Chemistry of Heterocyclic Compounds, Vol. 39, No. 4, 2003

REACTIONS OF 2,4-DISUBSTITUTED 5-NITRO-1,2,3-TRIAZOLE 1-OXIDES. 3*. DESTRUCTIVE NITRATION OF NITRO-SUBSTITUTED 2-ACETONYL-TRIAZOLE OXIDES AND AZOTRIAZOLE OXIDES

T. I. Godovikova, S. A. Vozchikova, E. L. Ignat'eva, L. I. Khmel'nitskii, and B. L. Korsunskii

We have studied destructive nitration of acetonyltriazole oxides and azotriazole oxides to the corresponding trinitromethyl derivatives.

Keywords: nitrotriazole oxides, hydroxypropyl group, trinitromethyl and acetonyl derivatives, destructive nitration, oxidation.

We previously carried out oxidation of substituted aminotriazole oxides to dinitro derivatives of triazole oxides and azotriazole oxides [1, 2].

This report is devoted to development of a method for synthesis of polynitrotriazole oxides based on degradative nitration of the corresponding acetonyl derivatives. Destructive nitration of nitrocarbonyl compounds of various classes is a novel and rather general method for obtaining polynitro derivatives [3, 4], and it has been shown that a large number of heteroatoms in the ring and also the presence of good acceptor substituents significantly increases the ability of the compound to enter into the indicated reaction. In particular, it has been used as the basis for a well-developed and widely used method for synthesis of N-polynitromethylazoles, 1,2,4-triazoles, and tetrazoles [4]. Until our work, destructive nitration had not been studied in the 1,2,3-triazole-1-oxide series.

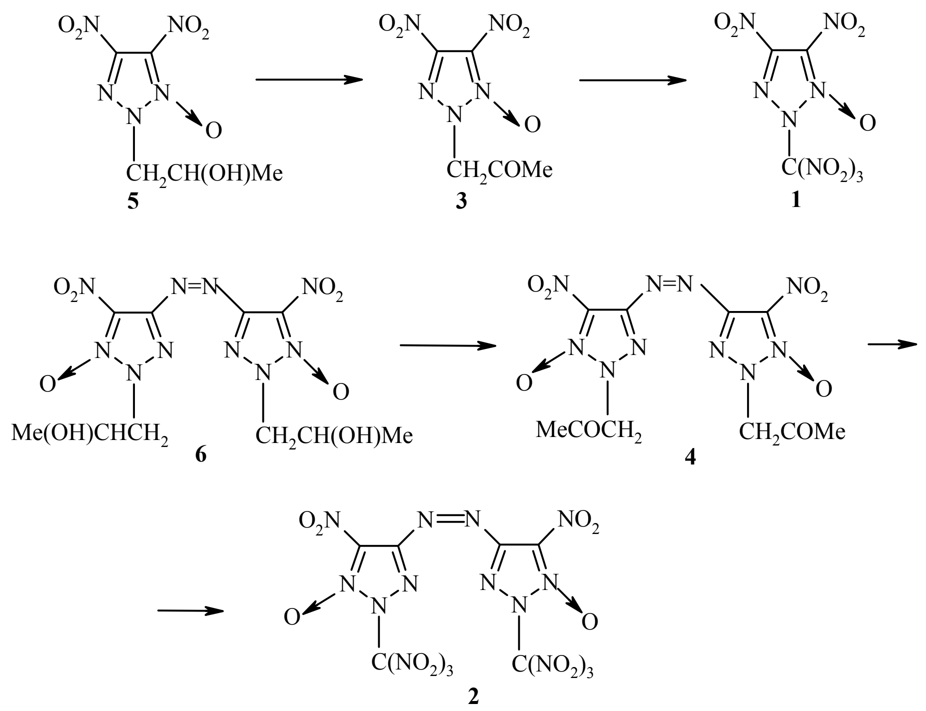
With the aim of synthesis of 4,5-dinitro-2-trinitromethyl-1,2,3-triazole 1-oxide (**1**) and 4,4'-azo-5-nitro-2-trinitromethyl-1,2,3-triazole 1-oxide (**2**), we selected as the objects of investigation 2-acetonyl-4,5-dinitro-1,2,3-triazole 1-oxide (**3**) and 4,4'-azo-2-acetonyl-5-nitro-1,2,3-triazole 1-oxide (**4**), which we obtained by using the Jones reagent (chromic anhydride in an aqueous solution of sulfuric acid [5, 6]) to oxidize 4,5-dinitro-2-(2-hydroxypropyl)-1,2,3-triazole 1-oxide (**5**) and 4,4'-azo-5-nitro-2-(2-hydroxypropyl)-1,2,3-triazole 1-oxide (**6**).

The Jones reagent, added to a solution of alcohol in acetone, has the advantage of rapid oxidation under mild conditions. This method is preferred if there are no easily oxidized functional groups and the reaction is carried out with a fairly small amount of material [5].

---

* For Communication 2, see [1].

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow 117913, e-mail: ogv@cacr.ioc.ac.ru. Institute of Problems in Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 548-551, April, 2003. Original article submitted January 12, 2000; revision submitted October 13, 2000.



When ketone **3** was reacted with a mixture of concentrated nitric and sulfuric acids, polynitrotriazole oxide **1** was obtained (yield 50%).

The analogous reaction of destructive nitration of azotriazole oxide **4** was not carried out because of the instability of the starting compound in sulfuric acid. So as the agents nitrating compound **4**, we studied concentrated (*d* 1.5) and 70% nitric acid, and also the following mixtures: trifluoroacetic acid – nitric acid (*d* 1.5), 3:2 (A); trifluoroacetic anhydride – nitric acid (*d* 1.5), 3:2 (B); trifluoroacetic acid – nitric acid (*d* 1.5) – nitrogen tetroxide, 2:2:1 (C).

In nitration of azotriazole oxide **4** by concentrated (*d* 1.5) or 70% nitric acid, we only detected formation of new products chromatographically and could not isolate them.

We followed the course of the reactions with nitrating mixtures A-C by means of UV spectroscopy. In the case of mixture B, the nature of the UV spectral curves for the reaction mass changed after 5 h, and a new peak with γ 315 nm (absorption in this region is assigned to compounds with a trinitromethyl group, i.e., to product **2**) appeared after 7.5 h. For mixture C, similar changes were observed in the spectrum after 4.0 and 6.5 h respectively.

The best yield of polynitroazotriazole oxide **2** (41%) was achieved by nitration with mixture A. When we used mixtures B and C, the yield of product **2** was respectively 10% and 15%.

In the studied reactions of destructive nitration of compounds **3** and **4**, we did not detect formation of the corresponding dinitromethyl derivatives either with UV spectroscopy or with TLC, which may be explained by their high reactivity, probably due to the presence of electron-acceptor substituents and an N-oxide moiety in the molecules.

EXPERIMENTAL

The IR spectra were taken on a Specord IR-75 and UR-20 apparatus in KBr disks. The ^{13}C and ^{14}N NMR spectra were obtained on a Bruker AM-300 instrument at frequencies of 75 MHz and 21.67 MHz respectively, internal standard TMS. The UV spectrum was taken on a Specord-UV spectrometer in absolute ethanol. The mass spectra were obtained on a Varian apparatus with direct injection of the sample into the ion source, with ionizing electron energy 70 eV, accelerating potential 1.75 kV, and emission current 100 mA. The melting points were determined on a Boetius stage with heating rate of 4°C/min at the melting point. TLC was carried out on Silufol UV-254 (eluent methylene chloride) with detection in UV light.

The synthesis of compounds **5** and **6** is described in [1].

Oxidation of Triazole Oxides 5 and 6 by the Jones Reagent. (General Procedure). Mixture (0.13 or 0.40 ml) prepared from chromic anhydride (0.25 g), concentrated H_2SO_4 (0.25 ml), and water (0.75 ml) was added dropwise with stirring to a solution of respectively triazole oxide **5** (0.1 g, 0.43 mmol) or azotriazole oxide **6** (0.1 g, 0.25 mmol) in acetone (20 ml) at 10-20°C. The reaction mass was held for 3 h at the same temperature, and its composition was monitored using TLC (eluent ether); then chromium sulfate was filtered off and washed with acetone (3 × 5 ml). After the washing, acetone was combined with the filtrate and the mixture was dried with calcined magnesium sulfate. The solvent was removed on a rotary evaporator; a fairly small amount of ether or alcohol was added to the residue, and the precipitate of product was filtered off. The following were obtained:

2-Acetonyl-4,5-dinitro-1,2,3-triazole 1-Oxide (3) from compound **5** in yield of 0.07 g (70%); mp 98°C. IR spectrum, ν, cm^{-1}: 3010, 2960, 1730, 1580, 1560, 1490, 1450, 1440, 1410, 1380, 1340, 1330, 1300, 1240, 1180, 1130, 1080, 1040, 980, 930, 800, 720. UV spectrum (MeOH), λ, nm: 228 and 335. Mass spectrum: 231 M^+, 143 [M – $NO_2^{\cdot}$ – CH_3CHO], 96 [143 – $NO_2^{\cdot}$ – $H^{\cdot}$]. Found, %: C 25.75; H 1.95; N 30.37. $C_5H_5N_5O_6$. Calculated, %: C 25.97; H 2.16; N 30.30;

4,4'-Azo-2-acetonyl-5-nitro-1,2,3-triazole 1-Oxide (4) from compound **6** in yield of 0.07 g (70%); mp 177°C (with decomposition). IR spectrum, ν, cm^{-1}: 2990, 2940, 1730, 1620, 1550, 1520, 1440, 1400, 1360, 1290, 1230, 1180, 1130, 1120, 1050, 1040, 990, 940, 860, 840, 810, 750. Mass spectrum: 398 M^+, 352 [M – $NO_2^{\cdot}$], 341 [M – $^{\cdot}CH_2COCH_3$], 335 [352 – $HO^{\cdot}$], 167 [$^{\cdot}N{=}NC_2HN(CH_2COCH_3)N{\rightarrow}O$], 57 [$^{\cdot}CH_2COCH_3$]. Found, %: C 29.92; H 2.60; N 35.30. $C_{10}H_{10}N_{10}O_8$. Calculated, %: C 30.15; H 2.51; N 35.18.

Nitration of Triazole Oxide 3. Triazole oxide **3** (0.6 g, 1.9 mmol) was added in portions at 0-5°C with rapid stirring to mixture of concentrated nitric acid (*d* 1.5) and concentrated sulfuric acid (*d* 1.84) (60 ml). The reaction mass was held at room temperature for 15-16 h and then poured over ice; the crystals were filtered off and dried in air. The following was obtained:

4,5-Dinitro-2-trinitromethyl-1,2,3-triazole 1-Oxide (1). Yield 0.3 g. The filtrate was extracted with hexane (2 × 20 ml), the solvent was removed, and an additional amount of the target product (0.1 g) was isolated. Total yield 0.4 g (50%); mp 38-40°C. IR spectrum, ν, cm^{-1}: 1650, 1620, 1595, 1575, 1540, 1495, 1470, 1365, 1320, 1280, 1270, 1170, 1060, 1040, 940, 875, 810, 795, 725. ^{14}N NMR spectrum ($CDCl_3$), δ, ppm: -43.70 (4-NO_2); -49.88 (5-NO_2); -49.80 [$C(NO_2)_3$]. Mass spectrum: 324 M^+, 232 [M – $NO_2^{\cdot}$ – $NO_2^{\cdot}$], 186 [232 – $NO_2^{\cdot}$], 174 [M – $C(NO_2)^{\cdot}_3$], 112 [174 – $O^{\cdot}$ – $NO_2^{\cdot}$], 66 [112 – $NO_2^{\cdot}$]. Found, %: C 11.11; N 34.79. $C_3N_8O_{11}$. Calculated, %: C 11.11; N 34.57.

Nitration of Azotriazole Oxide 4. (General Procedure). Compound **4** (0.05 g, 0.1 mmol) was added at 0°C with stirring to 0.5 ml of mixture A, B, or C. The reaction mass was held for 24 h at room temperature and then poured over ice, the precipitate was filtered off and then washed with water and hexane. When the nitrating mixture A was used, the following was obtained:

4,4'-Azo-5-nitro-2-trinitromethyl-1,2,3-triazole 1-Oxide (2). Yield 0.03 g (41%); mp 68-70°C. The material was unstable and decomposed during storage. IR spectrum, ν, cm^{-1}: 1640, 1625, 1610, 1580, 1556, 1555, 1505, 1380, 1360, 1330, 1280, 1245, 1175, 1120, 1035, 950, 855, 825, 795, 745. ^{13}C NMR spectrum (CD_2Cl_2), δ, ppm: 113.9 [$C(NO_2)_3$]; 127.6 [C–NO_2]; 147.9 [C–N=N]. ^{14}N NMR spectrum (CD_2Cl_2), δ, ppm: -37.90 [NO_2]; -47.81 [$C(NO_2)_3$].

REFERENCES

1. T. I. Godovikova, S. A. Vozchikova, E. L. Ignat'eva, L. I. Khmel'nitskii, and B. L. Korsunskii, *Khim. Geterotsikl. Soedin.*, 1356 (1999).
2. T. I. Godovikova, E. L. Ignat'eva, S. P. Golova, V. S. Kuz'min, and L. I. Khmel'nitskii, *Zh. Org. Khim.*, **33**, 1209 (1997).
3. E. L. Golod, I. K. Kukushkin, I. K. Moiseev, I. V. Tselinskii, *Zh. Vses. Khim. Obshch. im. D. I. Mendeleeva*, **41**, **B.I.**, 22 (1997).
4. V. V. Semenov, S. A. Shevelev, and L. G. Melnikova, *Mendeleev Commun.* 58 (1993).
5. C. A. Buehler and D. E. Pearson, *Survey of Organic Syntheses* [Russian translation], Mir, Moscow (1973), Vol. 2, p. 92.
6. L. Fieser and M. Fieser, *Reagents for Organic Synthesis* [Russian translation], Mir, Moscow (1971), Vol. 4, p. 176.