3-Ethoxy-2,2-bis(methoxy-*NNO*-azoxy)propan-1-ol. Synthesis and X-ray diffraction analysis

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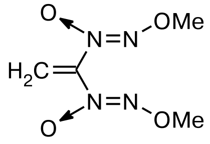
Reaction of bis(methoxy-*NNO*-azoxy)methane with formaldehyde in ethanol gives 3-ethoxy-2,2-bis(methoxy-*NNO*-azoxy)propan-1-ol as a minor product along with target 2,2-bis(methoxy-*NNO*-azoxy)ethanol. The structure of the former was confirmed by the counter synthesis and X-ray diffraction analysis.

Key words: azoxy compounds, oxymethylation, X-ray diffraction study.

Alkoxy-*NNO*-azoxy compounds (AAC) are known from the end of the XIX century,[1,2] however before the 1980s they were the poorly studied class of compounds. In recent years, the interest to AAC is greatly increased (see reviews[3—5]). Several AAC have been considered as the components for the gas generating compositions[6] and biologically active compounds (NO donors, antitumor pharmaceuticals).[5,7,8]

One of the fields in the AAC chemistry is the synthesis and study of the reactions of unsaturated AAC.[9—16] Thus, recently synthesized 1,1-bis(methoxy-*NNO*-azoxy)ethene (**1**)[16] turned out to be useful for the introduction of the 2,2-bis(methoxy-*NNO*-azoxy)ethyl group into various compounds by the Michael reaction.[16—19]

The key intermediate for the synthesis of 1,1-bis(methoxy-*NNO*-azoxy)ethene (**1**) is 2,2-bis(methoxy-*NNO*-azoxy)ethanol (**2**),[16] which is widely used in the other transformations.[16,18,20—22]



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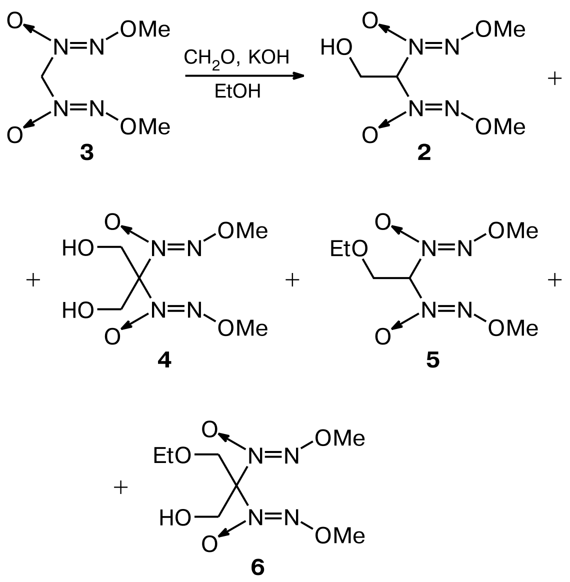
Alcohol **2** could be prepared[16,20] by oxymethylation of bis(methoxy-*NNO*-azoxy)methane (**3**) (Scheme 1). Our modification of the published synthetic procedure[20] for alcohol **2** serves to the considerable improvement in the purity of the target product.[16] However, a more detailed investigation of this reaction is necessary, namely, identification of the side products and study of the mechanisms of their formation.

Scheme 1



Oxymethylation of compound **3** resembles nitroaldol condensation (the Henry reaction),[23—28] since the effect of two geminal MeON=N(O) groups is similar to that of one NO_2 group.[16,29] However, compound **3** is a weaker CH acid in respect of nitromethane taking into account reactivity of the former toward electrophiles.[9,16,20,30,31]

Similar to oxymethylation of nitromethane,[32,33] the reaction of compound **3** with formaldehyde proceeds nonselectively. Analysis of the reaction mixture by TLC revealed the presence of target compound **2** (41%), unreacted starting compound **3** (~15%), and expected side product 2,2-bis(methoxy-*NNO*-azoxy)propan-1,3-diol (**4**)[16,20] (21%) as well as small amounts of two other side products,

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† Deceased.

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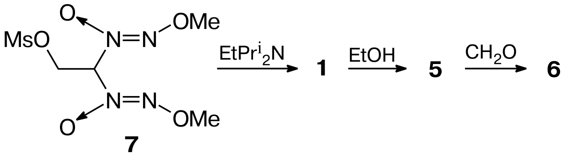
2-ethoxy-1,1-bis(methoxy-*NNO*-azoxy)ethane (**5**)[22] and hitherto unknown 3-ethoxy-2,2-bis(methoxy-*NNO*-azoxy)propan-1-ol (**6**) (see Scheme 1).

Compound **6** was synthesized in sufficient amount by treatment with formaldehyde and alkali in EtOH of the combined mother liquors obtained after isolation of compounds **2** and **4**; according to TLC data, these mother solutions contained a mixture of compounds **2**—**6**. Treatment of compounds **2** and **3** with formaldehyde resulted in easily isolable compound **4**, while compound **5** furnished compound **6** (see Scheme 1 and Experimental). The total yield of thus synthesized compound **6** is 2.6%.

Formation of compound **6** upon oxymethylation of compound **5** was confirmed by counter syntheses (Scheme 2). Compound **6** was prepared by oxymethylation of ether **5** in 72% yield and by a tree-step one-pot synthesis from 2,2-bis(methoxy-*NNO*-azoxy)ethyl methanesulfonate (**7**) in 30% total yield (see Experimental, procedures ***B*** and ***C***, respectively). The completion of the reactions on each step and formation of intermediates **1** and **5** were monitored by TLC using authentic reference samples.

Scheme 2



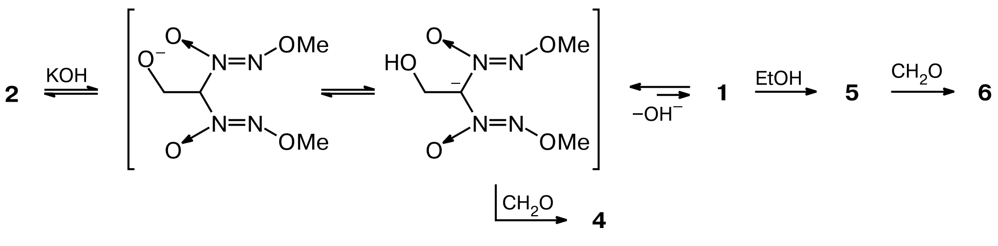
Transformation **1**→**5** (see Scheme 2) allows one to suggest that the most probable mechanism of formation of compound **5** involved the Michael addition of the EtOH molecule to activated olefin **1** (Scheme 3).

Similar side reactions giving 2-nitroalkyl ethers in the Henry reaction are known,[25] although the examples are limited by carbonyl compounds bearing bulky substituents. Thus, nearly in all cases, the Henry reaction of aromatic aldehydes are accompanied by dehydration of nitro alcohols,[25,26,34] which is used for the synthesis of nitroolefins[34] and products of their subsequent transformations by the Michael reaction often in one-pot syntheses.[28,35,36] Formation of α-nitro ethers by oxymethylation of nitro compounds under conditions of the Mannich reaction (1,1,1-trifluoro-2-nitroethane, paraformaldehyde, primary alcohol, diethylamine hydrochloride, 100 °C, 10 h) was documented.[37] However, the side processes of base-catalyzed oxymethylation under the Henry reaction conditions to give α-nitro ethers are unknown; usually there takes place the reverse reaction of the formaldehyde molecule removal from the nitro alcohol anion.[38]

Since the OH^- anion is a very poor leaving group, the carbanion generated from compound **2** reacts mainly with the second molecule of CH_2O (see Scheme 3) to give bis-hydroxymethylated compound **4** in the yield of 45% and does not produce the olefin **1** (the total yield of **6** is 2.6%). In contrary, treatment of alcohol **2** with KOH in EtOH without formaldehyde resulted mainly in compound **5** (*via* olefin **1**); this fact was confirmed by special experiment (see Experimental). At the same time, resinification of the reaction mixture occurred probably due to both the Michael addition of the carbanions to olefin **1** and decomposition of these anions.

The structure of compound **6** was unambiguously established by X-ray diffraction analysis and confirmed by the data from ^1H NMR spectroscopy and elemental analysis.[29] Molecules of compound **6** occupy the general position in the unit cell of a monoclinic crystal (Fig. 1). Geometry of the (C)N(O)=NO(C) group is very stable and nearly independent from the environment.[15,16,31] Distances and angles in the N(O)=NO fragment (Table 1) are virtually the same as those in the other geminal alkoxy-*NNO*-azoxy compounds.[16,22,39—43] Both oxydiazene oxide fragments, C(1)N(3)O(4)N(2)O(1) and C(1)N(1)O(3)N(4)O(5), have the *Z*-configuration. These fragments are nearly planar (a mean deviation of the atoms from the plane for both fragments is 0.010 Å) with an angle between the planes of 93.9° and twisted in opposite directions relative to the N(1)C(1)N(3) plane by 58.3 and 120.5°, respectively. The angle between the planes of the CN(O)=NO fragments is the most variable structural parameter in the molecules of this type (Table 2, *cf.* with the similar parameters for the described previously analogs $R^1R^2C[N(O)=NOAlk]_2$ **7**—**15**). In the molecule of **6**, as well as in the molecules of **8**, **10**, **11**, and **13**—**16**, the interplanar angles between the CN(O)=NO fragments are close to 90°, moreover the planes of these fragments are

Scheme 3



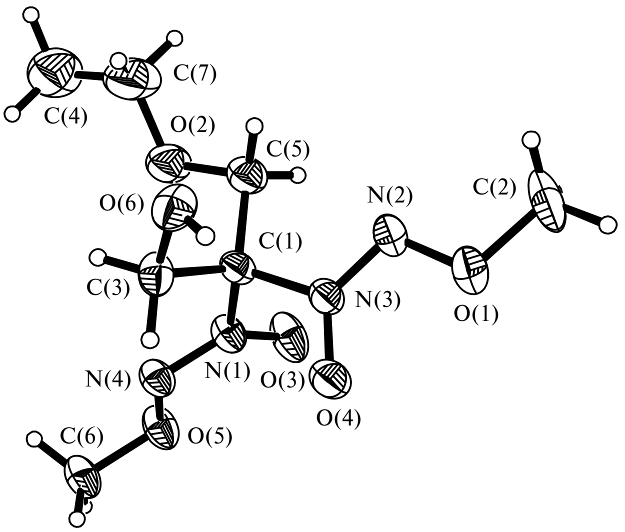


Fig. 1. Geometry of compound **6** with atomic thermal displacement ellipsoids (30% probability).

twisted in opposite directions relative to the N—C—N plane. In the molecules of **9** and **10**, the planes of the CN(O)=NO fragments twisted in the same direction relative to the N—C—N plane, the angles between them are much larger and close to the bond angle N—C—N (106.6° for compound **9**).

Compound **6** exhibited the O(6)—H...O(4) hydrogen bond, the O(6)...O(4) distance is 2.823(4) Å. This hydrogen bond is significantly shorter compared with similar contacts in compounds **10** (2.897 Å) and **14** (2.851 Å), which also contain one CH_2OH group per molecule,[41] and is comparable with similar hydrogen bonds in diols **15**[40] (2.80 and 2.84 Å) and **16**[41] (2.793 and 2.830 Å). In all structures of compounds **6**, **10**, and **14**—**16**, an electron donor for the proton of the CH_2OH group is the oxygen atom of the N-oxide fragment of a neighboring molecule, which suggested the highest basicity of this atom in the N(O)=NOMe moiety. Among other intermolecular contacts in structure of **6**, a short intermolecular C(6)...O(6) distance of 3.012(5) Å is should be noted.

Table 1. Bond lengths (*d*) and bond angles (ω) in the crystal structure of compound **6**

Bond	*d*/Å	Angle	ω/deg
O(1)—N(2)	1.370(5)	N(2)—O(1)—C(2)	108.2(3)
O(1)—C(2)	1.437(6)	O(3)—N(1)—N(4)	126.7(4)
O(6)—C(3)	1.425(5)	O(3)—N(1)—C(1)	117.4(3)
O(3)—N(1)	1.254(5)	N(4)—N(1)—C(1)	115.9(4)
O(4)—N(3)	1.261(4)	N(3)—C(1)—N(1)	103.8(3)
N(1)—N(4)	1.268(5)	N(3)—C(1)—C(5)	107.8(4)
N(1)—C(1)	1.504(6)	N(1)—C(1)—C(5)	111.0(3)
C(1)—N(3)	1.486(6)	N(3)—C(1)—C(3)	112.7(3)
C(1)—C(5)	1.529(7)	N(1)—C(1)—C(3)	107.3(3)
C(1)—C(3)	1.544(8)	C(5)—C(1)—C(3)	113.8(4)
N(2)—N(3)	1.272(5)	N(3)—N(2)—O(1)	108.2(3)
O(5)—N(4)	1.357(5)	O(4)—N(3)—N(2)	126.8(4)
O(5)—C(6)	1.443(7)	O(4)—N(3)—C(1)	117.9(3)
O(2)—C(7)	1.401(9)	N(2)—N(3)—C(1)	115.3(3)
O(2)—C(5)	1.413(6)	N(4)—O(5)—C(6)	109(3)
C(7)—C(4)	1.434(10)	N(1)—N(4)—O(5)	108.8(4)
		O(6)—C(3)—C(1)	107.7(3)
		C(7)—O(2)—C(5)	114.6(5)
		O(2)—C(5)—C(1)	105.5(4)
		O(2)—C(7)—C(4)	113.1(6)

Table 2. Angle between the planes of the CN(O)=NO fragments (φ) in geminal bis(alkoxy-*NNO*-azoxy) compounds $R^1R^2C[N(O)=NOAlk]_2$

Compound	Alk	R^1	R^2	φ/deg
6	Me	CH_2OH	CH_2OMe	93.9
8	Me	H	H	84.9[40]
9	Me	H	Me	106.8[31]
10	Me	H	CH_2OH	94.2[41]
11	Me	H	CH_2OMe	90.5[22]
12	Me	H	$CH_2N(NO_2)Me$	108.9[42]
13	Me	Me	Me	86.3[31]
14	Me	Me	CH_2OH	90.7[41]
15	Me	CH_2OH	CH_2OH	86.2[40]
16	Et	CH_2OH	CH_2OH	90.0[41]

In summary, in the present work hitherto unknown 3-ethoxy-2,2-bis(methoxy-*NNO*-azoxy)propan-1-ol (**6**) was synthesized employing three independent methods, the mechanisms of formation of this compound were proposed; the crystalline structure of **6** was established by X-ray diffraction analysis. The obtained results may be useful for the optimization of the synthesis of **2** and for the fundamental study in the chemistry of aliphatic azoxy compounds.

Experimental

^1H NMR spectrum (500.13 MHz) was recorded on a Bruker DRX 500 instrument. The signals for the protons were attributed according to the published data.[16,22,29] EtOH (rectificate) and KOH (pure per analysis, 90% pure) were used. Bis(methoxy-*NNO*-azoxy)methane (**3**)[44] and 2,2-bis(methoxy-*NNO*-azoxy)ethyl methanesulfonate (**7**)[16] were synthesized according to the known procedures.

Single crystals of compound **6** were prepared by crystallization from diethyl ether. X-ray diffraction data were collected on a Bruker AXS P4 diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, 293 K, ω/2θ scan mode). The crystal structure was solved by the direct method. The positions and temperature parameters of nonhydrogen atoms were refined first isotropically and then anisotropically using the full-matrix least square approximation. The positions of hydrogen atoms were defined in difference Fourier synthesis and refined in a riding model. All calculations were performed using SHELXS-97 software.[45]

The main crystallographic data and refinement parameters for compound **6**: $C_7H_{16}N_4O_6$, M = 252.24, monoclinic, space group $P2_1/n$, a = 8.3820(10) Å, b = 11.0610(10) Å, c = 13.910(2) Å, α = 90°, β = 99.840(10)°, γ = 90°, V = 1270.7(3) Å^3, Z = 4, d_{calc} = 1.319(6) g cm^{-3}, μ = 0.115 cm^{-1}, scan range 24.99°, number of measured reflections (R_{int}) 1975, number of reflections with $I > 2\sigma(I)$ 1086, number of refinement parameters 158, R_1 = 0.0593 for the reflections with $I > 2\sigma(I)$, wR_2 = 0.1743 (for all reflections).

2-Ethoxy-1,1-bis(methoxy-*NNO*-azoxy)ethane (5) was synthesized according to the known procedure[22] and purified by flash column chromatography on silica gel (Sapelko, 40—60 μm, elution with $CHCl_3$—AcOEt from 5 : 1 to 2 : 1) followed by recrystallization from Et_2O—Bu^{t}OMe. Yield 40%, m.p. 82.0—82.4 °C, which is by 11—12 °C higher than that documented (*cf.* Ref. 22: 70—71 °C) probably due to impure compound prepared previously.[22] Found (%): C, 32.38; H, 5.81; N, 25.12. $C_6H_{14}N_4O_6$. Calculated (%): C, 32.43; H, 6.35; N, 25.21.

3-Ethoxy-2,2-bis(methoxy-*NNO*-azoxy)propan-1-ol (6). ***A.*** To a boiling solution of compound **3** (30 g, 0.183 mol) in EtOH (100 mL), a solution of paraformaldehyde (6.66 g, 0.222 mol) and KOH (1.18 g, 0.019 mol) in EtOH (30 mL) was added and the mixture was refluxed for 30 min. The resulting yellow solution was cooled and neutralized with concentrated HCl (1.8 mL, 0.02 mmol). The precipitate of KCl that formed was filtered off and the filtrate was concentrated *in vacuo*. The residue (38 g) was heated at reflux in $CHCl_3$ (100 mL) for 15 min, the obtained solution was filtered hot to remove the precipitate of the remaining KCl and insoluble in $CHCl_3$ compound **4**. The precipitate was washed with $CHCl_3$ (40 mL), dried (10.92 g), and recrystallized from water (10 mL). Yield of 2,2-bis(methoxy-*NNO*-azoxy)propan-1,3-diol (**4**) is 8.60 g (21%), m.p. 192—194 °C (*cf.* Ref. 2: 191—192 °C), m.p. after the second recrystallization from water is 195—196 °C. Evaporation of the chloroform mother solution and successive recrystallization of the residue (27.4 g) from Pr^{i}OH (40 mL), $CHCl_3$ (40 mL), and EtOH (2×30 mL) yielded 2,2-bis(methoxy-*NNO*-azoxy)ethanol (**2**) (4.64 g, 41%), m.p. 115.5—116.1 °C (*cf.* Ref. 2: 106—107 °C, Ref. 21: 113 °C, Ref. 1: 114.5—115.2 °C). According to the TLC data (Silufol, elution with AcOEt), the combined mother solutions contained compounds **2—6**, R_f 0.62 for **6**, 0.47 for **2**, 0.69 for **5**, 0.54 for **3**, and 0.34 for **4**. The mother solutions were concentrated *in vacuo*, paraformaldehyde (4.5 g, 0.15 mol), KOH (0.5 g), and EtOH (40 mL) were added to the residue (9.6 g) and the mixture was refluxed for 1.5 h. Diol **4** was isolated as described above to give additional amount of 9.71 g. Total yield of diol **4** is 18.31 g (45%). The chloroform solutions were concentrated *in vacuo* and the residue (1.5 g) was subjected to column chromatography on silica gel (Sapelko, 40—60 μm, 30 g, elution with $CHCl_3$—AcOEt from 2 : 1 to 1 : 3). The eluates with R_f 0.62 (Silufol, elution with AcOEt) were recrystallized from Et_2O to give ethoxy alcohol **6** (1.19 g, 2.6%), m.p. 120.5—121.5 °C. Found (%): C, 33.40; H, 6.25; N, 22.35. $C_6H_{14}N_4O_6$. Calculated (%): C, 33.33; H, 6.39; N, 22.21. ^{1}H NMR (DMSO-d$_6$), δ: 1.09 (t, 3 H, OCH_2CH_3, J = 7.0 Hz); 3.34 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.0 Hz); 4.06 (s, 6 H, MeO); 4.16 (d, 2 H, $C\underline{H}_2OH$, J = 6.0 Hz); 4.17 (s, 2 H, CH_2OEt); 5.92 (t, 1 H, OH, J = 6.1 Hz).

B. To a solution of compound **5** (0.222 g, 0.001 mol) in EtOH (5 mL), a solution of paraformaldehyde (0.120 g, 0.004 mol) and KOH (0.062 g, 0.001 mol) in EtOH (5 mL) was added and the mixture was heated at 50—60 °C for 15 min. The obtained colorless solution was cooled, neutralized with concentrated HCl, and concentrated *in vacuo*. The residue was heated up to reflux in AcOEt (10 mL), the resulting solution was cooled down, filtered through thin layer of silica gel (Sapelko, 40—60 μm, 2 g), and washed with anhydrous AcOEt (10 mL). The solvent was removed to dryness and the residue was recrystallized from Bu^{t}OMe to give compound **6** (0.182 g, 72%), m.p. 119.1—120.0 °C. No depression of the melting point was observed for the mixed sample with compound **6**, obtained by method ***A***.

C. A solution of 2,2-bis(methoxy-*NNO*-azoxy)ethyl methanesulfonate (**7**) (0.272 g, 0.001 mol) and *N,N*-diisopropylethylamine (0.258 g, 0.002 mol) in anhydrous THF (5 mL) was refluxed for 30 min until complete consumption of compound **7** (TLC monitoring, R_f 0.25, Silufol, elution with AcOEt—C_6H_6, 1 : 1) and formation of olefin **1**. Then anhydrous EtOH (5 mL) was added and the mixture was refluxed for 3 h until complete consumption of olefin **1** (TLC monitoring, R_f 0.37). Then a solution of paraformaldehyde (0.09 g, 0.003 mol) and KOH (0.1 g, 0.0016 mol) in anhydrous EtOH (5 mL) was added, which resulted in formation of the precipitate of potassium methanesulfonate. The stirred reaction mixture was refluxed for 1 h, diluted with water (2 mL), concentrated to ~3 mL, neutralized with 5 *M* HCl, and the solvent was removed *in vacuo* to dryness. The residue was heated up to reflux in AcOEt (10 mL), cooled down, filtered through a thin layer of silica gel (Sapelko, 40—60 μm, 3 g), and washed with anhydrous AcOEt (10 mL). The solvent was removed *in vacuo*, the residue was recrystallized twice from CH_2Cl_2—Et_2O to give compound **6** (0.075 g, 30%), m.p. 121.1—121.7 °C. No depression of the melting point was observed for the mixed sample with compound **6**, obtained by method ***A***.

Reaction of 2,2-bis(methoxy-*NNO*-azoxy)ethanol (2) with KOH in ethanol. A mixture of compound **2** (0.2 g) and KOH (0.1 g) in EtOH (4 mL) was refluxed for 1.5 h. The color of the reaction mixture changed from yellow to light brown. According to the TLC data (Silufol, elution with AcOEt), the reaction mixture contained 1,1-bis(methoxy-*NNO*-azoxy)-2-ethoxyethane (**5**) (main product, R_f 0.69) and the starting compound **2** (R_f 0.47) along with the tongue-shaped spot of the resins (on the start).

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References

1. R. Behrend, E. König, *Liebigs Ann. Chem.*, 1891, **263**, 175.
2. W. Traube, *Liebigs Ann. Chem.*, 1898, **300**, 81.
3. V. N. Yandovskii, B. V. Gidaspov, I. V. Tselinskii, *Usp. Khim.*, 1980, **49**, 449 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1980, **49**, 237].
4. S. G. Zlotin, O. A. Luk´yanov, *Usp. Khim.*, 1993, **62**, 157 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1993, **62**, 143].
5. J. A. Hrabie, L. K. Keefer, *Chem. Rev.*, 2002, **102**, 1135.
6. I. N. Zyuzin, D. B. Lempert, *Propellants*, *Explos.*, *Pyrotech.*, 2007, **32**, 42.
7. V. G. Granik, N. B. Grigor´ev, *Izv. Akad. Nauk*, *Ser. Khim.*, 2002, 1268 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1375].
8. J. Brand, T. Huhn, U. Groth, J. C. Jochims, *Chem. Eur. J.*, 2006, **12**, 499.
9. R. B. Woodward, C. Wintner, *Tetrahedron Lett.*, 1969, **10**, 2689.

10. I. N. Zyuzin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2626 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1985, **34**, 2433].
11. I. N. Zyuzin, *Izv. Akad. Nauk*, *Ser. Khim.*, 1998, 1263 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1998, **47**, 1231].
12. O. A. Luk´yanov, N. I. Shlykova, *Izv. Akad. Nauk*, *Ser. Khim.*, 1998, 2262 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1998, **47**, 2193].
13. I. N. Zyuzin, G. N. Nechiporenko, *Izv. Akad. Nauk*, *Ser. Khim.*, 1998, 2390 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1998, **47**, 2317].
14. I. N. Zyuzin, *Zh. Prikl. Khim.*, 2009, **82**, 1677 [*Russ. J. Appl. Chem.* (*Engl. Transl.*), 2009, **82**, 1829].
15. I. N. Zyuzin, D. B. Lempert, G. N. Nechiporenko, *Izv. Akad. Nauk*, *Ser. Khim.*, 2003, 1354 [*Russ. Chem. Bull.*, *Int. Ed.*, 2003, **52**, 1431].
16. I. N. Zyuzin, N. I. Golovina, D. B. Lempert, G. N. Nechiporenko, G. V. Shilov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2008, 619 [*Russ. Chem. Bull., Int. Ed.*, 2008, **57**, 632].
17. I. N. Zyuzin, D. B. Lempert, *Izv. Akad. Nauk*, *Ser. Khim.*, 2009, 2108 [*Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 2173].
18. I. N. Zyuzin, *Zh. Prikl. Khim.*, 2009, **82**, 1647 [*Russ. J. Appl. Chem.* (*Engl. Transl.*), 2009, **82**, 1799].
19. I. N. Zyuzin, D. B. Lempert, *Tes. dokl., Vseross. konferenciya "Khimiya nitrosiedinenii i rodstvennykh azot-kislorodnykh sistem"* [*Abstrs*, *All-Russia Conf. "Chemistry of Nitro Compounds and Relative Nitrogen-Oxigen Systems"*] *(Moscow, October 21—23, 2009)*, Moscow, p. 48 (in Russian).
20. G. A. Marchenko, A. S. Mukhametzyanov, I. V. Tselinskii, *Zh. Org. Khim.*, 1985, **21**, 1426 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 1985, **21**].
21. G. A. Marchenko, A. S. Mukhametzyanov, I. V. Tselinskii, A. S. Ermoshkin, *Zh. Org. Khim.*, 1985, **21**, 1429 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 1985, **21**].
22. G. A. Marchenko, L. N. Punegova, L. F. Chertanova, T. G. Beskrovnaya, V. V. Cherevin, V. F. Sopin, *Zh. Org. Khim.*, 1990, **26**, 276 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 1990, **26**].
23. G. A. Shvekhgeimer, N. F. Pyatakov, S. S. Novikov, *Usp. Khim.*, 1959, **28**, 466 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1959, **28**].
24. L. M. Kozlov, V. I. Burmistrov, *Nitrospirty i ikh proizvodnye* [*Nitro Alcohols and their Derivatives*], izd-vo Kazanskogo Khim.-Tekhnol. Instituta, Kazan´, 1960 (in Russian).
25. S. S. Novikov, V. V. Sevast´yanova, G. A. Shvekhgeimer, V. A. Shlyapochnikov, *Khimiya alifaticheskikh i alitsiklicheskikh nitrosoedinenii* [*Chemistry of Aliphatic and Alicyclic Nitroso Compounds*], Khimiya, Moscow, 1974, 416 pp. (in Russian).
26. M.-G. A. Shvekhgeimer, *Usp. Khim.*, 1998, **67**, 39 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1998, **67**, 35].
27. N. Ono, *The Nitro Group in Organic Synthesis*, Wiley-VCH, New York, 2001, p. 30.
28. R. Ballini, L. Barboni, F. Fringuelli, A. Palmieri, F. Pizzo, L. Vaccaro, *Green Chem.*, 2007, **9**, 823.
29. Yu. A. Red´kin, G. A. Marchenko, L. N. Punegova, G. S. Stepanov, I. V. Tselinskii, *Zh. Org. Khim.*, 1988, **24**, 495 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 1988, **24**].
30. O. A. Luk´yanov, N. I. Shlykova, V. A. Tartakovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1656 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1982, **31**, 1475].
31. L. O. Atovmyan, N. I. Golovina, I. N. Zyuzin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1309 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1987, **36**, 1205].
32. W. E. Noland, M. S. Newman, S. S. Rawalay, in *Organic Syntheses*, coll. vol. **5**, Wiley, New York, 1973, p. 833.
33. I. M. Gorsky, S. P. Makarov, *Ber. Dtsch. Chem. Ges.*, 1934, **67**, 996.
34. V. V. Perekalin, E. S. Lipina, V. M. Berestovitskaya, D. A. Efremov, *Nitroalkenes: Conjugated Nitro Compounds*, John Wiley and Sons, Chichester, 1994, 256 pp.
35. R. Ballini, G. Bosica, D. Fiorini, A. Palmieri, *Synthesis*, 2004, 1938.
36. K. Motokura, M. Tada, Y. Iwasawa, *Angew. Chem.*, *Int. Ed.*, 2008, **47**, 9230.
37. I. L. Knunyants, L. S. German, I. N. Rozhkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1964, 1630 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1964, **13**, 1538)].
38. A. Baran´sky, M. Mikul´ska, R. Yasin´sky, *Izv. Vuz Khim. Khim. Tekhnol.*, 2009, **52**, No. 2, 3 [*Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhol.* (*in Russian*), 2009, **52**, No. 2, 3].
39. I. N. Zyuzin, D. B. Lempert, G. N. Nechiporenko, *Izv. Akad. Nauk*, *Ser. Khim.*, 2003, 726 [*Russ. Chem. Bull.*, *Int. Ed.*, 2003, **52**, 761)].
40. G. A. Marchenko, L. F. Chertanova, Yu. T. Struchkov, B. I. Buzykin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1777 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1987, **36**, 1646].
41. L. F. Chertanova, G. A. Marchenko, L. A. Gazikasheva, Yu. T. Struchkov, V. F. Sopin, L. N. Punegova, A. S. Mukhametzyanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 297 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1989, **38**, 250)].
42. L. F. Chertanova, A. I. Yanovskii, Yu. T. Struchkov, G. A. Marchenko, V. F. Sopin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1200 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1989, **38**, 1092].
43. G. A. Marchenko, L. F. Chertanova, M. Yu. Antipin, Yu. T. Struchkov, L. N. Punegova, *Dokl. Akad. Nauk SSSR*, 1987, **294**, 1169 [*Dokl. Chem.*, 1987, **294**].
44. V. N. Yandovskii, E. Yu. Dobrodumova, I. V. Tselinskii, *Zh. Org. Khim.*, 1980, **16**, 933 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 1980, **16**].
45. G. M. Sheldrick, *SHELXS-97, Program for the Solution of Crystal Structures*, University of Göttingen, Germany, 1997.

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