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Dedicated to Professor V.A.Ostrovskii on occasion of his sixtieth birthday

Synthesis and Properties of 1-Dinitromethyl-3-R-1,2,4-triazoles

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Abstract—Reductive denitration of 1-trinitromethyl-3-R-1,2,4-triazoles by KI or NH_2OH followed by the treatment of the formed 1-dinitromethyl-3-R-1,2,4-triazoles salts with sulfuric acid yielded dinitromethyl compounds (R = H, N_3, Cl, NO_2), sufficiently strong CH-acids (pK_a 1.37–0.12) whose typical reactions are similar to those of *gem*-dinitrocompounds from the aliphatic series. The spectral data and the analysis of correlation relations between pK_a of 1-dinitromethyl-3-R-1,2,4-triazoles and the substituent constants confirm that their structure is analogous to that of the majority of compounds belonging to the mentioned series.

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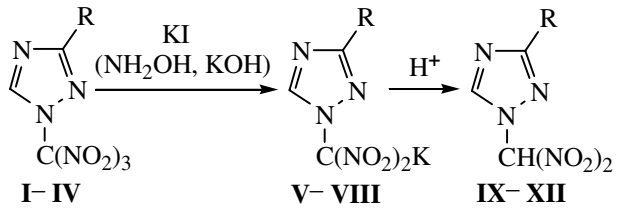
The successful preparation of 1-trinitromethyl-3-R-1,2,4-triazoles **I–IV** [1] provided a possibility to get over to their dinitromethyl analogs applying the classic method, a reduction of trinitromethyl compounds with potassium iodide or hydroxylamine in alkaline medium [2, 3] giving potassium salts of the corresponding 1-dinitromethyl-3-R-1,2,4-triazoles **V–VIII** (Scheme 1). The use of hydroxylamine like with other polyfunc-tional compounds [3] proved to be more favorable with the most 1-trinitromethyl-3-R-1,2,4-triazoles due to the high selectivity of the reaction that occurred prevailingly at the carbon atom of the trinitromethyl moiety practically excluding side processes: the reagent attack on the positions *1* or *3* of the ring. Only in the case of 3-azido-1-trinitro-methyl-1,2,4-triazole the application of the hydroxylamine resulted in a low yield of dinitromethyl compound **VI** evidently because of the probable reduction of the azido group. In this reaction application of KI was more feasible.

The high selectivity of the reaction with hydroxylamine for the majority of 1-trinitromethyl-3-R-1,2,4-triazoles was confirmed both by the high yield (up to 90%) and virtually analytical purity of salts obtained, and therefore it was possible to use them in further syntheses without additional purification. The latter opportunity is lucky, for the salts are very sensitive to mechanical forces.

Scheme 1.



I– IV **V– VIII** **IX– XII**

R = H (**I, V, IX**), N_3 (**II, VI, X**), Cl (**III, VII, XI**), NO_2 (**IV, VIII, XII**).

In reduction of 1-trinitromethyl-3-R-1,2,4-triazoles with potassium iodide the yield of salts was lower (60–70%), the products were contaminated with iodine and required an additional purification.

1-Dinitromethyl-3-R-1,2,4-triazoles salts **V–VIII** can be converted into the corresponding CH-acids **IX–XII** (Scheme 1), but only at the application of sufficiently concentrated sulfuric acid (over 20%) indicating the high acidity of the dinitromethyl compounds of this type.

In reaction of salts with acid the target compounds **IX–XII** should be quickly removed from the acidic environment: The long contact with the acid or the attempt at heating in order to increase the solubility of salts at the use of more dilute acid results in sharply decreased yield due to the hydrolysis of 1-dinitromethyl-3-R-1,2,4-triazoles to the corresponding NH-acids (in [4] is described the reaction version with conversion of the dinitromethyl group into a carboxyl followed by decarboxylation). We succeeded in removal of 1-dinitro-methyl-3-R-1,2,4-triazoles from the reaction zone and isolated them in good yield by extraction into ether or ethyl acetate; therewith the extractant should be added to the acid before the introduction of salt. Although the solubility of the target products in ethyl acetate is higher, the use of ethyl ether is preferable for ethyl acetate

considerably hydrolyzes in the conditions of the reaction, and the target product gets polluted with acetic acid.

All 1-dinitromethyl-3-R-1,2,4-triazoles obtained were characterized by the spectral and analytical data.

IR spectra of 1-dinitromethyl-3-R-1,2,4-triazoles like those of the corresponding trinitromethyl compounds [1] are characterized by a shift to higher frequencies of the bands of antisymmetric stretching vibrations of dinitromethyl fragment as compared with the aliphatic dinitromethyl compounds (ν_{as} 1610–1640 cm^{-1}); this is often a series of strong bands. This region of salts spectra lacks absorption bands in conformity to the published findings [5]. A similar shift of the absorption band of nitro groups from the dinitromethyl fragment was observed in the spectra of 1,1,1,2,2-pentanitroalkanes (ν_{as} 1595–1605 cm^{-1} [6]). Commonly in compounds lacking such strong electron-withdrawing groups contiguous to the dinitromethyl this band is located in the region 1575–1587 cm^{-1} [7]. The bands of symmetric stretching vibrations of dinitromethyl group of 1-dinitromethyl-3-R-1,2,4-triazoles are observed in the region 1300–1325 cm^{-1}, for 1,1,1,2,2-pentanitromethyl compounds, ν_s 1280–1295 cm^{-1} [6].

In the ^1H NMR spectra, as with N-trinitromethyl triazole derivatives [1], the signals of C^5H protons appear far downfield (δ 9.25–9.50 ppm), and the spectra of all 1-dinitromethyl-3-R-1,2,4-triazoles **IX–XII** contain an additional downfield signal (δ 9.10–9.58 ppm) capable of exchange with D_2O and therefore assigned to the proton of the dinitromethyl moiety. Evidently the signal is lacking in the salts spectra, and the position of the signal from H^5 proton is shifted upfield by nearly 1 ppm due to the sharp decrease in the acceptor properties of the substituent at N^1 atom in going from the covalent to the ionic form.

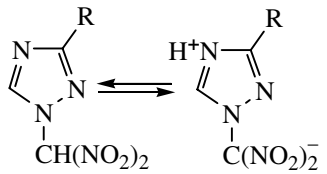
The UV spectra of 1-dinitromethyl-3-R-1,2,4-triazoles contain two intensive maxima. One maximum appears in the short-wave region as is common for the other nitro derivatives (λ_{max} 210–230 nm, log ε > 4) [8], and uts position and intensity is virtually insensitive to the acidity of the environment. The second, long-wave, maximum is observed in a very narrow range for all these substances notwithstanding the substituent range attached to the position *3* of the ring [λ_{max} 340–345 nm (log ε 4.1–4.2), see the table]. The intensity of this band essentially changed with varying acidity of the medium (pH from –4 to 3 and more). The intensity of the band significantly decreased with the growing acidity, and at attaining the pH (H_-) value individual for each substance the band disappeared. This phenomenon id characteristic of anions of aliphatic dinitro compounds [3, 9].

UV spectra and pK_a values of triazolyldinitromethanes **IX–XII**

Compound no.	λ_{max}, nm	ε, l/(mol· cm)	pK_a
IX	345	16 900	1.37 ± 0.03
X	345	19 300	1.22 ± 0.03
XI	345	18 240	0.97 ± 0.05
XII	340	17 000	0.12 ±0.03

Fundamentally, the dinitromethyl compounds of the triazole series might exist in a zwitter-ion structure that is the most probable for triazole **IX** with no acceptor substituent in the position *3* and with the most basic pyridine atom N^4 (Scheme 2).

Scheme 2.



The virtual identity of the long-wave maxima in position and intensity for all substances under study excludes the possibility of their protonation in the ring: In the opposite case in the environment whose acidity corresponds to the neutral (for triazole **IX** tis is H_- = –0.5, 15% H_2SO_4] the maximum in the region 340 nm should remain, but it is not observed.

For all known *Z*-dinitromethanes (*Z* is alkyl, substituted alkyl, aryl, substituted aryl etc.) a characteristic band is observed in the UV spectra (λ_{max} 340–400 nm [3, 9, 10]), but for 1-dinitromethyl-3-R-1,2,4-triazoles this band appears at shorter waves than for the majority of substances from this series. Its position is close to those of λ_{max} of anions of trinitromethane and dinitroacetonitrile (λ_{max} 350 and 345 nm respectively), i.e. to dinitro carbanions with a strong electron-withdrawing substituent (σ* 3.90 and 3.60 respectively) [3].

Thus the IR and UV findings suggest that the triazole ring possesses sufficiently strong electron-withdrawing character.

It is known that the λ_{max} in *Z*-dinitro carbanions at precisely constant steric effect of substituents depends essentially on their polar constants [3].

$$\lambda_{max} = 382 - 14.4\,\sigma^* \quad (1)$$

The steric effect in the series of 1-dinitromethyl-3-R-1,2,4-triazoles is permanent. Therefore the practically constant wavelength of the maximum for 1-dinitromethyl-3-R-1,2,4-triazoles suggests the close values of the electronic effects in all 3-R-1,2,4-triazol-1-yl substituents, namely, the main contribution into the overall polar effect originates from the triazole ring proper.

However the λ_{max} positions for anions of trinitromethane and dinitroacetonitrile do not coincide with those calculated by correlation equation (1) using Taft σ* values (λ_{max} 317 and 330 nm respectively) [3], in all likelihood because of steric factors in the first case and due to the effect of *p*-electrons repulsion in the second. The deviation from the position of λ_{max} calculated based on Taft σ* values (red shift by over 40 nm) is also characteristic of α-halodinitromethanes anions where a heteroatom with an unshared electron pair is contiguous to the *p*-electron system of the dinitro carbanion [3]. In 1-dinitromethyl-3-R-1,2,4-triazoles this effect also cannot be excluded for the 1,1-dinitro carbanion fragment is directly linked to the pyrrole nitrogen possessing an unshared electron pair involved into the *p*,π-conjugation.

Taking into consideration the above discussion it is interesting to estimate the polar constants of the 3-R-1,2,4-triazole substituent.

The values of the polar constants of 1,2,4-triazol-1-yl (σ_I, σ*) can be estimated from the pK_a magnitude of the corresponding 3-R-triazole-1-ylacetic acids applying Charton equation [11] for substituted acetic acids:

$$\sigma_I = -0.251\ pK_a + 1.186, \quad (2)$$

and σ*, from equation [12]:

$$\sigma_I = \sigma^*/6.23. \quad (3)$$

We measured potentiometrically the pK_a of 1,2,4-triazol-1-yl- and 3-nitro-1,2,4-triazol-1-ylacetic acids **XIII** and **XIV** (3.24 and 2.90 respectively) and calculated therefrom by equations (2, 3) the polar constants of 3-R-1,2,4-triazol-1-yl substituents (R = H, NO_2): σ_I 0.38 and 0.46; σ* 2.16 and 2.63 respectively.

Thus the polar constants evaluated for the first and the last members of the series in question 3-R-1,2,4-triazoles (R = H, NO_2) are quite close in value and similar to analogous constants of halogens [3].

Yet in contrast to halodinitromethanes anions the calculated λ_{max} obtained for 1-dinitromethyl-3-R-1,2,4-triazoles by equation (1) (351 and 344 nm respectively) are close to the corresponding experimental values. Therefore the compounds under study fit to the general series of *Z*-dinitromethanes and are essentially different in this respect from halodinitromethanes and from trinitromethane and dinitroacetonitrile.

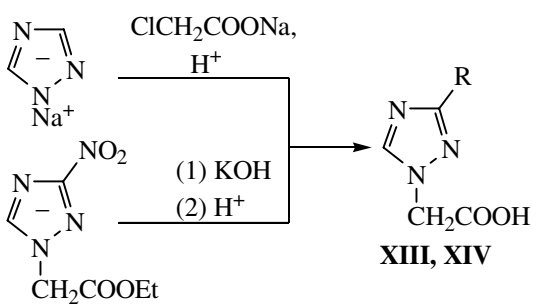
1,2,4-Triazol-1-ylacetic acid was obtained by alkylation of 1,2,4-triazole with chloroacetic acid in alkaline medium, 3-nitro-1,2,4-triazol-1- ylacetic acid, by alkaline hydrolysis of its ester[13] followed by acidifying the salt obtained with sulfuric acid (Scheme 3).

The 1,1-dinitro carbanion in 1-dinitromethyl-3-R-1,2,4-triazoles is likely to possess a planar structure as has been established for most *Z*-dinitromethanes, in particular, for the closest analogs of the series under consideration, *meta*- and *para*-susbtituted phenyldinitromethanes. In the latter the ring plane deviates considerably from the plane of the carbanion [3, 9], therefore the conjugation between the phenyl ring and the dinitro carbanion is virtually absent. This question remains unclear for 1-dinitromethyl-3-R-1,2,4-triazoles.

To get more information on the structure of N-dinitromethyl compounds of this series and to make a preliminary estimation of their reactivity we investigated with the use of spectrophotometry [14] their acid dissociation equilibrium and performed a correlation analysis.

It was established that 1-dinitromethyl-3-R-1,2,4-triazoles (R = H, Cl, N_3, NO_2) are fairly strong CH-acids in the polynitroalkanes series. Their acidity somewhat increased with growing acceptor character of the substituent at the position *3* of the ring (see the table), its value is close to that of trinitromethane (pK_a 0.17 [2], 0.22 [3]) and 1,1-dinitroalkanes with an electron-withdrawing substituent *Z*, and to phenyls with acceptor substituents [3, 10].

Scheme 3.



R = H (**XIII**), NO_2 (**XIV**).

The pK_a of 1-dinitromethyl-3-R-1,2,4-triazoles correlated well with the σ_p Hammett constants of substituents R:

$$pK_a = -1.59\ \sigma_p + 1.35\ (r\ 0.999,\ s\ 0.02), \quad (4)$$

worse with the σ_m constants of these substituents:

$$pK_a = -1.74\ \sigma_m + 1.55\ (r\ 0.902,\ s\ 0.29) \quad (5)$$

and did not fit to correlation with their σ_I constants (r 0.788, s 0.42).

These data show that unlike the series of phenyldinitromethane substituted in the ring the conjugation of 1,1-dinitro carbanion and N-triazolyl substituent occurred to a sufficient extent apparently because of the absence of one *ortho*-hydrogen.

Interestingly, a very good correlation is obtained taking into account inductive and conjugative effects of the substituent in the position *3* of the ring:

$$pK_a = -1.65\ \sigma_I^O - 1.67\ \sigma_R^O + 1.37\ (R\ 0.99,\ S\ 0.14). \quad (6)$$

The transfer of the substituent influence to the reaction center occurs apparently equally through both effects as shows the similar sensitivity of pK_a to the resonance and inductive constants of the substituents.

It was presumable that the reactivity of 1-dinitromethyl-3-R-1,2,4-triazoles would be similar to that of other CH-acids having close pK_a values, namely, they would be able to react with compounds with activated double bond (Michael reaction), with formaldehyde (Henry reaction), and their salts would undergo alkylation, halogenation etc. [2, 5].

We tested these reactions with the most available among the compounds of this series: 1-dinitromethyl-3-nitro-1,2,4-triazole (**XII**) and its salt **VIII**.

In reaction with methyl vinyl ketone in aprotic solvents (acetone, ether) at room temperature without catalysts 1-dinitromethyl-3-nitro-1,2,4-triazole (**XII**) readily formed 1-(1,1-dinitro-4-oxopentyl)-3-nitro-1,2,4-triazole (**XV**), and its reaction with formaldehyde in acetone also without catalyst resulted in 1-(2-hydroxy-1,1-dinitroethyl)-3-nitro-1,2,4-triazole (**XVI**) (Scheme 4).

The attempt to carry out the condensation with methyl vinyl ketone in water or water-ethanol mixture gave only trace amount of the target ketone because of the reversibility of the process, low thermodynamical stability of the reaction product, and its decomposition into the initial compounds in proton-donor environment.

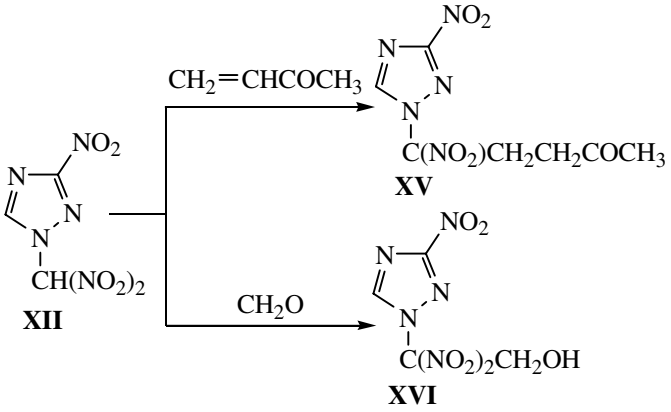
The alkylation of salt **VIII** with dimethyl sulfate in anhydrous acetone at 60°C resulted in the recovery of the initial salt, presumably due to its low solubility. The application of DMF and methyl iodide at prolonged storage in the dark at room temperature (7–8 days, UV monitoring by salt consumption) made it possible to obtain C-methylated product **XVII** in over 80% yield, and the chlorination of the salt in ether led to the formation of 1-dinitrochloromethyl-3-nitro-1,2,4-triazole (**XVIII**) (Scheme 5).

As a side product we obtained in this reaction 3-nitro-1,2,4-triazole showing that the salt suffered hydrolysis and decarboxylation in all likelihood by the residual moisture in the solvent ethyl ether. It is significant that in going to alcoholic media the yield of 3-nitro-1,2,4-triazole considerably grows.

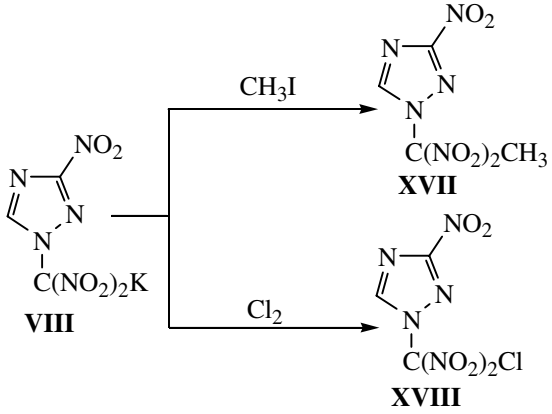
EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Perkin Elmer R-12 (60 MHz) from solutions in acetone-

Scheme 4.



Scheme 5.



d_6, internal reference HMDS. IR spectra were recorded on a spectrophotometer Specord 75IR from films. CH-Acidity of 1-dinitromethyl-3-R-1,2,4-triazoles was measured spectrophotometrically in water buffer media by a standard procedure [14] using a spectrophotometer SF-16 and a pH-meter pH-262. Elemental analysis was performed on a CHN-analyzer Hewlett Packard 185B, the molecular weight was measured by reversed ebulliometry in acetone.

1-Dinitromethyl-3-R-1,2,4-triazoles potassium salts V–VIII. *a*. To a solution of 0.87 g (0.005 mol) of potassium iodide in 7 ml of methanol was added by portions at room temperature while stirring 2.5 mmol of 1-trinitromethyl-3-R-1,2,4-triazole **I–IV**, the mixture was kept for 1 h and left overnight in a refrigerator. The precipitated salt was filtered off using a Teflon Nutsch filter, washed on the filter with cold methanol, dried in air and crystallized from aqueous ethanol Yield of crude products 60–70%, after recrystallization, 50–60%.

b. To a solution of 0.25 g (3.7 mmol) of hydroxylamine hydrochloride in 8 ml of methanol was added a solution of 0.78 g (14 mmol) of potassium hydroxide in 10 ml of methanol, the mixture was cooled to 0°C, the precipitated KCl was filtered off, washed on the filter with a cold methanol, and at stirring the solution cooled to 0°C was poured by portions to a solution of 3.6 mmol of azole **I–IV**. The reaction mixture was kept at 0°C for 1 h, then it was warmed to room temperature and left under fume hood for partial evaporation of methanol (to 0.25 of the initial volume). The residue was diluted with 50 ml of ether and left overnight in a refrigerator. The precipitated salt was filtered off using a Teflon Nutsch filter, washed on the filter with ether, dried in air and recrystallized in case of need from ethanol or aqueous methanol. Yield of salts 85–95%.

1-Dinitromethyl-3-chloro-1,2,4-triazole potassium salt (VI). Yield 60 (*a*), 85% (*b*), mp 110–111°C (MeOH–H_2O, 3:1). IR spectrum, ν, cm^{-1}: 845, 875, 995 s, 1075, 1150 s, 1160 s, 1235 s 1285 s, 1380, 1410 s, 1445, 1540. ^1H NMR spectrum, δ, ppm: 8.90 s (1H, C^5H). Found, %: C 14.66, 14.95; H 0.40, 0.56; N 28.51, 28.09. $C_3HClKN_5O_4$. Calculated, %: C 14.92; H 0.29; N 28.38.

1-Dinitromethyl-3-azido-1,2,4-triazole potassium salt (VII). Yield 50 (*a*), 30% (*b*), mp 98–99°C (MeOH–H_2O, 1:2). IR spectrum, ν, cm^{-1}: 850, 880, 990, 1060, 1170, 1200, 1240, 1350, 1400 s, 1450, 1480, 1500 s, 1550, 2170 s. ^1H NMR spectrum, δ, ppm: 8.50 s (1H, C^5H). Found, %: C 14.69, 14.35; H 0.25, 0.36; N 44.91, 44.65. $C_3HKN_8O_4$. Calculated, %: C 14.28; H 0.39; N 44.44.

1-Dinitromethyl-3-nitro-1,2,4-triazole potassium salt (VIII). Yield 65 (*a*), 92% (*b*), mp 194°C (ethanol). IR spectrum, ν, cm^{-1}: 830 s, 840, 1160 v.s, 1215, 1240 v.s, 1260, 1305 v.s, 1490 v.s, 1530, 1570 s. ^1H NMR spectrum, δ, ppm: 8.90 s (1H, C^5H). Found, %: C 14.16, 14.35; H 0.45, 0.58; N 32.62, 33.06. $C_3HClKN_5O_4$. Calculated, %: C 14.12; H 0.39; N 32.94.

1-Dinitromethyl-3-R-1,2,4-triazoles IX–XII. To 7.5 ml of 30% sulfuric acid was added at room temperature while stirring 15 ml of ether (or ethyl acetate) and then by portions 0.5 g of salt **V–VIII**, the mixture was maintained for 3–5 min, the ether layer was separated, and the inorganic part was additionally extracted with ether (5×15 ml). The combined extracts were washed with water, the solvent was evaporated in air, the residue was crystallized.

1-Dinitromethyl-1,2,4-triazole (IX). Yield 70%, mp 106–107°C ($CHCl_3$). IR spectrum, ν, cm^{-1}: 750, 780, 825, 845, 890, 910, 980, 1040, 1140 s, 1240 s, 1300, 1340, 1385, 1430, 1500 (ring), 1610 s [$C(NO_2)_2$]. ^1H NMR spectrum, δ, ppm: 8.50 s (1H, H^3), 9.25 s (1H, H^5), 9.30 (1H, CH, exchange in D_2O). Found, %: C 21.00, 20.95; H 1.47, 1.86; N 41.07, 40.89. $C_3H_3N_5O_4$. Calculated, %: C 20.78; H 1.74; N 40.39.

3-Azido-1-dinitromethyl-1,2,4-triazole (X). Yield 75%, mp 72–73°C (petroleum ether). IR spectrum, ν, cm^{-1}: 740, 760, 810, 890, 930, 995, 1030, 1080, 1140, 1185, 1220, 1255, 1270, 1325 s, 1435 s, 1470 s, 1540 v.s (ring), 1610 v.s [$C(NO_2)_2$], 2160 v.s (N_3). ^1H NMR spectrum, δ, ppm: 9.50 s (1H, H^5), 9.10 (1H, exchange in D_2O). Found, %: C 16.53, 16.49; H 0.82, 0.88; N 52.32, 52.55. $C_3H_2N_8O_4$. Calculated, %: C 16.84; H 0.94; N 52.34.

1-Dinitromethyl-3-chloro-1,2,4-triazole (XI). Yield 45%, mp 37–38°C ($CHCl_3$). IR spectrum, ν, cm^{-1}: 800, 840 s, 890, 950, 1050, 1300 s, 1350, 1415, 1430, 1520 (ring), 1615–1640 s [$C(NO_2)_2$]. ^1H NMR spectrum, δ, ppm: 9.30 s (1H, H^5), 9.25 (1H, CH, exchange in D_2O). Found, %: C 17.47, 17.72; H 0.84, 0.82; Cl 17.65, 17. 20; N 32.94, 32.88. $C_3H_2ClN_5O_4$. Calculated, %: 17.36; 0.97; Cl 17.12; N 33.75.

1-Dinitromethyl-3-nitro-1,2,4-triazole (XII). Yield 75%, mp 115–116°C (dichloroethane). IR spectrum, ν, cm^{-1}: 750 s, 800, 840 s, 870, 885, 900, 1005, 1030, 1080, 1115, 1135, 1180, 1225, 1260, 1305 v.s, 1350, 1410, 1440, 1530 s (ring), 1575 v.s (NO_2), 1600–1640 v.s [$C(NO_2)_2$]. ^1H NMR spectrum, δ, ppm: 9.63 s (1H, H^5), 9.58 (1H, CH, exchange in D_2O). Found, %: C 16.84, 16.43; H 1.00, 0.87; N 38.82, 38.32. $C_3H_2N_6O_6$. Calculated, %: C 16.52; H 0.93; N 38.54.

1,2,4-Triazol-1-ylacetic acid (XIII). To a solution of 1.5 g (0.022 mol) of 1,2,4-triazole and 3.12 g (0.033 mol) of chloroacetic acid in 20 ml of water was added 2.6 g (0.065 mol) of sodium hydroxide, the mixture was boiled for 20 h, cooled, acidified with 10% sulfuric acid to pH 1, and extracted with ethyl acetate (3×50 ml). The extract was washed with water, dried with calcined magnesium sulfate, the solvent was removed, and the residue was crystallized. Yield 60%, mp 201–202°C (2-propanol). IR spectrum, ν, cm^{-1}: 800, 870, 880, 940, 1020, 1080, 1090, 1130, 1215 s, 1290 s, 1300, 1350, 1370, 1420, 1450, 1480, 1520 (ring), 1720 s [C=O]. ^1H NMR spectrum, δ, ppm: 8.50 s (2H, H^3, H^5), 6.62 (1H, COOH, exchange in D_2O), 5.12 (2H, CH_2). Found, %: C 37.79, 37.96; H 3.94, 4.01; N 33.07, 33.57. *M* 125. $C_4H_5N_3O_2$. Calculated, %: C 37.80; H 3.97; N 33.06. *M* 127.10.

3-Nitro-1,2,4-triazol-1-ylacetic acid (XIV). To a solution of 1 g (0.038 mol) of ethyl 3-nitro-1,2,4-triazol-1-ylacetate [12] in 15 ml of methanol was added a solution of potassium hydroxide in ethanol till pH 10, the mixture was heated to boiling, cooled, and left standing at room temperature for 2 h. The solvent was evaporated, the residue was treated with 10 ml of 2% sulfuric acid, stirred for 10 min, and extracted with ethyl acetate (3×15 ml). The combined extracts were washed with water, the solvent was evaporated, the residue was crystallized. Yield 55%, mp 188–189°C (ethanol). IR spectrum, ν, cm^{-1}: 810, 840, 880, 890, 965, 980, 1050, 1170, 1230 v.s, 1320 s 1350, 1390, 1435, 1530 s (ring), 1575 v.s (NO_2), 1735 s (C=O). ^1H NMR spectrum, δ, ppm: 8.80 s (1H, H^5), 9.90 (1H, COOH, exchange in D_2O), 5.42 (2H, CH_2). Found, %: C 27.83, 28.04; H 2.55, 2.58; N 32.59, 32.79. *M* 166. $C_4H_4N_4O_4$. Calculated, %: C 28.24; H 2.37; N 32.94. *M* 170.10.

1-(1,1-Dinitro-4-oxopentyl)-3-nitro-1,2,4-triazole (XV). To a solution of 0.2 g (0.9 mmol) of triazole **XII** in 5 ml of aceyone was added 0.5 ml (1.5 mmol) of freshly distilled methyl vinyl ketone, and the mixture was left standing in a closed flask at room temperature for 72 h. The solution was evaporated, the residue was crystallized. Yield 77%, mp 80–81°C (ethanol). IR spectrum, ν, cm^{-1}: 820 s, 840 m, 870 s, 930 w, 950 w, 1000 m, 1020 w, 1040 w, 1080 m, 1180 w, 1240 w, 1320 s, 1430 w, 1530 m (ring), 1570 s (NO_2), 1600 s [$C(NO_2)_2$], 1725 s (C=O). ^1H NMR spectrum, δ, ppm: 2.20 s (CH_3), 3.08 t (CH_2, £ 7 Hz), 3.74 t (CH_2, £ 7 Hz), 9.72 s (C^5H). Found, %: C 29.44, 29.37; H 3.00, 2.91; N 29.45, 29.49. *M* 295. $C_7H_8N_6O_7$. Calculated, %: C 29.18; H 2.80; N 29.16. *M* 288.18.

1-(2-Hydroxy-1,1-dinitroethyl)-3-nitro-1,2,4-triazole (XVI). To a solution of 0.1 g (0.45 mmol) of triazole **XII** in 5 ml of acetone was added 0.5 ml (6 mmol) of 35% formaldehyde solution, the mixture was stirred at room temperature for 4 h and left overnight. The reaction mixture was diluted with an equal volume of water, the solvent was evaporated in air, the precipitated reaction product was filtered off, dissolved in ether, and precipitated with tetrachloromethane. Yield 56%, mp 127–128°C. IR spectrum, ν, cm^{-1}: 820 m, 840 m, 860 s, 880 m, 1000 m, 1020 m , 1090 m, 1110 w, 1200 w, 1230 m, 1280–1310 s, 1340 m, 1435 w, 1520 m (ring), 1575 s (NO_2), 1590–1605 v.s [$C(NO_2)_2$], 3400 m.br (OH). ^1H NMR spectrum, δ, ppm: 5.35 s (CH_2), 6.48 t (OH, exchange in D_2O), 9.30 s (C^5H). Found, %: C 19.56, 19.62; H 1.65, 1.60; N 34.08, 33.77. *M* 249. $C_4H_4N_6O_7$. Calculated, %: C 19.36; H 1.00; N 33.87. *M* 248.11.

1-(1,1-Dinitroethyl)-3-nitro-1,2,4-triazole (XVII). To a solution of 0.5 g (1.9 mmol) of salt **VIII** in 5 ml of DMF was added at stirring 0.25 ml (0.04 mol) of methyl iodide, and the mixture was kept in a stoppered weighing bottle till disappearance of the salt (7–8 days, UV monitoring). The mixture was diluted with 25 ml of water, the precipitate was filtered off, washed with water, and crystallized from ethanol. Yield 83%, mp 132–133°C. IR spectrum, ν, cm^{-1}: 780, 830 s, 900, 1020, 1215 s, 1130, 1250, 1285, 1320 v.s, 1360, 1400, 1410, 1450 s, 1460, 1545 m (ring), 1585 s (NO_2), 1615 v.s, 1625 v.s [$C(NO_2)_2$]. ^1H NMR spectrum, δ, ppm: 9.50 s (C^5H), 3.15 s (CH_3). Found, %: C 20.79, 20.87; H 2.07, 1.83; N 36.52, 36.54. *M* 228. $C_4H_4N_6O_6$. Calculated, %: C 20.70; H 1.74; N 36.21. *M* 232.11.

1-Dinitrochloromethyl-3-nitro-1,2,4-triazole (XVIII). Through a dispersion of 0.5 g (1.9 mmol) of salt **VIII** in 10 ml of ether while stirring at 0–5°C was bubbled chlorine for 3–4 h till the salt turned colorless. The mixture was left overnight, KCl was filtered off and washed withether on the filter, the solution was evaporated, and the residue was crystallized. Yield 75%, mp 126–127°C (CCl_4–$CHCl_3$). IR spectrum, ν, cm^{-1}: 805 s, 835 s, 870, 890, 915 s, 975 s, 1005, 1045, 1215 s, 1240, 1310 v.s, 1340, 1380, 1440, 1530 (ring), 1575 s (NO_2), 1620 v.s, 1635 v.s [$C(NO_2)_2$]. ^1H NMR spectrum, δ, ppm: 9.90 s (C^5H). Found, %: C 14.31, 14.18; H 0.30, 2.78; Cl 14.62, 14.14; N 33.51, 33.65. *M* 249. $C_3HClN_6O_6$. Calculated, %: C 14.26; H 0.31; Cl 13.79; N 32.62. *M* 252.63.

REFERENCES

1. Kofman, T.P., Kartseva, G.Yu., Glazkova, E.Yu., and Krasnov, K.N., *Zh. Org. Khim.*, 2005, vol. 41, p. 767.
2. *The Chemistry of the Nitro and Nitroso Groups*, Feuer, H., Ed., New York: Wiley-Interscience, 1969, Pt. 1; 1970, Pt. 2.
3. Tselinskii, I.V., *Doctoral Sci. (Chem.) Dissertation,* Leningrad, 1974.
4. 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.