

## Nitration of Triazolyl-substituted Ketones

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**Abstract**—By nitration of 3-R-1,2,4-triazol-1-ylalkanones with a mixture of concentrated sulfuric and nitric acids a series of compounds was obtained containing a trinitromethyl fragment at the nitrogen of the ring.

The nitration of compounds possessing a methylene fragment activated by a carbonyl group may be regarded as a fairly general synthetic procedure for preparation of aliphatic mono-, di-, and trinitromethyl compounds [1–6].

Treating simple aliphatic ketones with nitric acid is known [1] to result in the rupture of the chain and in formation of 1,1-dinitroalkanes that were however obtained in a low yield. The nitration of ketones possessing a methylene group activated by additional acceptor (ethyl acetoacetate, acetylacetone) under mild conditions (with a mixture of sulfuric and nitric acids in chloroform at low temperature) afforded the corresponding mononitrocompounds [2], and treating polynitroalkyl-substituted ketones of the general formula  $R(\text{CH}_2)_n\text{COCH}_3$  with mixtures of concentrated sulfuric and nitric acids resulted in the synthesis of the corresponding R-dinitro and R-trinitro derivatives [ $R = \text{CH}(\text{NO}_2)_2, \text{RC}(\text{NO}_2)_3$ ] [3–6].

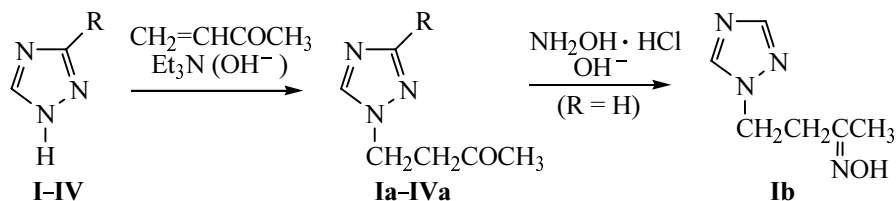
Mononitro-substituted ketones as well as 1-aryl-1,1-dinitro-4-pentanones were not involved into the reaction [4]. In no case Golod et al. [3–6] succeeded in isolation of compounds with the terminal dinitromethyl group.

Alongside the nitration of polynitroalkyl-substituted ketones an example was described of a successful nitration carried out with N-heteryl-substituted propanones [7]: At treating the N-methylated N-(2-oxopropyl)azoles with a diluted mixture of sulfuric and nitric acids ylides were obtained with a dinitromethyl fragment at the nitrogen of the five-membered ring.

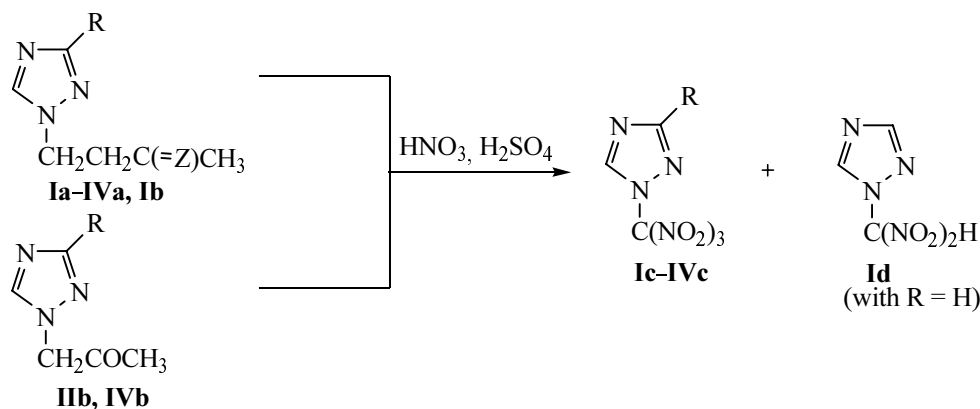
The reaction of destructive nitration of aliphatic ketones was thoroughly investigated by an example of 1,1,1-trinitro-4-pentanone nitration into hexanitroethane [5, 6]. It was established that the use of concentrated nitric acid alone did not result in nitration, but the mixtures of sulfuric and nitric acids at the optimum components ratio [ $\text{HNO}_3:\text{H}_2\text{SO}_4 = (1-2):1$  (by weight), low water content (up to 3%), and high liquor ratio of the acid bath (acids mixture: ketone = 15–20:1)] afforded the hexanitroethane in a high yield. The presence of nitrogen oxides did not affect the process. The kinetic data on this reaction were published in [6], and based thereon the mechanism of ketones destructive nitration was suggested. In keeping with the data the reaction was represented as a multistage sequential-parallel process whose kinetics were plausibly described by an equation of a double-stage reaction. In both rate-determining stages the nitronium cation is involved, and the non-protonated form of the ketone enters into the reaction.

The short survey of the above studies suggested that the nitration of N-oxoalkyl-1,2,4-triazole with mixtures of sulfuric and nitric acids would provide nitro derivatives with a polynitroalkyl fragment attached to the nitrogen atom of the ring.

We selected for the study a series of ketones mono-substituted in the ring, both previously synthesized by us [8, 9] and newly prepared: 3-R-1,2,4-triazol-1-ylbutan-3-ones  $R = \text{H}$  (**Ia**),  $\text{N}_3$  (**Ia**) [9],  $\text{Cl}$  (**IIIa**),  $\text{NO}_2$  (**IVa**) [8],



$R = \text{H}$  (**I**),  $\text{N}_3$  (**II**),  $\text{Cl}$  (**III**),  $\text{NO}_2$  (**IV**).  $Z = \text{O}$  (**Ia-IVa**),  $\text{NOH}$  (**Ib**).



and 3-R-1,2,4-triazol-1-ylpropan-2-ones: R = N<sub>3</sub> (**IIb**) [9], NO<sub>2</sub> (**IVb**) [8].

Compounds **IIa–IVa** were obtained by condensation of 3-R-1,2,4-triazoles **I–IV** with methyl vinyl ketone. The isolation and identification of triazol-1-ylbutanone (**Ia**) was performed by conversion of the crude product into oxime **Ib**.

3-R-1,2,4-Triazol-1-ylpropan-2-ones **IIb** and **IVb** were prepared as described in [8, 9] by alkylation of triazole **II** and **IV** with bromoacetone or propylene oxide followed by oxidation of the alcohols obtained with Jones' reagent.

Nitration conditions for 3-R-1,2,4-triazol-1-ylalkanones were taken at the beginning as described in [5].

We established that under the chosen conditions the destructive nitration of triazolyl-substituted ketones, like that of polynitroalkylbutanones, afforded trinitromethyl derivatives **Ic–IVc**, but in contrast to the polynitro-substituted ketones the nitration of ketone **Ia** gave rise also to dinitromethyl compound **Id**, the natural precursor of 1-trinitromethyl-1,2,4-triazole (**Ic**). Nitration to trinitromethyl compounds is a very slow process with the 3-R-1,2,4-triazol-1-ylalkanones.

The nitration products of the first compound in this series, 1,2,4-triazol-1-ylbutanone (**Ia**) or its oxime **Ib** were isolated only in small overall yield, up to 10% (extraction from the diluted nitrating mixture) and after long exposure time (1–7 days); therewith the yield did not grow at prolonging the exposure to 20 days.

The introduction of an electron-acceptor substituent into the triazole ring (compounds **IIa–IVa**) significantly accelerated the process and increased the yield of the corresponding 1-trinitromethyl-1,2,4-triazoles **IIc–IVc**. The latter precipitated in a virtually pure state on diluting the nitrating mixture and did not contain the corresponding 1-dinitromethyl-1,2,4-triazoles. The extraction of diluted nitrating mixture with ethyl acetate after nitration of

compound **IVa** furnished a negligible amount (less than 1%) of 1-trinitromethyl-3-nitro-1,2,4-triazole (**IVc**).

In nitration with mixtures of concentrated sulfuric and nitric acid we varied the liquor ratio of the acid bath: acids mixture: ketone = 20–40:1 (by weight), the ratio of acids in the mixture HNO<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub> = 1:1–1:4 (by weight), temperature 0–20°C, reaction time from several hours to 5–7 days. The reaction progress was monitored by weight of the accumulating final product that was isolated by diluting an aliquot of the nitrating mixture under standard conditions.

Some regular trends in the reaction and also the effect of substrate structure on the process were investigated by varying the nitration conditions by the example of triazol-1-ylbutanones **IIa**, **IVa**, R = N<sub>3</sub>, NO<sub>2</sub> and 3-nitro-1,2,4-triazol-1-ylpropanone (**IVb**, R = NO<sub>2</sub>) (Fig. 1–3).

It was established that ketones nitration into the trinitromethyl compounds is accompanied by decomposition of the target product in the nitrating mixture: the accumulation curves reached a maximum, and then the yield of the target product notably decreased (Figs. 1–3) with the greatest speed for the most active ketone (Fig. 1, curves 1, 2, 4). Therefore the workup of the reaction mixture should be done at a proper time. Therewith for each ketone a certain exposure time exists where the yield remains sufficiently stable under the given conditions. For instance, the exposure intervals in the nitrating mixture may be regarded as optimum for the following ketones: 36–48 h for triazolylpropanone **IVb**, 70–96 h for triazolylbutanone **IVa**, and 120 h for triazolylbutanone **IIa** (HNO<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub> = 1:1, liquor ratio 20).

In the general case the maximum yield of the product and the time required to obtain it is governed by the ketone structure and the reaction temperature and also depends on the liquor ratio of the acid bath and the proportion of the acids in the nitrating mixture. Triazolylpropanone **IVb**

is nitrated faster than homologous **IVa** (Fig. 1, curves 1, 2) in good agreement with the ease of destruction of a shorter chain, and in the butanone series the activity grows with the increasing electron-acceptor effect of the substituent in the ring: nitro-substituted triazolylbutanone **IVa** is notably more reactive than the corresponding azido analog **IIa** and affords the trinitromethyl compound in a higher yield (Fig. 1, curves 2, 4). The reaction rate considerably decreased at lower temperature (Fig. 1, curves 2, 3) and although the stability of the trinitromethyl compound grew under these conditions, carrying out the nitration at 0°C is unfeasible due to the long duration of the process and low yield of the target product.

The yield and reaction time can be adjusted by varying the liquor ratio of the acid bath and the acids proportion (Fig. 2, 3). For compounds **IVa** and **IIa** the maximum yield of trinitromethyl compounds (63 and 45% respectively) was attained at sufficiently stringent conditions [ $\text{HNO}_3:\text{H}_2\text{SO}_4 = 1:2$ , liquor ratio = 30, 20°C (sulfuric acid content in the mixture 64%, water content up to 3%)]. With the growing proportion of sulfuric acid in the nitrating mixture ( $\text{HNO}_3:\text{H}_2\text{SO}_4 = 1:1, 1:2$ ) (Fig. 2, curves 2, 1; Fig. 3, curves 1, 3) at the constant liquor ratio (20) the process notably accelerated, but the yield increased only for the azido derivative. Raising of the liquor ratio at the high content of the sulfuric acid in the mixture (liquor ratio = 20–30,  $\text{HNO}_3:\text{H}_2\text{SO}_4 = 1:2$ ) resulted both in a faster process and a greater yield (Fig. 2, curves 1, 3; Fig. 3, curves 3, 4) and it is especially pronounced with the nitro derivative. The attempt to increase the yield of azido compound **IIc** by applying even higher liquor ratio (40) was not successful: The process accelerated but the yield was decreased (Fig. 3, curve 2).

Just these conditions of the destructive nitration (liquor ratio = 30,  $\text{HNO}_3:\text{H}_2\text{SO}_4 = 1:2$ , 20°C) we believe to be optimum for the N-azolyl-substituted ketones, and we have carried out under these conditions the nitration of the chlorine-substituted ketone **IIIa**.

The structure of all compounds obtained was confirmed by their analyses and spectral data. Their IR spectra are characterized by a certain shift of the absorption bands from the asymmetrical stretching vibrations of the trinitromethyl fragment to the high-frequency region (1600–1640  $\text{cm}^{-1}$ ) with respect to the spectra of the other aliphatic polynitro derivatives (1597–1603  $\text{cm}^{-1}$ ) [10]. This phenomenon was previously observed for pentanitroethyl compounds and hexanitroethane (1595–1636  $\text{cm}^{-1}$ ) [6]: therewith in the latter spectra a strong

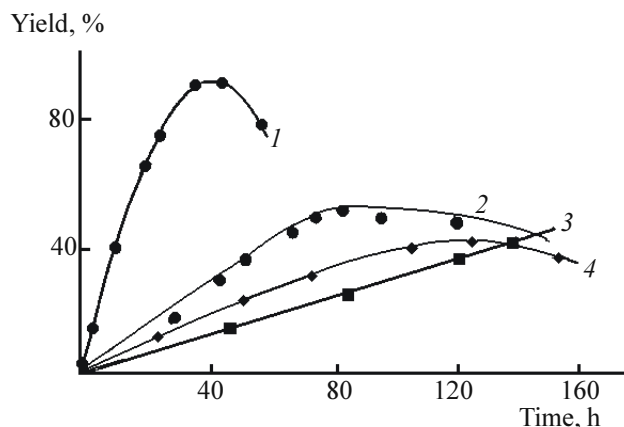


Fig. 1. Yield of trinitromethyl compounds at nitration of compounds **IVb** (1), **IVa** (2, 3), **IIa** (4). Liquor ratio 20.  $\text{HNO}_3:\text{H}_2\text{SO}_4 = 1:1$ ; 20°C (1, 2, 4); 3–0°C (3).

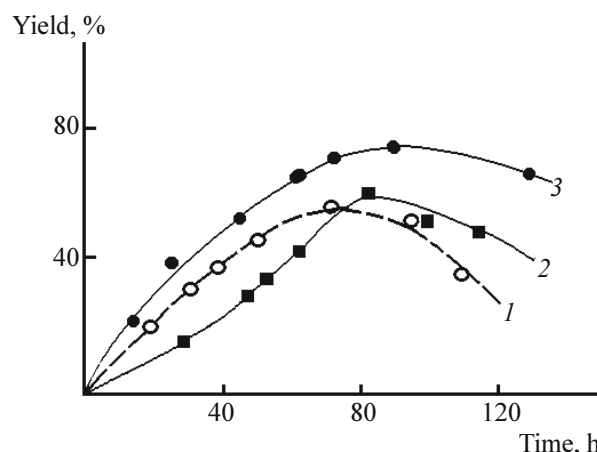


Fig. 2. Nitration of triazolylbutanone **IVa** at variable liquor ratio and the ratio of acids in the nitrating mixture, 20°C: (1) liquor ratio = 20,  $\text{HNO}_3:\text{H}_2\text{SO}_4 = 1:1$ ; (2) liquor ratio = 20,  $\text{HNO}_3:\text{H}_2\text{SO}_4 = 1:1$ ; (3) liquor ratio = 1:30,  $\text{HNO}_3:\text{H}_2\text{SO}_4 = 1:2$ .

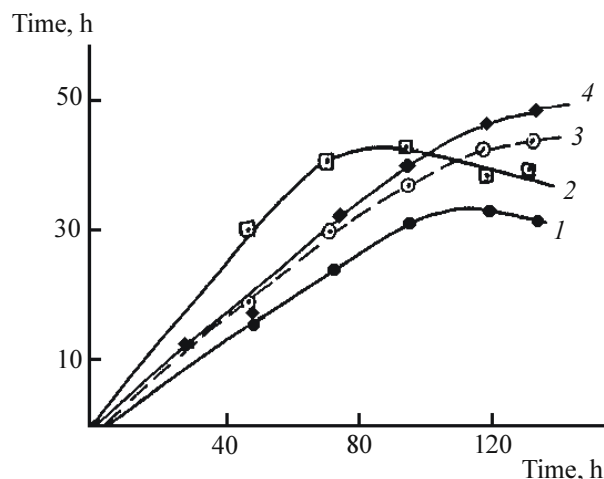


Fig. 3. Nitration of butanone **IIa** at variable liquor ratio and the ratio of acids in the nitrating mixture, 20°C: (1) liquor ratio = 20,  $\text{HNO}_3:\text{H}_2\text{SO}_4 = 1:1$ ; (2) liquor ratio = 40,  $\text{HNO}_3:\text{H}_2\text{SO}_4 = 1:2$ ; (3) liquor ratio = 1:20,  $\text{HNO}_3:\text{H}_2\text{SO}_4 = 1:2$ ; (4) liquor ratio = 30,  $\text{HNO}_3:\text{H}_2\text{SO}_4 = 1:2$ .

dublet was observed in this region. In our case similarly for trinitromethyl compounds **IIIc–IVc** possessing electron-acceptor substituents 2–3 very strong bands were observed in this region. This fact evidences most likely the spatial nonequivalence of the nitro groups in the trinitromethyl fragment.

In the  $^1\text{H}$  NMR spectra the signal from  $\text{C}^5\text{H}$  proton is located typically in a very weak field ( $\delta$  9.30–9.98 ppm) as compared to the initial triazoles ( $\delta$  8.0–8.6 ppm) due to introduction of a very strong electron-acceptor into the position 1 of the triazole ring. The characteristic feature of the UV spectra is the presence of a single maximum of high intensity:  $\lambda_{\text{max}}$ , nm, ( $\log \epsilon$ ): 231 (4.1) (**IIc**), 212 (4.17) (**IVc**).

It should be remarked that all trinitromethyl compounds of this series are exceedingly sensitive to heating and mechanical effects and therefore they should be handled with special care and the syntheses and purification should be performed with small charges.

## EXPERIMENTAL

$^1\text{H}$  NMR spectra were registered on a spectrometer Perkin Elmer R-12 (60 MHz) in acetone- $d_6$ , internal reference HMDS. IR spectra were recorded on a spectrophotometer Specord 75IR (from films), UV spectra were measured on SF-4A device from solutions in ethanol of concentration about  $10^{-4}$  mol/l, cell thickness 1 cm.

**3-R-1,2,4-Triazol-1-ylbutan-3-ones Ia–IVa.** To a solution of 0.044 mol of substituted triazole **I–IV** was added 1 ml of triethylamine and 4.5 ml (0.054 mol) of methyl vinyl ketone, the mixture was kept for 48 h at room temperature, the solvent was removed, and the residue was crystallized.

**1,2,4-Triazol-1-ylbutan-3-one oxime (Ib).** To a solution of 10 g (0.145 mol) of 1,2,4-triazole **Ia** in 50 ml of ethanol was added 18 ml (0.22 mol) of methyl vinyl ketone and 3 ml of triethylamine. The mixture was kept at room temperature for 3 days, the solvent was evaporated, and to the residue was added hydroxylamine solution prepared in methanol from 10 g (0.145 mol) of hydroxylamine hydrochloride and 8.1 g (0.145 mol) of KOH. The mixture was kept at room temperature for 24 h, the solvent was evaporated, and the residue was crystallized from 1-pentanol. Yield 11.2 g (50%), mp 113–114°C, IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1480 (cycle), 1520 (C=N).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 8.52 s (1H,  $\text{H}^5$ ), 8.0 s (1H,  $\text{H}^3$ ), 4.50 t (2H,  $\text{CH}_2$ ), 2.75 t (2H,  $\text{CH}_2$ ), 1.80 s (3H,  $\text{CH}_3$ ). Found, %: C 46.18; H 6.44; N 36.69.  $\text{C}_6\text{H}_{10}\text{N}_4\text{O}$ . Calculated, %: C 46.7; H 6.5; N 36.4.

**3-Azido-1,2,4-triazol-1-ylbutan-3-one (IIa).** Yield 65%, mp 34–35°C (freezing out from ether) [9].

**3-Chloro-1,2,4-triazol-1-ylbutan-3-one (IIIa).** Oily substance, yield 60%, isomers 9:1 (reprecipitation from ether with petroleum ether). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1180 (C=O), 1515 (cycle), 1730 (C=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 8.42 s (1H,  $\text{H}^5$ ), 7.95 s (1H,  $\text{H}^3$ ), 4.48 t (2H,  $\text{CH}_2$ ), 4.40 t (2H,  $\text{CH}_2$ ), 3.15 t (2H,  $\text{CH}_2$ ), 2.18 s (3H,  $\text{CH}_3$ ). Found, %: C 41.33; H 4.66; N 24.55.  $\text{C}_6\text{H}_8\text{ClN}_3\text{O}$ . Calculated, %: C 41.5; H 4.6; N 24.2.

**3-Nitro-1,2,4-triazol-1-ylbutan-3-one (IVa).** Yield 82%, mp 60–61°C (from aqueous methanol) [8].

**3-Azido-1,2,4-triazol-1-ylpropan-2-one (IIb).** Yield 75%,  $n_D^{20}$  1.577 (reprecipitation from ether with petroleum ether) [9].

**3-Nitro-1,2,4-triazol-1-ylpropan-2-one (IVb).** Yield 70%, mp 100–101°C (from chloroform) [8].

**1-Dinitromethyl- and 1-trinitromethyl-1,2,4-triazoles (Id and Ic). General procedure.** To a mixture of 13 ml of nitric ( $d$  1.51  $\text{g}/\text{cm}^3$ ) and 12 ml of sulfuric acid ( $d$  1.84  $\text{g}/\text{cm}^3$ ) at 0–5°C was added while stirring by portions a solution of 2 g of ketone **Ia** (oxime **Ib**) in 10 ml of concn.  $\text{H}_2\text{SO}_4$ . The reaction mixture was stirred at 0–5°C for 1 h, then the temperature was raised to ambient, and the mixture was kept for 1–20 days. Then the nitrating mixture was poured into a 4-fold amount of finely crushed ice with water, extracted with dichloromethane (4×25 ml) (compound **Id**) and then with ethyl acetate (4×25 ml) (a mixture of compounds **Ic** and **Id**). Both extracts were washed with water (2×50 ml). The ethyl acetate from the second extract was evaporated, the residue was treated with hot dichloromethane (2×25 ml) to extract compound **Id**, and this solution was combined with the first extract containing the main portion of the compound. The residue after extraction was crystallized from chloroform. From the combined dichloromethane solutions the solvent was evaporated, and the product obtained was crystallized from chloroform.

**1-Dinitromethyl-1,2,4-triazole (Id).** Yield 5–7%, mp 106–107°C ( $\text{CHCl}_3$ ). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1500 (cycle), 1610 s [ $\text{C}(\text{NO}_2)_2$ ].  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 9.25 s (1H,  $\text{H}^5$ ), 8.50 s (1H,  $\text{H}^3$ ), 8.40 s [1H,  $\text{C}(\text{NO}_2)_2\text{H}$ ], exchange in  $\text{D}_2\text{O}$ . Found, %: C 20.95; H 1.86; N 40.89.  $\text{C}_3\text{H}_3\text{N}_5\text{O}_4$ . Calculated, %: C 20.8; H 1.73; N 40.5.

**1-Trinitromethyl-1,2,4-triazole (Ic).** Yield 7%, mp 101–102°C ( $\text{CHCl}_3$ ). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1480 s (cycle), 1560 s, 1630 s [ $\text{C}(\text{NO}_2)_3$ ].  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 9.30 s (1H,  $\text{H}^5$ ), 8.50 s (1H,  $\text{H}^3$ ). Found, %: C 16.58;



H 0.99; N 38.77.  $C_3H_2N_6O_6$ . Calculated, %: C 16.50; H 0.92; N 38.50.

**1-Trinitromethyl-1,2,4-triazoles IIc–IVc.**

*General procedure.* To a mixture of 13 ml of nitric ( $d$  1.51 g/cm<sup>3</sup>) and 12 ml of sulfuric acid ( $d$  1.84 g/cm<sup>3</sup>) at 0–5°C was added while stirring by portions a solution of 2 g of ketone **IIa–IVa**, **IIb**, and **IVb**. The reaction mixture was stirred at 0–5°C for 1 h, then the temperature was raised to ambient and the reaction mixture was kept at intermittent stirring. The reaction progress was monitored by weight of the accumulating final product that was isolated by sampling an aliquot of the nitrating mixture (5 ml). The aliquot of the nitrating mixture was poured into a 4-fold amount of finely crushed ice with water, the precipitated product was filtered off through a teflon nutsch filter and fiber-glass and washed with ice water (2×5 ml), dried in air, and weighed. A fair yield was obtained by keeping the nitrating mixture for 1.5 or 3 days (ketones **IVb** and **IVa** respectively) or 5 days (ketones **IIa**, **IIb**, and **IIIa**). Recrystallization of products was performed with the use of a water bath.

**1-Trinitromethyl-3-azido-1,2,4-triazole (IIc).** Yield 45%, mp 58–59°C (from petroleum ether). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1540 s (cycle), 1600 s, 1630 v.s [C(NO<sub>2</sub>)<sub>3</sub>], 2155 s (N<sub>3</sub>). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 9.50 s (C<sup>5</sup>H). Found, %: C 14.09; H 0.38; N 48.72.  $C_3HN_9O_6$ . Calculated, %: C 13.9; H 0.4; N 48.7.

**1-Trinitromethyl-3-chloro-1,2,4-triazole (IIIc).** Yield 45%, mp 37–38°C (CHCl<sub>3</sub>). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1520 m (cycle), 1615 s, 1645 s [C(NO<sub>2</sub>)<sub>3</sub>]. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 9.85 s (C<sup>5</sup>H). Found, %: C 14.32; H 0.43; N 32.94.  $C_3ClHN_6O_9$ . Calculated, %: C 14.25; H 0.39; N 33.3.

**1-Trinitromethyl-3-nitro-1,2,4-triazole (IVc).** Yield 63% (from triazolylbutanone **IVa**), 90% (from

triazolylpropanone **IVb**), mp 99–100°C (CHCl<sub>3</sub>). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1520 sc (cycle), 1570 v.s (NO<sub>2</sub>), 1610 v.s, 1620 v.s, 1625 v.s [C(NO<sub>2</sub>)<sub>3</sub>]. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 9.98 s (C<sup>5</sup>H). Found, %: C 13.63; H 0.37; N 37.22.  $C_3HN_7O_8$ . Calculated, %: C 13.7; H 0.4; N 37.3.

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## REFERENCES

1. Chancel, M.G., *C.r.*, 1882, vol. 94, p. 399; Fileti, M.F. and Ponzio, G.J., *Pr. Chem.*, 1895, vol. 55, p. 1862.
2. Laikhter, A.L., Kislyi, V.P., and Semenov, V.V., *Mendeleev Commun.*, 1993, p. 20; Lukashevich, O.V., Novatskii, G.N., Golod, E.L., and Bagal, L.I., *Zh. Org. Khim.*, 1972, vol. 8, p. 908; Golod, E.L., Novatskii, G.N., and Bagal, L.I., *Zh. Org. Khim.*, 1973, vol. 9, p. 1111; Tselinskii, I.V., Shokhor, I.N., and Bagal, L.I., *Zh. Org. Khim.*, 1994, vol. 30, p. 983; Stepanova, O.P., and Golod, E.L., *Zh. Org. Khim.*, 1997, vol. 33, p. 1521.
3. Stepanova, O.P., Poryadkova, M.A., and Golod, E.L., *Zh. Org. Khim.*, 1994, vol. 30, p. 1458.
4. Stepanova, O.P. and Golod, E.L., *Zh. Org. Khim.*, 1994, vol. 30, p. 1521.
5. Golod, E.L. and Bagal, L.I., *Zh. Org. Khim.*, 1994, vol. 30, p. 29.
6. Golod, E.L., Kukushkin, I.K., Moiseev, I.K., and Tselinskii, I.V., *Ros. Khim. Zh.*, 1997, vol. 41, p. 22.
7. Semenov, V.V., Shevelev, S.A., and Mel'nikova, L.S., *Mendeleev Commun.*, 1993, p. 58.
8. Kofman, T.P., Uspenskaya, T.L., Medvedeva, N.Yu., and Pevzner, M.S., *Kh. Geterotsykl. Soed.*, 1976, p. 991.
9. Kofman, T.P. and Krasnov, K.K., *Zh. Org. Khim.*, 2004, vol. 40, p. 1699.
10. Noble, R., Borgardt, F., and Reed, W.L., *Chem. Rev.*, 1964, vol. 64, p. 19.