5-azido-3-nitro-1*H*-1,2,4-triazol-1-yl)-dinitromethanide (IX). A solution of 0.87 g (5 mmol) of potassium iodide in 7 ml of methanol was added to a solution of 0.75 g (2.5 mmol) of 5-azido-3-nitro-1-trinitromethyl-1*H*-1,2,4-triazole (**III**) in 5 ml of methanol under stirring at 0°C, the mixture was stirred for 15 min, and the precipitate was filtered off through a Teflon nutsch filter, washed on a filter with cold methanol, and dried in air. Yield 60%, mp 112–113°C (reprecipitated from water with methanol, 1:2). IR spectrum, ν, cm^{-1}: 890, 1030, 1050, 1065, 1140, 1175, 1230 s, 1269 s, 1320, 1335, 1390, 1415, 1440, 1500 s, 1545 (ring), 1580 (NO_2), 2170 s (N_3). Found, %: C 12.06; N 42.42. $C_3KN_9O_6$. Calculated, %: C 12.12; N 42.42.

5-Substituted 1-dinitromethyl-3-nitro-1*H*-1,2,4-triazoles XII–XVI (*general procedure*). Diethyl ether, 15 ml, was added under stirring at room temperature to 7.5 ml of 30% sulfuric acid, 0.5 g of potassium salt **VII–XII** was then added in portions, the mixture was stirred for 3–5 min, the organic phase was separated, and the aqueous phase was additionally extracted with diethyl ether (5×15 ml). The extracts were combined, washed with water, and evaporated in air, and the residue was recrystallized from appropriate solvent.

1-Dinitromethyl-3-nitro-1*H*-1,2,4-triazole. Yield 70%, mp 115–116°C (from $CHCl_3$) [5].

1-Dinitromethyl-5-methyl-3-nitro-1*H*-1,2,4-triazole (XII). Yield 90%, mp 132–133°C (from $CHCl_3$–CH_2Cl_2, 1:1). IR spectrum, ν, cm^{-1}: 850, 920, 935, 950, 1020, 1050, 1140, 1260, 1325 s, 1380, 1410, 1460, 1520, 1560 (ring), 1590 s (NO_2), 1620 s, 1630 s [$C(NO_2)_2$]. ^1H NMR spectrum, δ, ppm: 2.85 s (3H, CH_3), 9.48 s (1H, CH, exchangeable with D_2O). Found, %: C 21.12; H 1.57; N 36.47. *M* 224. $C_4H_4N_6O_6$. Calculated, %: C 20.70; H 1.74; N 36.21. *M* 232.11.

1-Dinitromethyl-3-nitro-1*H*-1,2,4-triazol-5-amine (XIII). Yield 60%, mp 168–169°C (from $CHCl_3$–MeOH, 1:2). IR spectrum, ν, cm^{-1}: 850, 910, 940, 960, 1035, 1085, 1150 s, 1295 s, 1325 s, 1425, 1545 s (ring), 1580 s (NO_2), 1610 s, 1660 s [$C(NO_2)_2$], 3385 (NH_2). ^1H NMR spectrum, δ, ppm: 9.00 s (1H, CH), 7.75 (2H, NH_2), both signals disappeared upon addition of D_2O. Found, %: C 15.63; H 1.32; N 42.12.

M 239. $C_3H_3N_7O_6$. Calculated, %: C 15.46; H 1.39; N 42.06. *M* 233.10.

5-Azido-1-dinitromethyl-3-nitro-1*H*-1,2,4-triazole (XIV). Yield 60%, mp 91–92°C (from acetone, –30°C). IR spectrum, ν, cm^{-1}: 840, 870, 940, 950, 1030, 1100, 1220 s, 1275, 1320 s, 1375, 1425 s, 1530 s (ring), 1580 s (NO_2), 1620 s [$C(NO_2)_2$], 2190 s (N_3). ^1H NMR spectrum, δ, ppm: 9.20 s (1H, CH), exchangeable with D_2O. Found, %: C 14.33; H 0.42; N 49.12. *M* 247. $C_3HN_9O_6$. Calculated, %: C 13.91; H 0.39; N 48.66. *M* 259.13.

5-Chloro-1-dinitromethyl-3-nitro-1*H*-1,2,4-triazole (XV). Yield 70%, mp 142–143°C (from CCl_4). IR spectrum, ν, cm^{-1}: 820 s, 845 s, 870 s, 900 s, 950, 1025 s, 1085 s, 1100, 1195 s, 1260, 1289, 1320 s, 1380, 1410 s, 1460 s, 1530 s (ring), 1580 s (NO_2), 1615 s, 1625 s [$C(NO_2)_2$]. ^1H NMR spectrum, δ, ppm: 9.20 s (1H, CH), exchangeable with D_2O. Found, %: C 14.22; H 0.44; Cl 14.66; N 33.34. *M* 254. $C_3HClN_6O_6$. Calculated, %: C 14.27; H 0.49; Cl 14.04; N 33.28. *M* 252.53.

5-Bromo-1-dinitromethyl-3-nitro-1*H*-1,2,4-triazole (XVI). Yield 70%, mp 89–90°C (from CCl_4). IR spectrum, ν, cm^{-1}: 820 s, 870, 910, 930, 1020, 1080, 1135, 1180, 1265, 1310 s, 1390, 1450, 1510, 1555 (ring), 1580 s (NO_2), 1610 s, 1630 s [$C(NO_2)_2$]. ^1H NMR spectrum, δ, ppm: 9.35 (1H, CH), exchangeable with D_2O. Found, %: C 12.14; H 0.22; Br 26,9; N 28.3. *M* 285. $C_3HBrN_6O_6$. Calculated, %: C 12.13; H 0.34; Br 26.91; N 28.30. *M* 296.98.

Dipotassium 2-(dinitromethanidyl)-3-methyl-5-oxo-2,5-dihydro-1,2,4-triazol-1-ide (XVII). 3,5-Dinitro-1-trinitromethyl-1H-1,2,4-triazole (**VI**), 0.75 g (2.5 mmol), was added in portions to a solution of 0.87 g (5 mmol) of potassium iodide in 7 ml of methanol under stirring and cooling. The mixture was kept for 1 h and left overnight in a refrigerator. The precipitate was filtered off through a Teflon nutsch filter, washed with cold methanol on a filter, dried in air, and recrystallized from methanol. The product was carefully added in portions under stirring and cooling to 10 ml of 10% sulfuric acid. The resulting solution was extracted with diethyl ether (3×15 ml), the extract was dried over calcined magnesium sulfate, the drying agent was filtered off, and a solution of potassium acetate was added to the filtrate to pH 7. The salt thus obtained was again dissolved in 10% sulfuric acid, and the above operation was repeated. The residue (about 100 mg) was recrystallized from water. mp 240°C (with decomposition, according to thermal gravimetric analysis). IR spectrum, ν, cm^{-1}: 860, 1020, 1040, 1140 s, 1180 s, 1240, 1320 s, 1340 s, 1390 s, 1460, 1495 s, 1520 (ring), 1570 s (NO_2), 1660–1670 s (C=O). Found, %: C 11.33; H 0.52; N 25.91; H_2O 6.1 (TGA). $C_3H_2K_2N_6O_7$. Calculated, %: C 10.97; H 0.61; N 25.60; H_2O 5.49.

Potassium 7-nitro-4-oxo-3,4-dihydro[1,2,4]triazolo[5,1-*d*][1,2,3,5]tetrazin-3-ide (XVIII). Potassium salt **XI**, 0.5 g, was added to 10 ml of 50% aqueous ethanol, the mixture was heated to the boiling point and cooled, and the precipitate was filtered off. Yield 83%, mp 192°C (decomp.). IR spectrum, ν, cm^{-1}: 830, 850 s, 900, 1020, 1130, 1250, 1285, 1320 v.s, 1360, 1400, 1410, 1450 s, 1460, 1545 (ring), 1585 s (NO_2), 1615 v.s., 1620 v.s (C=O). Found, %: C 16.57; N 43.95. $C_3KN_7O_3$. Calculated, %: C 16.29; N 44.33.

7-Nitro-1,2,4-triazolo[5,1-*d*][1,2,3,5]tetrazin-4(3*H*)-one (XIX). *a*. A mixture of 0.5 g of compound **XIV** and 10 ml of water was heated to the boiling point, cooled, and extracted with ethyl acetate (4× 25 ml). The extracts were combined, washed with water, and dried over calcined magnesium sulfate, the solvent was removed, and the residue was recrystallized from alcohol. Yield 70%, mp 166–167°C. IR spectrum, ν, cm^{-1}: 860 s, 960, 1040, 1095, 1150, 1210 s, 1320 s, 1400 s, 1420, 1450, 1460, 1540 s (ring), 1570 s (NO_2), 1790 v.s (C=O). ^1H NMR spectrum: δ 11.2 ppm, s (NH), exchangeable with D_2O. Found, %: C 19.87; H 0.56; N 53.35. *M* 188 (in acetone). $C_3HN_7O_3$. Calculated, %: C 19.67; H 0.55; N 53.55. *M* 183.08.

b. Potassium salt **XVIII**, 0.5 g, was added to 10 ml of 5% sulfuric acid, the mixture was carefully heated until it became homogeneous (40–50°C) and cooled, and the product was isolated as described above in *a*. Yield 75%.

Methylammonium (5-amino-3-nitro-1*H*-1,2,4-triazol-1-yl)dinitromethanide (XX). Azide **III** or **XIV** or amine **II** or **XIII**, 0.2 g, was added in portions under stirring and cooling to 5 ml of 25% aqueous methylamine, the mixture was allowed to warm up to room temperature and stirred for 3 h, the aqueous phase and excess methylamine were evaporated, and the residue was purified by recrystallization. Yield 50–55% (from **II** or **III**), 70–75% (from **XIII** or **XIV**); mp 191–192°C (from methanol). IR spectrum, ν, cm^{-1}: 850, 875 s, 930, 950, 990, 1015, 1090, 1150, 1160, 1250–1310 s, 1340, 1390, 1420, 1450, 1500 s, 1550 s (ring), 1580 s (NO_2), 1640 s, 1660 v.s (NH_2), 3350, 3440 (NH_2). ^1H NMR spectrum, δ, ppm: 2.50 s (3H, CH_3), 7.30 s (NH_2^+). Found, %: C 18.72; H 2.82;

N 42.51. $C_4H_8N_8O_6$. Calculated, %: C 18.19; H 3.05; N 42.42.

5,5-Dinitro-5-(5-R-3-nitro-1*H*-1,2,4-triazol-1-yl)-pentan-2-ones XXI–XXIII (*general procedure*). Freshly distilled methyl vinyl ketone, 0.5 ml (1.5 mol), was added to a solution of 1 mmol of triazole **XII**, **XIII**, or **XVI** in 5 ml of acetone, and the mixture was left to stand for 72 h at room temperature in a closed vessel. The solvent was evaporated, and the residue was recrystallized from ethanol.

5-(5-Methyl-3-nitro-1*H*-1,2,4-triazol-1-yl)-5,5-dinitropentan-2-one (XXI). Yield 75%, mp 99–100°C (from EtOH). IR spectrum, ν, cm^{-1}: 800 s, 860, 870, 890, 960, 970, 990, 1030, 1040, 1090, 1110, 1190, 1230, 1260, 1290, 1335 s, 1350 s, 1370, 1420, 1440, 1510 s (ring), 1585 s (NO_2), 1610 s [$C(NO_2)_2$], 1740 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.15 s and 2.60 s (CH_3), 3.08 t (CH_2, J = 6 Hz), 3.74 t (CH_2, J = 6 Hz). Found, %: C 31.61; H 3.40; N 27.65. M 298. $C_8H_{10}N_6O_7$. Calculated, %: C 31.80; H 3.33; N 27.81. M 302.20.

5-(5-Amino-3-nitro-1*H*-1,2,4-triazol-1-yl)-5,5-dinitropentan-2-one (XXII). Yield 60%, mp 183–184°C (from EtOH). IR spectrum, ν, cm^{-1}: 800 s, 845, 860 s, 1010, 1050, 1185, 1195, 1230, 1320 s, 1380 s, 1415, 1440, 1520 (ring), 1550 s (NO_2), 1600 (NH_2), 1665 v.s [$C(NO_2)_2$], 1720 v.s (C=O). ^{1}H NMR spectrum, δ, ppm: 2.15 s (CH_3), 2.90 t (CH_2, J = 10 Hz), 3.50 t (CH_2, J = 10 Hz), 7.20 s (NH_2, exchangeable with D_2O). Found, %: C 27.32; H 2.67; N 32.62. M 297. $C_7H_9N_7O_7$. Calculated, %: C 27.73; H 2.99; N 32.34. M 303.19.

5-(5-Bromo-3-nitro-1*H*-1,2,4-triazol-1-yl)-5,5-dinitropentan-2-one (XXIII). Yield 90%, mp 119–129°C (from EtOH). IR spectrum, ν, cm^{-1}: 800 s, 830, 855, 880, 960, 1070, 1110, 1190, 1270, 1360, 1440, 1520 (ring), 1590 s (NO_2), 1615 s [$C(NO_2)_2$], 1730 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.15 s (3H, CH_3), 3.03 t (2H, CH_2, J = 10 Hz), 3.70 t (2H, CH_2, J = 10 Hz). Found, %: C 22.71; H 2.13; Br 21.35; N 23.26. M 362. $C_7H_7BrN_6O_7$. Calculated, %: C 22.90; H 1.92; Br 21.77; N 22.90. M 367.07.

2-(5-Bromo-3-nitro-1*H*-1,2,4-triazol-1-yl)-2,2-dinitroethanol (XXIV). Compound **XVI**, 0.1 g (0.045 mmol), was dissolved in 5 ml of acetone, 0.5 ml (6 mmol) of a 35% formaldehyde solution was added, and the mixture was stirred for 4 h at room temperature and left overnight. The mixture was diluted with an equal volume of water, the solvent was evaporated in air, and the precipitate was filtered off, dissolved in diethyl ether, and reprecipitated with carbon tetrachloride. Yield 90%, mp 104–105°C (from ethanol). IR spectrum, ν, cm^{-1}: 800 s, 830 s, 860 s, 880, 1040, 1060, 1110, 1150, 1220, 1290, 1320 s, 1350, 1380, 1400, 1450, 1530 (ring), 1590 s (NO_2), 1620 s [$C(NO_2)_2$], 3500 (OH). ^{1}H NMR spectrum, δ, ppm: 5.35 t (CH_2), 5.85 t (J = 7 Hz), 6.2 (OH, exchangeable with D_2O). Found, %: C 14.35; H 0.74; Br 24.62; N 25.26. M 332. $C_4H_3BrN_6O_7$. Calculated, %: C 14.69; H 0.92; Br 24.43; N 25.70. M 327.01

5-Substituted 1-chlorodinitromethyl-3-nitro-1*H*-1,2,4-triazoles XXV–XXVII (*general procedure*). Gaseous chlorine was bubbled over a period of 3–4 h through a suspension of 0.5 g of salt **VIII**, **IX**, or **XI** in 10 ml of diethyl ether under stirring at 0–5°C until the precipitate turned colorless. The mixture was left overnight, the precipitate of KCl was filtered off and washed with diethyl ether on a filter, the filtrate was evaporated, and the residue was recrystallized from appropriate solvent.

1-Chlorodinitromethyl-3-nitro-1*H*-1,2,4-triazol-5-amine (XXV). Yield 50%, mp 83–84°C (from dichloroethane). IR spectrum, ν, cm^{-1}: 835 s, 850, 940, 1000 s, 1095, 1160, 1310 s, 1320 v.s, 1390, 1430, 1550 (ring, NO_2), 1625 v.s, 1640 s, 1670 s [$C(NO_2)_2$]. ^{1}H NMR spectrum: δ 7.95 ppm, s (NH_2), exchangeable with D_2O. Found, %: C 13.68; H 0.55; Cl 14.00; N 36.90. M 276. $C_3H_2ClN_7O_6$. Calculated, %: C 13.47; H 0.75; Cl 13.25; N 36.65. M 267.54.

5-Azido-1-chlorodinitromethyl-3-nitro-1*H*-1,2,4-triazole (XXVI). Yield 70%, mp 109–110°C (from CCl_4). IR spectrum, ν, cm^{-1}: 810, 840, 870, 900, 950, 1000, 1030, 1230, 1300 s, 1325 s, 1365, 1410, 1520 (ring), 1570 (NO_2), 1600 s, 1630 s [$C(NO_2)_2$], 2200 s (N_3). Found, %: C 12.60; Cl 11.95; N 43.11. M 295. $C_3ClN_9O_6$. Calculated, %: C 12.28; Cl 12.08; N 42.95. M 293.54.

5-Bromo-1-chlorodinitromethyl-3-nitro-1*H*-1,2,4-triazole (XXVII). Yield 70%, mp 98–99°C (from CCl_4). IR spectrum, ν, cm^{-1}: 830, 850, 930, 990, 1030, 1120, 1240 s, 1310 s, 1395, 1440, 1520 (ring), 1580 s (NO_2), 1620 s [$C(NO_2)_2$]. Found, %: C 11.02; Br 24.60; Cl 9.96; N 25.52. M 325. $C_3BrClN_6O_6$. Calculated, %: C 10.87; Br 24.11; Cl 10.70; N 25.36. M 331.43.

REFERENCES

1. Kofman, T.P., Uspenskaya, T.L., Malygina, L.V., and Pevzner, M.S., USSR Inventor's Certificate no. 1840302, 2006; *Byull. Izobret.*, 2006, no. 24.

2. Kofman, T.P., Kartseva, G.Yu., Glazkova, E.Yu., and Krasnov, K.N., *Russ. J. Org. Chem*., 2008, vol. 44, p. 870.
3. Kaplan, L.A., *The Chemistry of the Nitro and Nitroso Groups*, Feuer, H., Ed., New York: Wiley, 1970, part 2. Translated under the title *Khimiya nitro- i nitrozogrupp*, Moscow: Mir, 1972, vol. 2, p. 221.
4. Tselinskii, I.V., *Doctoral (Chem.) Dissertation*, Leningrad, 1974.
5. Kofman, T.P., Trubitsin, E.A., Dmitrienko, I.V., Glazkova, E.Yu., and Tselinskii, I.V., *Russ. J. Org. Chem*., 2007, vol. 43, p. 758.
6. Novikov, S.S., Shvekhgeimer, G.A., Sevost'yanova, V.V., and Shlyapochnikov, V.A., *Khimiya alifaticheskikh i alitsiklicheskikh nitrosoedinenii* (Chemistry of Aliphatic and Alicyclic Nitro Compounds), Moscow: Khimiya, 1974, p. 355.
7. Bagal, L.I., Pevzner, M.S., Samarenko, V.Ya., and Egorov, A.P., *Khim. Geterotsikl. Soedin*., 1970, p. 703; Kofman, T.P., Kartseva, G.Yu, Namestnikov, V.I., and Paketina, E.A., *Russ. J. Org. Chem*., 1998, vol. 34, p. 1032; Kofman, T.P., *Russ. J. Org. Chem*., 2001, vol. 37, p. 1158.
8. Kamlet, M.J. and Glover, D.J., *J. Org. Chem*., 1962, vol. 27, p. 537; Kaplan, L.A., *J. Org. Chem*., 1964, vol. 29, p. 2256.
9. Kofman, T.P., Pakhomov, K.E., and Pevzner, M.S., *Khim. Geterotsikl. Soedin*., 1982, p. 848.
10. Albert, A. and Serjeant, E., *Ionization Constants of Acids and Bases*, London: Methuen, 1962. Translated under the title *Konstanty ionizatsii kislot i osnovanii*, Moscow: Khimiya, 1964, p. 21.
11. Kolesetskaya, G.I., Tselinskii, I.V., and Bagal, L.I., *Reakts. Sposobn. Org. Soedin*., 1968, vol. 6, p. 386.