# Synthesis and study of thermal stability of 3-nitro-1,2,4-triazole *N*-nitroxy- and *N*-azidomethyl derivatives*

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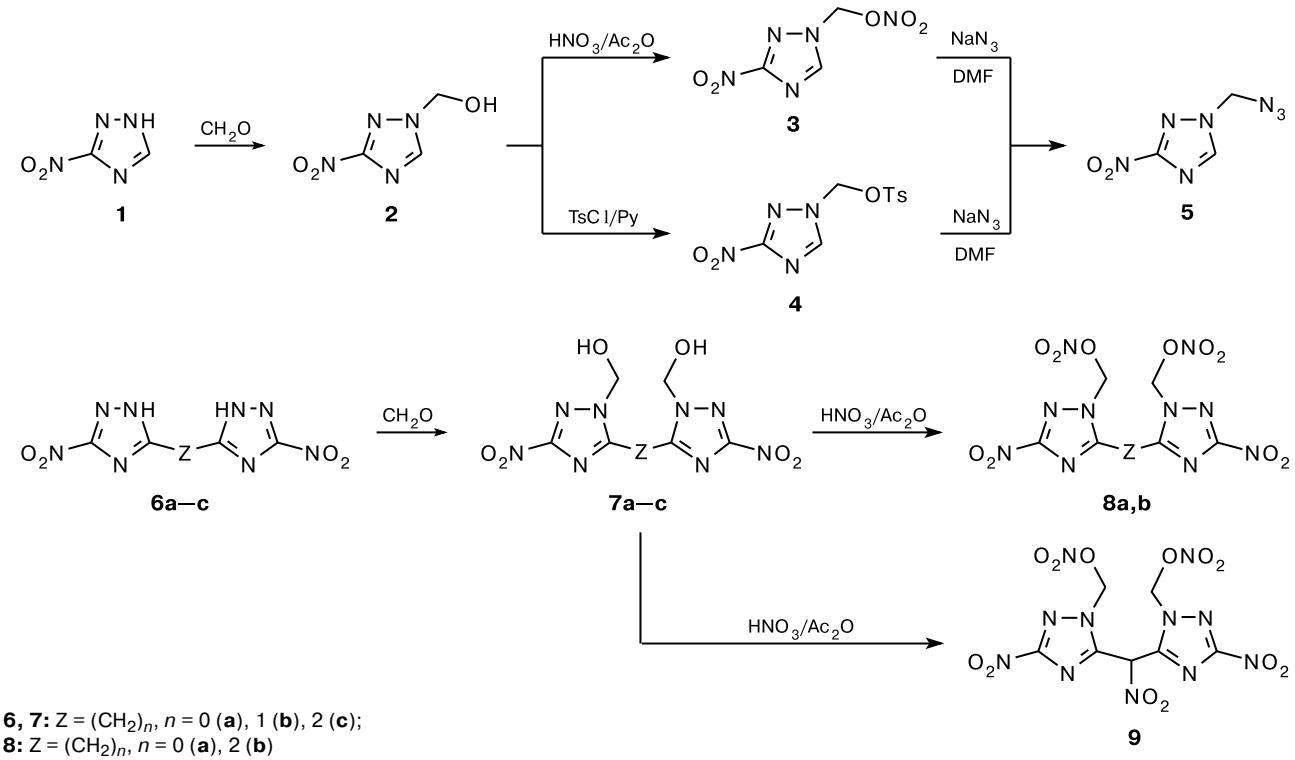
A method for the preparation of new 3-nitro-1,2,4-triazole derivatives has been suggested based on modification of the *N*-hydroxymethyl group by nitration and nucleophilic substitution reactions. Thermal stability of 3-nitro-1,2,4-triazole *N*-nitroxy- and *N*-azidomethyl derivatives, as well as of dinitrates, 5,5´-dinitro-2,2´-bisnitroxymethyl-2*H*,2´*H*-3,3´-bi(1,2,4-triazole) and -(nitromethylene)bis(1,2,4-triazole), has been studied.

**Key words:** 1,2,4-triazole, 3-nitro-1,2,4-triazole, dinitromethane, hydroxymethylation, nitration, nitrates, nucleophilic substitution, azidomethylation, thermal stability.

A possibility of preparation of 3-nitro-1,2,4-triazole 1-nitroxymethyl and 1-azidomethyl derivatives has been studied in the present work. Such compounds can be of interest as energy-rich materials used in pyrotechnic compositions of safety systems,[1,2] as well as they can serve as intermediates in the synthesis of other 3-nitro-1,2,4-triazole derivatives.[3] A combination of 3-nitro-1,2,4-triazole heterocycle and nitroxymethyl or azidomethyl groups has not been earlier studied.

* Dedicated to the memory of Corresponding Member of the Academy of Sciences of the USSR S. S. Novikov on the occasion of his 100th anniversary.

**Scheme 1**




**6, 7:** Z = $(CH_2)_n$, $n$ = 0 (**a**), 1 (**b**), 2 (**c**);
**8:** Z = $(CH_2)_n$, $n$ = 0 (**a**), 2 (**b**)

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The synthesis of such compounds included preparation of 3-nitro-1,2,4-triazole 1-hydroxymethyl derivatives, nitration or tosylation of the hydroxy group and nucleophilic replacement of the nitroxy and tosylate groups by the azide anion (Scheme 1).

The reactivity and thermodynamic properties of 3-nitro-1,2,4-triazole *N*-hydroxymethyl derivatives have been studied earlier.[4,5] Some specific features in behavior of such compounds were found, in particular, lability of the hydroxymethyl group in the halogenation and acylation reactions. At the same time, conditions for successful performing these reactions were selected,[4] as well as tosyloxymethyl derivatives were obtained.

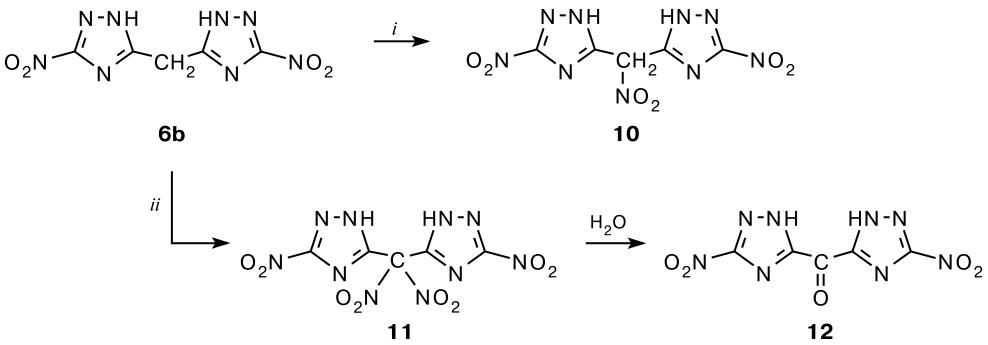
1-Hydroxymethyl-3-nitro-1*H*-1,2,4-triazoles **2** and **7a—c** were synthesized using an improved procedure[4] by the reaction of the starting compounds **1** and **6a—c** with formaline in aqueous or ethanol solution. When the nitration is carried out in concentrated nitric acid, the starting compounds do not react, whereas in the mixture of sulfuric and nitric acids, the N—$CH_2OH$ bond is cleaved to yield triazoles unsubstituted at position 1. Hydroxymethyl compounds **2** and **7a—c** were nitrated in the conc. nitric acid—acetic anhydride system at 0 °C similarly to the procedure suggested earlier[6] for the synthesis of close in structure and chemical properties (5-nitro-2*H*-tetrazol-2-yl)methyl nitrate. The reaction results in obtaining expected derivatives **3** and **8a,b**, whereas in the case of compound **7b**, the nitration also occurred at the methylene group and led to nitromethylene derivative **9**. The $^1$H NMR spectrum of compound **9** exhibits a signal at $\delta_H$ 7.2 characteristic of the C—H proton together with two signals at $\delta_H$ 6.92 and 6.80 assigned to the $CH_2$ protons. The nonequivalence of the proton in the $CH_2$ groups is explained by the steric strain of the molecules and different spatial interaction of the nitroxymethyl group with the nitro group at the "bridged" carbon atom, which results in the molecule to acquire properties of the chiral nonequivalence.

The IR spectrum exhibits absorption bands of the stretching vibrations for both the nitro- ($\nu$/cm$^{-1}$: 1566, 1319) and nitroxy groups ($\nu$/cm$^{-1}$: 1693, 1240). Compound **9** slowly decomposes in air at room temperature with evolution of nitrogen oxides. Nitration of compound **6b** unsubstituted at the nitrogen atom heterocycle, also proceeds at the methylene group. In this case, nitration with the mixture of sulfuric and nitric acids leads to the formation and isolation of mononitro derivative **10**, whereas under more drastic conditions, unstable *gem*-dinitro derivative **11** was obtained, which hydrolyzes in water at 25 °C to ketone **12** (Scheme 2). These results agree with the reported data,[7] which, however, contain no reaction conditions.

We suggested that it would be simple enough to synthesize triazole *N*-azidomethyl derivatives by tosylation of the hydroxy group with subsequent nucleophilic substitution of the tosylate group for the azide anion. However, it turned out that such a way of transformation can be recommended only for compound **4**. The activities of bis-triazole 1-tosyloxymethyl derivatives proved so high that the reaction products could not be even isolated from the reaction mixture: only unsubstituted at position 1 bis-nitrotriazoles **6a—c** were obtained instead of expected tosylates. Compound **4** was synthesized according to the procedure described earlier[4] with modifications to avoid rapid decomposition of the products obtained: the reaction time was reduced to 0.5 h and the isolation was performed by pouring the reaction mixture onto ice, rather than into aqueous hydrochloric acid, with subsequent cooling and careful acidification with hydrochloric acid to neutrality. Nucleophilic substitution for the azide anion in compound **4** takes place in DMF with sodium azide in the presence of catalytic amount of benzyltriethylammonium chloride for 5—8 h at 20 °C without any complications.

As to the rest of compounds of the nitrotriazole series studied, we attempted to involve 1-nitroxymethyl derivatives into this reaction in order to synthesize 1-azidomethyl derivatives. Substitution of the nitroxy group for the azide anion, similarly to tosylates, was performed in DMF at room temperature over a long period of time, however,

**Scheme 2**




*i*. $HNO_3$, dilute $H_2SO_4$; *ii*. $HNO_3$, conc. $H_2SO_4$.

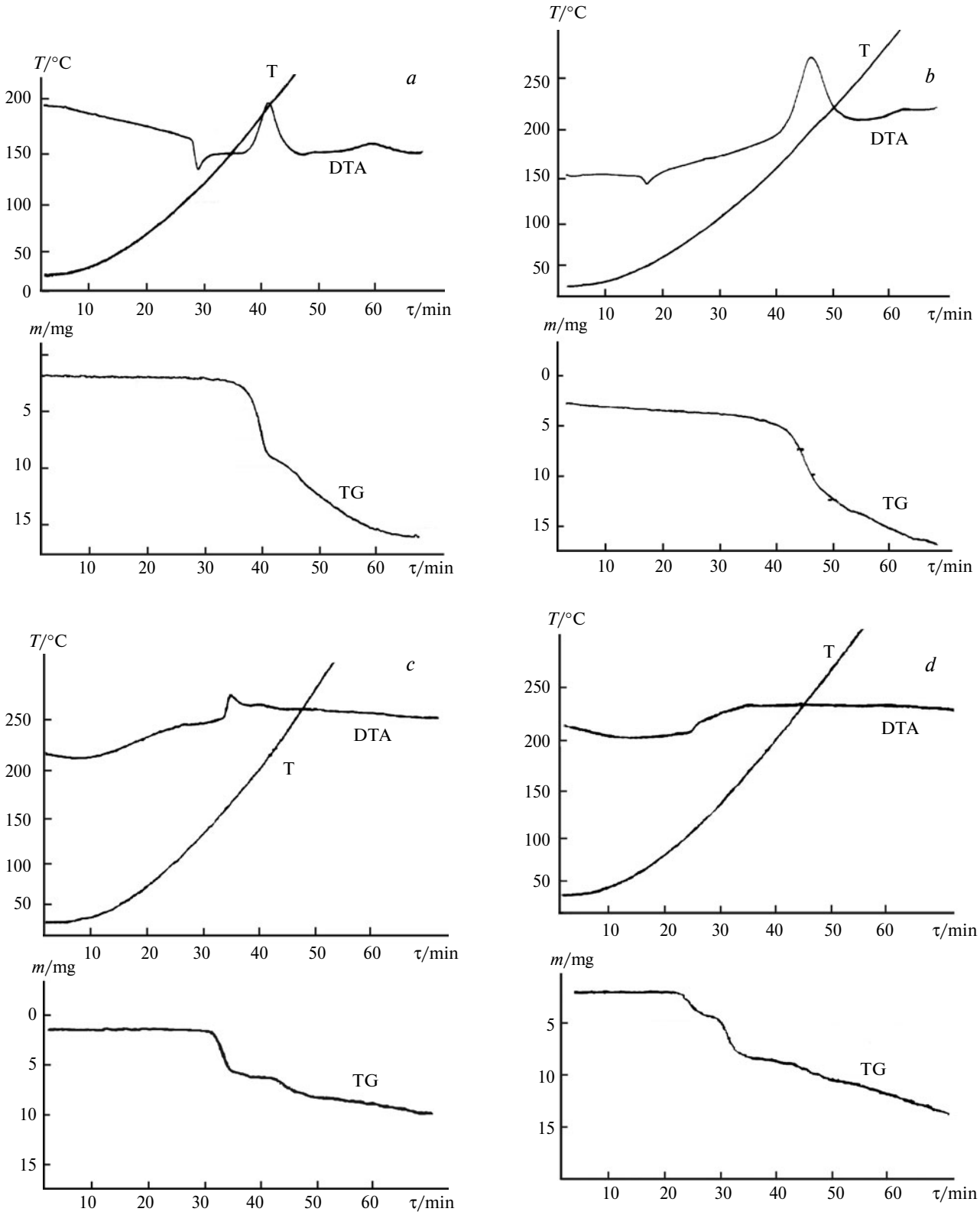



**Fig. 1.** Thermogravimetric (TG), temperature (T), and thermal differential (DTA) curves of (3-nitro-1*H*-1,2,4-triazol-1-yl)methyl nitrate (**3**) (*a*), 1-(azidomethyl)-3-nitro-1*H*-1,2,4-triazole (**5**) (*b*), 5,5′-dinitro-2,2′-di(nitroxymethyl)-2*H*,2′*H*-3,3′-bi(1,2,4-triazole) (**8a**) (*c*), 5,5′-dinitro-2,2′-di(nitroxymethyl)-2*H*,2′*H*-3,3′-(nitromethylene)bis(1*H*-1,2,4-triazole) (**9**) (*d*).

we succeeded only in obtaining compound **5**. In the case of bis-triazole derivatives **8a,b** involved into this reaction, the $N—CH_2ONO_2$ bond was found to be extremely unstable and only sodium salts **6a** and **6c** were isolated as the reaction products.

For the most energy-rich from the point of view of oxygen balance compounds **3**, **5**, **8a**, and **9**, studies of their thermal stability have been carried out, since it is the most important physico-chemical characteristic governing their practical use. Derivatographic analysis includes thermographic and thermogravimetric studies of compounds in the regime of programmed heating. The temperature curve T in Fig. 1 corresponds to the sample temperature, the TG curve, to the sample mass change with time, the DTA curve, to the temperature difference between the sample and the standard (it allows one to make qualitative and quantitative evaluation of physico-chemical processes). Thus, the direction of the peak deviation on the DTA curve determines character of the thermal effect (endo- or exothermic, the lower and upper peaks, respectively). The peak area on the DTA curve is proportional to the enthalpy effect. To make conclusions on physico-chemical transformations taking place in the sample, we performed co-analysis of the TG and DTA curves with orientation in coordinates by the T curve.[8]

As the thermal differential analysis data show, compound **3** is stable enough in the liquid state, virtually involatile to the decomposition onset ($t$ = 0—38 min) and intensively decomposes at the temperatures above 150 °C, which is characteristic of compounds containing nitroxy group. On the contrary, azidomethyl derivative **5** is somewhat volatile starting from 20 °C and loses ~7 wt.% to the melting onset (50 °C, the peak at $t$ = 16—18 min), the mass loss reaches already ~50% to the moment of decomposition onset. It is necessary to note that the temperature of intensive decomposition onset for compound **5** is 175—180 °C, which is higher than that for nitroxy derivative **3**.

Compound **8a** begins to slowly decompose before melting (at ~130 °C). The decomposition proceeds in two steps, the first step begins to be visible at 160 °C (with melting), whereas intensive decomposition starts at 187 °C, the second step begins at 210 °C, the peak is observed at 230 °C. Judging from the mass loss, the $N—CH_2ONO_2$ bond cleavage occurs in the first step (the mass loss is 40—45%), the rest of the molecules decompose in the second step. It is quite difficult to interpret thermal decomposition of compound **9**, though, the general picture of decomposition is similar to that for **8a**. Both compounds decompose in two steps, whereas the presence of the nitromethylene bridge in compound **9** causes the melting point and the intensive decomposition onset temperature to decrease by ~60 °C.

In conclusion, 3-nitro-1,2,4-triazole 1-nitroxymethyl and 1-azidomethyl derivatives have rather high thermal stability and are prospective for further study in the field of pyrotechnic composition applications.

## Experimental

$^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker DPX-300 (300 MHz) and Bruker AM-200 (200 MHz) spectrometers using residual signals of the solvent (DMSO-$d_6$, δ 2.50) as the reference. IR spectra were recorded on a Perkin—Elmer Spectrum 1000 spectrometer in KBr pellets. Elemental analysis was performed on a Hewlett—Packard 185, C,H,N-Analyser automatic instrument. Melting points were determined on a PTP instrument at the rate of heating of 1 °C $min^{-1}$ in the melting interval. The reaction progress was monitored by TLC on Merck Kieselgel $60F_{245}$ plates with visualization by the UV light.

Compounds **3**, **5**, **8a**, and **9** were analyzed on a F. Paulik, J. Paulik, L. Erdey derivatograph under the following conditions: the nonisothermic regime, the temperature range of 20—500 °C, the rate of heating of 5 °C $min^{-1}$, air as the medium, a quartz crucible. The weights of the compounds **3**, **5**, **8a**, and **9** samples were 20, 20, 11, and 20 mg, respectively. Compounds **5** and **9** were diluted with the inert compound $Al_2O_3$ (dilution of 1 : 10), compound **8a** with $Al_2O_3$, (1 : 50). The starting compounds **1** and **6a—c** were synthesized according to the procedure described earlier.[9]

**(3-Nitro-1*H*-1,2,4-triazol-1-yl)methanol (2).** Formaline (30% aq. solution, 10 mL) was added to 3-nitro-1*H*-1,2,4-triazole (**1**) (1.44 g, 0.01 mol) in water (100 mL). The reaction mixture was stirred for 16 h at 20—25 °C, then it was placed into a refrigerator. A precipitate formed was filtered off, washed with water (3S20 mL), and dried in air. Crystallization from chloroform yielded product **2** (11.2 g, 78%), m.p. 80—81 °C (*cf.* Ref. 4: m.p. 80—81 °C). $^1H$ NMR, δ: 8.75 (s, 1 H, C(5)H); 7.30 (s, 1 H, OH); 5.55 (s, 2 H, $CH_2$). IR, ν/$cm^{-1}$: 3352, 3161, 2341, 1558, 1515, 1417, 1311, 1220, 1186, 1107, 1053, 1012, 875, 840. Found (%): C, 24.9; H, 2.5; N, 39.0. $C_3H_4N_4O_3$. Calculated (%): C, 25.0; H, 2.8; N, 38.9.

**[5,5′-Dinitro-2*H*,2′*H*-3,3′bi(1,2,4-triazole)-2,2′-diyl]-dimethanol (7a).** For the synthesis of this product, compound **6a** (0.01 mol) and 30% aq. formaline (20 mL) were used, with ethanol as the solvent; the reaction and isolation conditions were similar to those described for compound **2**. The yield was 2.11 g (70%), m.p. 179 °C. $^1H$ NMR, δ: 6.05 (s, 2 H, OH); 6.00 (s, 4 H, $CH_2$). IR, ν/$cm^{-1}$: 3230, 1560, 1520, 1490, 1400, 1380, 1310, 1220, 1150, 850. Found (%): C, 25.2; H, 2.1; N, 39.0. $C_6H_6N_8O_6$. Calculated (%): C, 25.2; H, 2.1; N, 39.2.

**[5,5′-Methylenebis(3-nitro-1*H*-1,2,4-triazole)-1,1′-diyl]-dimethanol (7b).** For the synthesis of this product, compound **6b** (0.01 mol) and 30% aq. formaline (20 mL) were used with ethanol as the solvent; the reaction and isolation conditions were similar to those described for compound **2**. The yield was 2.64 g (88%), m.p. 154—155 °C. $^1H$ NMR, δ: 4.09 (s, 2 H, $CH_2$); 5.63 (s, 4 H, $CH_2$); 5.67 (s, 2 H, OH). IR, ν/$cm^{-1}$: 3120, 3000, 2966, 1560, 1520, 1400, 1310, 1270, 1200, 1040, 970. Found (%): C, 28.1; H, 2.5; N, 37.1. $C_7H_8N_8O_6$. Calculated (%): C, 28.0; H, 2.7; N, 37.3.

**[5,5′-(1,2-Ethylene)bis(3-nitro-1*H*-1,2,4-triazole-1,1′-diyl]-dimethanol (7c).** For the synthesis of this product, compound **6c** (0.01 mol) and 30% aq. formaline (20 mL) were used with ethanol as the solvent; the reaction and isolation conditions

were similar to those described earlier for compound **2**. The yield was 2.70 g (80%), m.p. 186 °C. $^1$H NMR, δ: 7.50 (s, 2 H, OH); 5.60 (s, 2 H, $CH_2$); 3.45 (s, 4 H, $CH_2$). IR, ν/cm$^{-1}$: 3248, 3000, 2974, 1523, 1558, 1423, 1315, 1134, 1087, 852. Found (%): C, 30.4; H, 3.2; N, 35.6. $C_8H_{10}N_8O_6$. Calculated (%): C, 30.6; H, 3.2; N, 35.7.

**Synthesis of 3-substituted 1-nitroxymethyl 1*H*-1,2,4-triazoles (general procedure).** Hydroxymethyl derivative **2** (0.025 mol) or hydroxymethyl derivative **7a—c** (0.0125 mol) was added with stirring to the mixture consisting of 97% aq. nitric acid (40 mL) and acetic anhydride (40 mL) at temperatures no higher than 0 °C. The reaction mixture was stirred at this temperature for 5 h, then poured onto finely crashed ice (200 g). A solution obtained was carefully neutralized with 10% aq. sodium bicarbonate to pH 4—5. A precipitate formed (for **7a—c**) was filtered off, washed with water to neutrality, and dried in air or (for **2**) extracted with ethyl acetate (3×50 mL), ethyl acetate was evaporated in air, and then the residue was dried for 12 h in vacuum-dessicator over phosphorus pentoxide.

**(3-Nitro-1*H*-1,2,4-triazol-1-yl)methyl nitrate (3).** Crystallization from diethyl ether yielded compound **3** (2.7 g, 50%), m.p. 104—105 °C. $^1$H NMR, δ: 9.05 (s, 1 H, C(5)H); 6.75 (s, 2 H, $CH_2$). Found (%): C, 19.4; H, 1.8; N, 36.6. $C_3H_3N_5O_5$. Calculated (%): C, 19.1; H, 1.6; N, 37.0.

**5,5′-Dinitro-2,2′-di(nitroxymethyl)-2*H*,2′*H*-3,3′-bi(1,2,4-triazole) (8a).** The yield was 2.70 g (72%), m.p. 163 °C. $^1$H NMR, δ: 7.04 (s, 4 H, $CH_2$). IR, ν/cm$^{-1}$: 3062, 2997, 1685, 1558, 1481, 1454, 1319, 1280, 983. Found (%): C, 19.4; H, 1.2; N, 37.2. $C_6H_4N_{10}O_{10}$. Calculated (%): C, 19.2; H, 1.1; N, 37.2.

**5,5′-Dinitro-2,2′-di(nitroxymethyl)-2*H*,2′*H*-3,3′-(nitromethylene)bis(1,2,4-triazole) (9).** The yield was 2.0 g (27.5%), m.p. 108—109 °C. $^1$H NMR, δ: 7.20 (s, 1 H, CH); 6.92 (s, 2 H, $CH_2$); 6.80 (s, 2 H, $CH_2$). IR, ν/cm$^{-1}$: 3005, 2995, 1693, 1566, 1575, 1438, 1319, 1240, 1234, 1072, 968. Found (%): C, 19.2; H, 1.2; N, 35.6. $C_7H_5N_{11}O_{12}$. Calculated (%): C, 19.3; H, 1.2; N, 35.4.

**5,5′-Dinitro-2,2′-di(nitroxymethyl)-2*H*,2′*H*-3,3′-ethylenebis(1,2,4-triazole) (8b).** The yield was 1.25 g (90%), m.p. 174 °C. $^1$H NMR, δ: 6.80 (s, 4 H, $CH_2$); 3.65 (s, 4 H, $CH_2$). IR, ν/cm$^{-1}$: 3051, 2982, 1678, 1566, 1523, 1423, 1134, 1049, 991, 856. Found (%): C, 24.0; H, 1.8; N, 34.9. $C_8H_8N_{10}O_{10}$. Calculated (%): C, 23.8; H, 2.0; N, 34.7.

**(3-Nitro-1*H*-1,2,4-triazol-1-yl)methyl 4-methylbenzenesulfonate (4).** Freshly recrystallized *p*-toluenesulfonyl chloride (98.04 g, 0.042 mol) was added to a solution of (3-nitro-1*H*-1,2,4-triazol-1-yl)methanol (**2**) (6 g, 0.042 mol) in anhydrous pyridine (20 mL) at −5—0 °C. The reaction mixture was stirred for 0.5 h at 0 °C and poured onto finely crushed ice (50 g). The mixture obtained was carefully neutralized with 10% aq. hydrochloric acid (~150 mL), a precipitate formed was filtered off, washed with water, dried, and recrystallized from acetone—ethanol solvent mixture (1 : 1). The yield was 5.16 g (41.2%), m.p. 140 °C (*cf.* Ref. 4: m.p. 140 °C). $^1$H NMR, δ: 2.4 (s, 3 H, Me); 6.35 (s, 2 H, $CH_2$); 7.38 (d, 2 H, $C_6H_4$, $J$ = 8.5 Hz); 7.74 (d, 2 H, $C_6H_4$, $J$ = 7.9 Hz); 8.9 (s, 1 H, C(5)H). IR, ν/cm$^{-1}$: 3138, 1664, 1558, 1515, 1471, 1440, 1425, 1380, 1309, 1284, 1234, 1199, 1134, 1056, 1033, 966. Found (%): C, 40.3; H, 3.5; N, 18.9. $C_{10}H_{10}N_4O_5S$. Calculated (%): C, 40.3; H, 3.4; N, 18.8.

**1-(Azidomethyl)-3-nitro-1*H*-1,2,4-triazole (5).** A mixture of compound **4** (3.0 g, 0.01 mol) and sodium azide (1.6 g, 0.024 mol) in DMF (30 mL) with the additive of benzyltriethylammonium chloride (0.1 g) was stirred for 8 h at ~20 °C. The reaction course was monitored by TLC. Then the reaction mixture poured into water (200 mL) and extracted with ethyl acetate (4×30 mL). The extract was dried with $MgSO_4$ and concentrated in a Petri dish *in vacuo*. The oily residue was placed into a freezer (temperature −20 °C) for 5—6 h. Diethyl ether (5—6 mL) was added to the crystalline product formed, which was filtered off and washed on the filter with diethyl ether (1—2 mL). The yield was 1.2 g (71%), m.p. 51—52 °C. $^1$H NMR, δ: 5.81 (s, 2 H, $CH_2$); 9.0 (s, 1 H, C(5)H). IR, ν/cm$^{-1}$: 3128, 2165, 2123, 1560, 1548, 1512, 1452, 1433, 1407, 1382, 1363, 1298, 1244, 1197, 1122, 1043, 1029, 1010, 916, 861. Found (%): C, 20.9; H, 1.9; N, 58.0. $C_3H_3N_7O_2$. Calculated (%): C, 21.3; H, 1.8; N, 58.0.

**5,5′-(Nitromethylene)bis(3-nitro-1*H*-1,2,4-triazole) (10).** Compound **6b** (1.2 g, 0.005 mol) was added to a nitrating mixture consisting of 65% aq. nitric acid (7 mL) and 94% sulfuric acid (11 mL) at 0—5 °C. The reaction mixture was stirred for 8 h at 20—25 °C, then poured onto finely crashed ice (70 g), and extracted with ethyl acetate (5×30 mL). The organic layer was washed with water and dried with anhydrous $MgSO_4$. Ethyl acetate was evaporated in the flow of air, the residue was recrystallized from chloroform—carbon tetrachloride mixture. The yield was 0.59 g (42%), m.p. 118 °C (*cf.* Ref. 7: m.p. 118 °C). $^1$H NMR, δ: 10.05 (br.s, 2 H, NH); 7.10 (s, 1 H, CH). IR, ν/cm$^{-1}$: 3100, 3010, 2966, 1556, 1430, 1323, 1250, 1050, 960. Found (%): C, 21.1; H, 1.0; N, 44.7. $C_5H_3N_9O_6$. Calculated (%): C, 21.2; H, 1.1; N, 44.5.

**Dinitrobis(3-nitro-1*H*-1,2,4-triazole-5-yl)methane (11).** Compound **6b** (1.2 g, 0.005 mol) was added to a nitrating mixture consisting of 96% nitric acid (7 mL) and 99.5% sulfuric acid (11 mL) at 0—5 °C. The reaction mixture was stirred for 8 h at 20—25 °C, then poured onto finely crashed ice (70 g), and extracted with ethyl acetate (5×30 mL). The organic layer was washed with water and dried with anhydrous $MgSO_4$. Ethyl acetate was evaporated in the flow of air. The yield was 0.93 g (57%), m.p. 52 °C (with decomp.). $^1$H NMR, δ: 10.68 (br.s, 2 H, NH). IR, ν/cm$^{-1}$: 1565, 1510, 1420, 1315, 1248, 1210, 1070, 950. Found (%): C, 19.5; H, 0.5; N, 43.0. $C_5H_2N_{10}O_8$. Calculated (%): C, 19.3; H, 0.6; N, 42.7.

**Bis(3-nitro-1*H*-1,2,4-triazole-5-yl)methanone (12).** Freshly obtained compound **11** (0.82 g, 0.0025 mol) was added to water (50 mL) at 20—25 °C. The reaction mixture was stirred for 5 h at the temperature indicated, then extracted with ethyl acetate (5×20 mL). The organic layer was dried with anhydrous $MgSO_4$. Ethyl acetate was evaporated in the flow of air, the residue was recrystallized from methanol—chloroform. The yield was 0.47 g (75%), m.p. 175 °C (*cf.* Ref. 7: m.p. 175 °C). $^1$H NMR, δ: 10.00 (br.s, 2 H, NH). $^{13}$C NMR, δ: 173.8 (C=O); 156.6 (C(3)—$NO_2$); 147.2 (C(5)—C=O). IR, ν/cm$^{-1}$: 1680, 1540, 1410, 1320, 1230, 1110, 1040, 980. Found (%): C, 23.9; H, 0.7; N, 44.3. $C_5H_2N_8O_5$. Calculated (%): C, 23.8; H, 0.8; N, 44.4.

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