

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

## 5-Substituted 3-Nitro-1-trinitromethyl-1,2,4-triazoles

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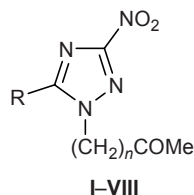
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**Abstract**—A number of 5-R-substituted 3-nitro-1-trinitromethyl-1*H*-1,2,4-triazoles (R = Me, Cl, Br, N<sub>3</sub>, NH<sub>2</sub>, NO<sub>2</sub>) were synthesized by nitration of the corresponding ω-(5-R-3-nitro-1*H*-1,2,4-triazol-1-yl)alkan-2-ones with mixtures of concentrated sulfuric and nitric acids.

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Successful nitration of 3-R-substituted 1*H*-1,2,4-triazol-1-ylalkanones (R = H, Cl, N<sub>3</sub>, NO<sub>2</sub>) with mixtures of concentrated sulfuric and nitric acids to 1-trinitromethyl-3-R-1*H*-1,2,4-triazoles and elucidation of some specific features of this reaction [1] prompted us to extend the substrate series and examine nitration under analogous conditions of 5-substituted ω-(3-nitro-1*H*-1,2,4-triazol-1-yl)alkan-2-ones **I–VIII**.



**I–III**,  $n = 1$ ; **IV–VIII**,  $n = 2$ ; **I, VI**, R = Br; **II**, R = H<sub>2</sub>N;  
**III, VIII**, R = O<sub>2</sub>N; **IV**, R = Me; **V**, R = Cl; **VII**, R = N<sub>3</sub>.

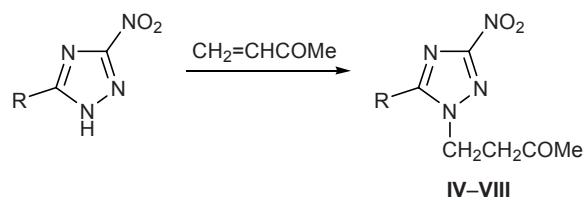
Initial triazolylpropanones **I–III** were synthesized either by alkylation of the corresponding 5-substituted 3-nitro-1*H*-1,2,4-triazoles with 1,2-epoxypropane, followed by oxidation of triazolylpropan-2-ols with Jones' reagent, or by reaction of 3-nitro-1*H*-1,2,4-triazol-5-amine sodium salt with bromoacetone as described in [2, 3].

Ketones **IV–VIII**, including previously unknown 4-(5-chloro- and 5-azido-3-nitro-1*H*-1,2,4-triazol-1-yl)butan-2-ones **V** and **VII**, were obtained by condensation of the corresponding 1-unsubstituted triazoles with methyl vinyl ketone according to the procedures described in [2] (Scheme 1).

Taking into account that the acidity of 5-chloro- and 5-azido-3-nitro-1*H*-1,2,4-triazoles is fairly high ( $pK_a =$

3.00 [4] and 3.85 [5], respectively), condensation of these compounds with methyl vinyl ketone in aprotic medium (diethyl ether, acetone) was expected to occur in the absence of a base, as in the synthesis of 4-(3,5-dinitro-1*H*-1,2,4-triazol-1-yl)butan-2-one [2]. However, under these conditions the yield of compounds **V** and **VII** did not exceed 15%; therefore, the presence of a base was necessary, as in the reaction with a weaker NH acid, 5-methyl-3-nitro-1*H*-1,2,4-triazole ( $pK_a > 6$ ).

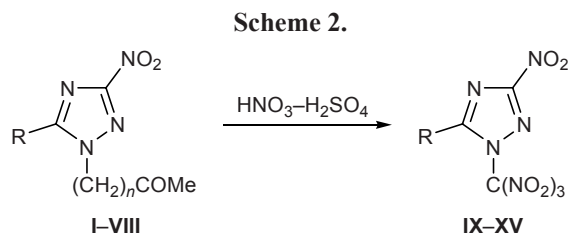
**Scheme 1.**



**IV**, R = Me; **V**, R = Cl; **VI**, R = Br; **VII**, R = N<sub>3</sub>; **VIII**, R = O<sub>2</sub>N.

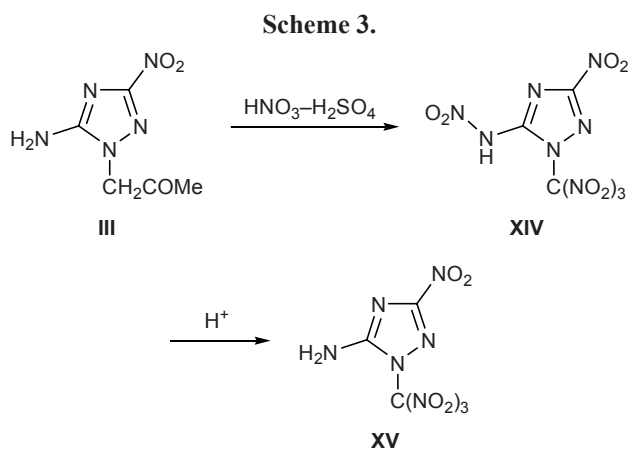
Unlike previously studied ω-(3-R-1*H*-1,2,4-triazol-1-yl)alkan-2-ones [1], the triazole ring in compounds **I–VIII** contained an additional substituent which was fairly large (in some cases; R = Me, Br, NO<sub>2</sub>) and was located in the vicinity of the reaction center. Therefore, some steric hindrances could appear during the multi-step degradative nitration process, and the possibility for synthesizing 3-nitro-1-trinitromethyl-1*H*-1,2,4-triazoles, as well as stability of the product, casted doubt. Nevertheless, the nitration of ω-(5-R-3-nitro-1*H*-1,2,4-triazol-1-yl)alkan-2-ones **I–VIII** with mixtures of concentrated sulfuric and nitric acids under the conditions described previously for the synthesis of 3-substituted

1-trinitromethyl-1*H*-1,2,4-triazoles [1] [weight ratio nitrating mixture–substrate  $M = (20-30):1$ ,  $\text{HNO}_3\text{--H}_2\text{SO}_4$  weight ratio 1:(1–2), reactant mixing at 0–5°C, reaction temperature 20°C, reaction time 12–72 h] in all cases gave the corresponding 5-substituted 3-nitro-1-trinitromethyl-1*H*-1,2,4-triazoles **IX–XV** in 40–75% yield (Scheme 2).



**I–III**,  $n = 1$ ; **IV–VIII**,  $n = 2$ ; **I, VI, XI**,  $R = \text{Br}$ ; **II, XV**,  $R = \text{H}_2\text{N}$ ; **III, VIII, XIII**,  $R = \text{O}_2\text{N}$ ; **IV, IX**,  $R = \text{Me}$ ; **V, X**,  $R = \text{Cl}$ ; **VII, XII**,  $R = \text{N}_3$ ; **XIV**,  $R = \text{O}_2\text{NNH}$ .

When the time of nitration of amine **III** was shorter than 12 h, a mixture of 5-amino- and 5-nitroamino-3-nitro-1-trinitromethyl-1*H*-1,2,4-triazoles **XIV** and **XV** was formed. After 72 h, the only reaction product was 5-amino derivative **XV**, i.e., the reaction involves initial formation of *N*-nitroaminotriazole **XIV** which then undergoes denitration in acid medium (Scheme 3). 5-Amino-3-nitro-1-trinitromethyl-1*H*-1,2,4-triazole (**XV**) was also formed when compound **XIV** was kept in sulfuric acid. *N*-Nitroamine **XIV** was isolated as crystal hydrate; its thermogravimetric analysis showed an endothermic peak at about 100°C with a weight loss corresponding to the presence of one molecule of crystallization water.



The nitration of  $\omega$ -(5-*R*-3-nitro-1*H*-1,2,4-triazol-1-yl)alkan-2-ones occurred in a way similar to the nitration of their analogs having no substituent in position 5

of the triazole ring. Moreover,  $\omega$ -(3-nitro-1*H*-1,2,4-triazol-1-yl)alkan-2-ones ( $n = 1, 2$ ) may be regarded as belonging to both  $\omega$ -(3-*R*-1*H*-1,2,4-triazol-1-yl)alkan-2-one and  $\omega$ -(5-*R*-3-nitro-1*H*-1,2,4-triazol-1-yl)alkan-2-one ( $R = \text{H}$ ) series. Therefore, we believed that comparison of the data on the nitration of these compounds is relevant. The formation of 5-substituted 3-nitro-1-trinitromethyl-1*H*-1,2,4-triazoles was monitored by weighing the products isolated under identical conditions by diluting a sample withdrawn from the reaction mixture.

Accumulation of trinitromethyltriazoles in the nitrating mixture follows the same pattern as in the nitration of 3-substituted analogs: the yield initially increases, passes through a maximum, and falls down as a result of decomposition. A typical example is illustrated by the data given in table for the nitration of 4-(5-bromo-3-nitro-1*H*-1,2,4-triazol-1-yl)butan-2-one (**VI**). The maximal yield of 5-substituted derivatives is attained in a shorter time and is lower than the yield of 3-substituted trinitromethyltriazoles. In the reactions with 1-(3-nitro-5-*R*-1*H*-1,2,4-triazol-1-yl)propan-2-ones, the maximal yield of the nitration products is attained in 12–18 h (60–75%), whereas the nitration of 1-(3-nitro-1*H*-1,2,4-triazol-1-yl)propan-2-one gives 90% of the corresponding 1-trinitromethyl derivative in 36–40 h [1] ( $M = 20$ ,  $\text{HNO}_3\text{--H}_2\text{SO}_4$  ratio 1:1). The difference for 4-triazolybutan-2-ones is somewhat smaller, but the general pattern is the same: under analogous conditions ( $M = 30$ ,  $\text{HNO}_3\text{--H}_2\text{SO}_4$  ratio 1:2) the maximal yield of 5-substituted 1-trinitromethyltriazoles (40–60%) is lower than the yield of 3-nitro-1-trinitromethyl-1*H*-1,2,4-triazole (70% [1]), but it is reached in a shorter time (30–40 h against 96 h [1]). Thus both nitration and decomposition of the nitration products in the series of 5-substituted 3-nitrotriazoles occur at a higher rate.

As in the nitration of  $\omega$ -(3-nitro-1*H*-1,2,4-triazol-1-yl)alkan-2-ones [1], it is advisable to apply more severe conditions for less reactive 4-(3-nitro-5-*R*-1*H*-1,2,4-triazol-1-yl)butan-2-ones ( $M = 30$ ,  $\text{HNO}_3\text{--H}_2\text{SO}_4$  ratio 1:2). The nitration of triazolypropanones occurs with a good yield at  $M = 20$  ( $\text{HNO}_3\text{--H}_2\text{SO}_4$  ratio 1:1).

The structure of the isolated compounds was confirmed by the analytical and spectral data. It should be noted that all trinitromethyl derivatives of the 3-nitrotriazole series are very sensitive to thermal and mechanical effects; therefore, specific precautions should be taken while handling these compounds, and their synthesis and purification should be performed with

Yields (%) of 5-bromo-3-nitro-1-trinitromethyl-1*H*-1,2,4-triazole (XI) in the nitration of compound VI under different conditions

Reactant ratio <sup>a</sup>	10 h <sup>b</sup>	24 h <sup>b</sup>	30 h <sup>b</sup>	40 h <sup>b</sup>	60 h <sup>b</sup>	72 h <sup>b</sup>	96 h <sup>b</sup>
H <sub>2</sub> SO <sub>4</sub> -HNO <sub>3</sub> , 2:1, <i>M</i> = 30	23	47	55	48	24	–	–
H <sub>2</sub> SO <sub>4</sub> -HNO <sub>3</sub> , 2:1, <i>M</i> = 20	18	38	45	48	42	35	26
H <sub>2</sub> SO <sub>4</sub> -HNO <sub>3</sub> , 1:1, <i>M</i> = 20	13	35	41	45	42	38	–

<sup>a</sup> *M* stands for the nitrating mixture–substrate weight ratio.

<sup>b</sup> Reaction time.

limited amounts of substrates. The procedure for the synthesis of 5-substituted 1-trinitromethyl-1*H*-1,2,4-triazoles was covered by inventor's certificate [6].

## EXPERIMENTAL

The <sup>1</sup>H NMR spectra were measured on a Perkin-Elmer R-12 instrument at 60 MHz using acetone-*d*<sub>6</sub> as solvent and HMDS as internal reference. The IR spectra were recorded on a Specord 75 IR spectrometer (from films). The UV spectra were obtained on an SF-4A spectrophotometer from solutions in ethanol. Thermal gravimetric analysis was performed on a Paulik–Paulik–Erdey derivatograph.

**4-(3-Nitro-1*H*-1,2,4-triazol-1-yl)butan-2-ones V and VII (general procedure).** 5-Chloro- or 5-azido-3-nitro-1*H*-1,2,4-triazole, 0.044 mol, was dissolved in acetone, 1 ml of triethylamine and 4.5 ml (0.054 mol) of methyl vinyl ketone were added, and the mixture was kept for 48 h at room temperature. The solvent was removed, and the residue was purified by reprecipitation (compound V) or recrystallization (VII).

**4-(5-Chloro-3-nitro-1*H*-1,2,4-triazol-1-yl)butan-2-one (V).** Yield 60%, oily substance (reprecipitated from diethyl ether with petroleum ether), *R*<sub>f</sub> 0.53 (acetone–ethyl acetate–hexane, 2:1:5). IR spectrum, *v*, cm<sup>-1</sup>: 850 s, 1030, 1070, 1115, 1185, 1315 v.s, 1430 s, 1460, 1500 s (ring), 1570 v.s (NO<sub>2</sub>), 1725 v.s (C=O). <sup>1</sup>H NMR spectrum, *δ*, ppm: 4.65 t (2H, CH<sub>2</sub>), 3.40 (2H, CH<sub>2</sub>), 2.25 s (3H, CH<sub>3</sub>). Found, %: C 22.33; H 2.67; Cl 16.87; N 25.95. *M* 225. C<sub>6</sub>H<sub>7</sub>ClN<sub>4</sub>O<sub>3</sub>. Calculated, %: C 32.97; H 3.22; Cl 16.22; N 25.63. *M* 218.61.

**4-(5-Azido-3-nitro-1*H*-1,2,4-triazol-1-yl)butan-2-one (VII).** Yield 62%, mp 118–119°C (from propan-2-ol). IR spectrum, *v*, cm<sup>-1</sup>: 830 s, 850, 895, 1040, 1080, 1130 s, 1150 s, 1180 s, 1260 s, 1320 v.s, 1340, 1360, 1380, 1410, 1440, 1460, 1530 s (ring), 1570 v.s (NO<sub>2</sub>), 1720 v.s (C=O), 2180 v.s (N<sub>3</sub>). <sup>1</sup>H NMR spectrum, *δ*, ppm: 4.70 t (2H, CH<sub>2</sub>), 3.30 (2H, CH<sub>2</sub>), 2.20 s (3H,

CH<sub>3</sub>). Found, %: C 31.93; H 3.02; N 46.60. *M* 227. C<sub>6</sub>H<sub>7</sub>N<sub>7</sub>O<sub>3</sub>. Calculated, %: C 32.01; H 3.13; N 43.54. *M* 225.17.

**5-Substituted 3-nitro-1-trinitromethyl-1*H*-1,2,4-triazoles IX–XIII (general procedure).** Ketone I–VIII, 2 g, was added in portions to a mixture of 13 ml of concentrated nitric acid (*d* = 1.51 g/cm<sup>3</sup>) and 12 ml of concentrated sulfuric acid (*d* = 1.84 g/cm<sup>3</sup>) under stirring at 0–5°C. The mixture was stirred for 1 h at that temperature, allowed to warm up to room temperature, and kept at room temperature with intermittent stirring. The product formation was monitored by withdrawing a 5-ml sample of the reaction mixture; the sample was poured onto 4-fold amount of finely crushed ice, and the precipitate was filtered off through a glass fiber using a Teflon filter, washed with ice water (2 × 5 ml), dried in air, and weighed. The yield was determined in 12–18 (I, III, VIII), 30–40 (IV–VII), or 48–72 h (II). The products were purified by recrystallization on heating on a water bath.

**5-Methyl-3-nitro-1-trinitromethyl-1*H*-1,2,4-triazole (IX).** Yield 57%, mp 55–56°C (from CCl<sub>4</sub>). IR spectrum, *v*, cm<sup>-1</sup>: 790 s, 840, 850, 1050, 1170, 1240, 1300 s, 1325, 1380, 1500, 1550 (ring), 1580 s (NO<sub>2</sub>), 1595, 1630 v.s [C(NO<sub>2</sub>)<sub>3</sub>]. <sup>1</sup>H NMR spectrum: *δ* 2.93 ppm, s (CH<sub>3</sub>). UV spectrum: *λ*<sub>max</sub> 212 nm, log *ε* = 4.08. Found, %: C 17.62; H 1.01; N 35.32. *M* 272. C<sub>4</sub>H<sub>3</sub>N<sub>7</sub>O<sub>8</sub>. Calculated, %: C 17.34; H 1.10; N 35.38. *M* 277.11.

**5-Chloro-3-nitro-1-trinitromethyl-1*H*-1,2,4-triazole (X).** Yield 40%, mp 139–140°C (from CHCl<sub>3</sub>). IR spectrum, *v*, cm<sup>-1</sup>: 805 s, 850 s, 910, 990, 1190, 1280, 1310 s, 1350, 1400, 1480, 1520 s (ring), 1590 s (NO<sub>2</sub>), 1620 v.s, 1655 v.s [C(NO<sub>2</sub>)<sub>3</sub>]. Found, %: C 12.41; Cl 11.70; N 32.79. *M* 298. C<sub>3</sub>ClN<sub>7</sub>O<sub>8</sub>. Calculated, %: C 12.11; Cl 11.95; N 32.95. *M* 297.53.

**5-Bromo-3-nitro-1-trinitromethyl-1*H*-1,2,4-triazole (XI).** Yield 65% (from I), 50% (from VI); mp 73–74°C (from CCl<sub>4</sub>). IR spectrum, *v*, cm<sup>-1</sup>: 795 v.s, 830, 840, 970, 1010, 1120, 1240, 1300 s,

1350, 1380 v.s, 1440, 1520 s (ring), 1580 s (NO<sub>2</sub>), 1600 s, 1635 v.s [C(NO<sub>2</sub>)<sub>3</sub>]. UV spectrum:  $\lambda_{\max}$  217 nm,  $\log \epsilon = 4.19$ . Found, %: C 10.83; N 26.25. *M* 340. C<sub>3</sub>BrN<sub>7</sub>O<sub>8</sub>. Calculated, %: C 10.54; N 26.67. *M* 341.98.

**5-Azido-3-nitro-1-trinitromethyl-1H-1,2,4-triazole (XII).** Yield 63%, mp 114–115°C (from CCl<sub>4</sub>). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 795 v.s, 815, 840, 860, 1020, 1130, 1240, 1270, 1310 s, 1330, 1350, 1400, 1518 v.s, 1550 s (ring), 1585 s (NO<sub>2</sub>), 1610 v.s, 1660 v.s [C(NO<sub>2</sub>)<sub>3</sub>], 2185 v.s (N<sub>3</sub>). UV spectrum:  $\lambda_{\max}$  223 nm,  $\log \epsilon = 4.12$ . Found, %: C 12.00; N 46.30. *M* 300. C<sub>3</sub>N<sub>10</sub>O<sub>8</sub>. Calculated, %: C 11.85; N 46.06. *M* 304.09.

**3,5-Dinitro-1-trinitromethyl-1H-1,2,4-triazole (XIII).** Yield 60% (from III), 45% (from VIII); mp 77–78°C (from CCl<sub>4</sub>). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 795 v.s, 830 s, 840, 850, 980, 1020, 1270 s, 1310 s, 1330, 1390, 1550 (ring), 1590 v.s (NO<sub>2</sub>), 1615 v.s, 1640 s, 1650 s [C(NO<sub>2</sub>)<sub>3</sub>]. UV spectrum:  $\lambda_{\max}$  217 nm,  $\log \epsilon = 4.03$ . Found, %: C 11.60; N 36.52. *M* 306. C<sub>3</sub>N<sub>8</sub>O<sub>10</sub>. Calculated, %: C 11.79; N 36.37. *M* 308.

**3,N-Dinitro-1-trinitromethyl-1H-1,2,4-triazol-5-amine (XIV).** Yield 75% (reaction time 12 h), mp 92–93°C (from CH<sub>2</sub>Cl<sub>2</sub>). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 815 s, 850 s, 915, 945, 960, 970, 1060, 1010, 1020, 1030, 1190 s, 1215, 1290 s, 1330, 1365, 1450, 1470, 1530 (ring), 1570 s (NO<sub>2</sub>), 1590 s (NO<sub>2</sub>), 1625 s, 1660 s, 1635 s, 1665 s [C(NO<sub>2</sub>)<sub>3</sub>]. <sup>1</sup>H NMR spectrum:  $\delta$  8.50 ppm, s (NH), exchangeable with D<sub>2</sub>O. Found,

%: C 10.62; H 0.93; N 36.5; water 4.7. C<sub>3</sub>HN<sub>9</sub>O<sub>10</sub>·H<sub>2</sub>O. Calculated, %: C 10.56; H 0.89; N 37.20; water 5.2.

**3-Nitro-1-trinitromethyl-1H-1,2,4-triazol-5-amine (XV).** Yield 50–55% (reaction time 48–72 h), mp 110–111°C (from CHCl<sub>3</sub>). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 815 s, 860, 885, 985, 1060, 1100, 1130, 1150, 1260, 1280, 1290 s, 1335 s, 1385, 1430, 1500 (ring), 1570 s (NO<sub>2</sub>), 1615 s, 1640 s, 1660 s, 1675 [C(NO<sub>2</sub>)<sub>3</sub>, NH<sub>2</sub>], 3260, 3485 (NH<sub>2</sub>). <sup>1</sup>H NMR spectrum:  $\delta$  8.25 ppm, s (NH<sub>2</sub>), exchangeable with D<sub>2</sub>O. Found, %: C 12.52; H 0.76; N 40.44. *M* 272. C<sub>3</sub>H<sub>2</sub>N<sub>8</sub>O<sub>8</sub>. Calculated, %: C 12.96; H 0.73; N 40.30. *M* 278.10.

## REFERENCES

1. Kofman, T.P., Kartseva, G.Yu., Glazkova, E.Yu., and Krasnov, K.K., *Russ. J. Org. Chem.*, 2005, vol. 41, p. 753.
2. Kofman, T.P., Uspenskaya, T.L., Medvedeva, N.Yu., and Pevzner, M.S., *Khim. Geterotsikl. Soedin.*, 1976, p. 991.
3. Kofman, T.P. and Paketina, E.A., *Russ. J. Org. Chem.*, 1995, vol. 31, p. 987.
4. Kofman, T.P., Uspenskaya, T.L., and Pevzner, M.S., *Zh. Org. Khim.*, 1993, vol. 29, p. 2328.
5. Pevzner, M.S., Martynova, M.N., and Timofeeva, T.N., *Khim. Geterotsikl. Soedin.*, 1974, p. 1288.
6. Kofman, T.P., Uspenskaya, T.L., Malygina, L.V., and Pevzner, M.S., USSR Inventor's Certificate no. 1 840 302, 2006; *Byull. Izobret.*, 2006, no. 24.