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A New Method for the Synthesis of 1,2,3-Triazole 1-Oxides

Tamara I. Godovikova,[a] Svetlana P. Golova,[a] Svetlana A. Vozchikova,[b] Elena L. Ignat'eva,[b] Mikhail V. Povorin,[a] Vladimir S. Kuz'min[c] and Lenor I. Khmel'nitskii[†a]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation. Fax: +7 095 135 5328*
[b] *Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 096 51 53588*
[c] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 117907 Moscow, Russian Federation. Fax: +7 095 954 1279*

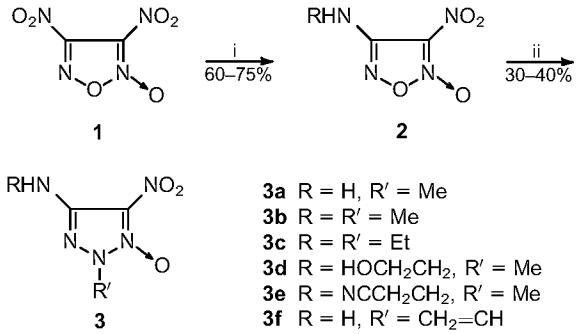
The synthesis of uncondensed 1,2,3-triazole 1-oxides from 4-aminofuroxans has been pioneered.

The most studied and widely used method for the preparation of 1,2,3-triazole 1-oxides prior to our work was the oxidative cyclization of hydrazone oximes of 1,2-dicarbonyl compounds.[1] Nitro-1,2,3-triazole 1-oxides, however, were not obtained in this way.

We now propose a new method for the synthesis of uncondensed 1,2,3-triazole 1-oxides containing a nitro group in the ring.

According to our earlier publications[2,3] 3,4-dinitrofuroxan **1** readily reacts with nucleophilic reagents to give the correspondingly substituted 3-nitrofuroxans. To gain access to di(alkylamino)furoxans we investigated the interaction of 4-alkylamino-3-nitrofuroxans **2** with primary aliphatic amines and showed that 2-alkyl-4-alkylamino-5-nitro-1,2,3-triazole 1-oxides **3** formed in all the cases studied.

The product **3** may also be obtained directly from **1**, the intermediate **2** not being isolated from the reaction mixture (Scheme 1). 1,2,3-Triazole 1-oxides with different alkyl substituents may be obtained by this method using alkylamines of various structure in the first and second stages. If ammonia is used as a nucleophile in the first stage and alkylamines in the second, the reaction affords 4-amino-2-alkyl-5-nitro-1,2,3-triazole 1-oxides:

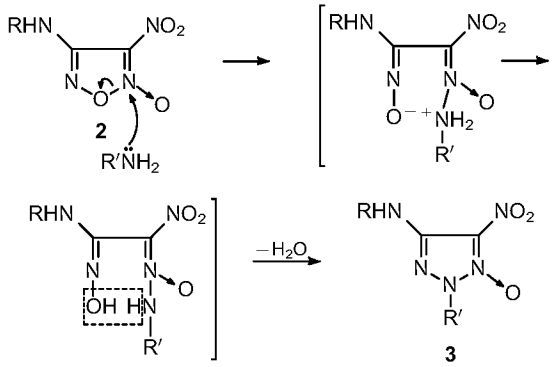


Scheme 1 *Reagents and conditions:* i, RNH_2, CH_2Cl_2, −20 °C; ii, $R'NH_2$, CH_2Cl_2, 20 °C (TLC to control reaction stages).

[†] Professor Lenor I. Khmel'nitskii, renowned scientist in the field of chemistry of nitrogen-containing heterocycles, died on the 20th April 1995.

We suppose that the primary amine attacks the nitrogen atom of the *N*-oxide entity to open the furoxan ring, then dehydrative cyclization follows to form the 1,2,3-triazole 1-oxide ring (Scheme 2).

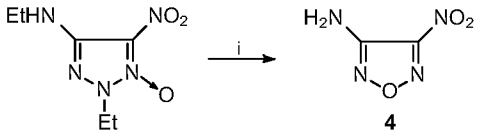
Reactions involving transformation of the uncondensed furoxan ring into a 5-nitro-1,2,3-triazole 1-oxide ring have not been reported in the literature.[1,4]



Scheme 2

In the area of condensed systems, benzofuroxan was transformed into 2-aryl-2*H*-benzo-1,2,3-triazole 1-oxides by the action of Na or K salts of substituted formanilides.[5]

Aminonitrofurazan **4** was isolated as a side product for **3** in all runs. Special experiments showed that compound **4** is generated from **3**, *e.g.*, **3c** with excess ethylamine transforms quantitatively into **4** (Scheme 3).



Scheme 3 *Reagents and conditions*: i, $EtNH_2$, CH_2Cl_2, 18–20 °C, 48 h; compound **4**, m.p. 124–125 °C (*cf.* ref. 6).

Such a recyclization was not known earlier for 1,2,3-triazole 1-oxides.[1]

All newly prepared compounds have satisfactory elemental analyses and are characterized by IR, NMR and mass spectra (molecular ion peaks were observed in all mass spectra). The prevailing fragmentation mode is extrusion from the molecular ion of first $NO_2^{\cdot}$ and then a neutral diazoalkane molecule. Precisely this fragmentation route is a general feature of all investigated triazole 1-oxides of this structure; therefore, combination of the respective peaks may be used to identify compounds of this type.

X-Ray analysis, using as an example **3a**, offered a conclusive verification of the structure of substituted 5-nitro-1,2,3-triazole 1-oxides.‡ The structure of **3a** is shown in Fig. 1.

The molecule of **3a** is nearly planar, except that the H(13), H(23) and H(33) atoms of the Me group deviate from the ring plane by 0.505, 0.918 and 0.324 Å, respectively. Distribution of bond lengths in the triazole ring is indicative of ring aromaticity. Coplanarity of the nitro group with the ring plane (the corresponding angle is 1.8°) is caused by intramolecular H-bond O(121)...H(111)...N(11) (the O...N distance is 2.851 Å). This fact also explains an elongation of the N(21)–O(121) bond (1.233 Å) relative to N(21)–O(221) (1.225 Å). The amine atom N(11) has planar trigonal geometry; deviation of the N(11) atom from the H(111), H(211) and C(1) plane is 0.05 Å.

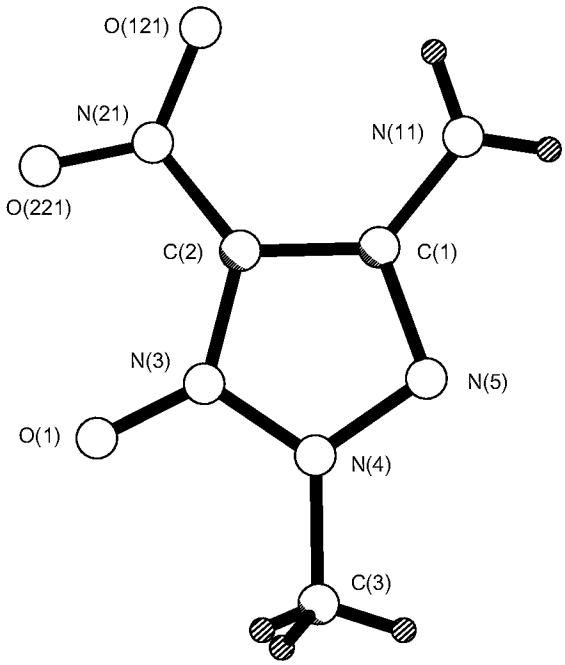


Fig. 1 Molecular structure of **3a**.

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‡ *Crystal data for* **3a**: $C_3H_5N_5O_3$, monoclinic, space group $P2_1/C$, $a = 4.6011(4)$, $_3$ $b = 9.518(2)$, $c = 14.461(2)$ A, $\beta = 100.64(1)°$, $V = 622.4(2)$ A , $D_c = 1.698$ g cm^{-3}, $z = 2$. The intensities of 838 reflections (781 observed): I_{hkl} were measured on a Syntex-$P2_1$ diffractometer (graphite monochromated λCu-Kα, λ = 1.5405 A) using the θ/2θ scan technique (2θ⩽120°). The structure was solved by direct methods and refined by a full-matrix least-squares method in an anisotropic approximation for all atoms. The final R_F was 0.042 for 775 reflections. All calculations were performed on an IBM PC using SHELX software. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, see Notice to Authors, *Mendeleev Commun.*, 1995, Issue 1.

3a R = H, R′ = Me, m.p. 218–219 °C (decomp.), ^{13}C NMR ([$^2H_6$]DMSO): 39.5 (Me), 123.8 (C–NO_2), $\Delta\nu_{1/2}$ 13Hz), 144.7 (CNH_2, $\Delta\nu_{1/2}$ 5Hz). ^{14}N NMR ([$^2H_6$]DMSO): −83.9 (N→O, $\Delta\nu_{1/2}$ 120Hz), −30.42 (NO_2, $\Delta\nu_{1/2}$ 37Hz). IR, ν/cm^{-1} (KBr pellets): 3410, 3320, 3270, 3210, 2940, 2700, 1650, 1640, 1580, 1510, 1490, 1450, 1360, 1290, 1240, 1180, 1030, 950, 830, 750.

3b R = R′ = Me, m.p. 187 °C (decomp.), ^{1}H NMR ($CDCl_3$): 3.0 d (MeNH), 3.87 s (Me). ^{14}N NMR ([$^2H_6$]DMSO): −85 (N→O, $\Delta\nu_{1/2}$ 300 Hz), −30.73 (NO_2, $\Delta\nu_{1/2}$ 25 Hz). IR, ν/cm^{-1} (KBr pellets): 3420, 3050, 2965, 2930, 1625, 1522, 1508, 1480, 1467, 1425, 1417, 1372, 1351, 1333, 1280, 1226, 1168, 1150, 1058, 1017, 940, 890, 830.

3c R = R′ = Et, m.p. 126 °C (decomp.), ^{1}H NMR ($CDCl_3$): 1.35 m (Me), 3.55 m (CH_2 in EtNH), 4.3 q (CH_2 in $MeCH_2$), 5.8 br.s. (NH). IR, ν/cm^{-1} (KBr pellets): 3420, 2995, 2960, 2900, 1620, 1534, 1510, 1485, 1470, 1390, 1338, 1317, 1295, 1250, 1187, 1166, 1146, 1079, 1009, 931, 895, 825.

3d R = $HOCH_2CH_2$, R′ = Me, m.p. 167–168 °C, ^{1}H NMR (CD_3OD): 3.91 q (CH_2N), 3.77 m (CH_2CH_2), 3.54 s (MeN), 3.34 s (OH), 4.96 br.s (NH). IR, ν/cm^{-1} (KBr pellets): 3440, 3400, 2975, 2950, 1645, 1520, 1470, 1420, 1390, 1370, 1350, 1320, 1260, 1220, 1185, 1150, 1080, 1020, 980, 900, 875, 820, 750.

3e R = $NCCH_2CH_2$, R′ = Me, m.p. 168–170 °C, ^{1}H NMR ($CDCl_3$): 3.93 s (Me), 3.77 q (CH_2NH), 2.79 t (CH_2CN), 6.2 br.s (NH). IR, ν/cm^{-1} (KBr pellets): 3395, 3045, 2970, 2255, 1630, 1536, 1500, 1490, 1450, 1435, 1395, 1345, 1322, 1264, 1230, 1205, 1170, 1095, 1040, 860, 820, 740.

3f R = H, R′ = CH_2=$CHCH_2$, m.p. 151–152 °C, ^{1}H NMR ($CDCl_3$): 5.27 br.s (NH_2), 4.48 d (CH_2N), 5.90 m (CH), 5.45 d (CH_2=CH). IR, ν/cm^{-1} (KBr pellets): 3470, 3280, 1620, 1560, 1480, 1420, 1350, 1320, 1300, 1240, 1160, 1130, 1080, 1000, 940, 810.