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Electrochemical synthesis of geminal azidonitro compounds

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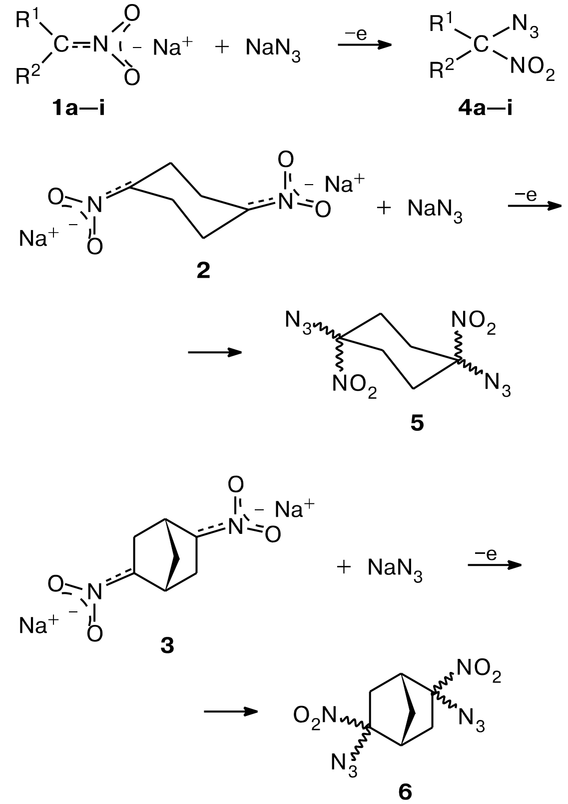
An electrochemical method for the synthesis of geminal azidonitro compounds was developed. The method involves electrooxidative coupling of azide anions with salts of nitro compounds and affords geminal azidonitroalkanes, azidonitrocycloalkanes, and diazidodinitrocycloalkanes in 45—92% yields.

Key words: salts of nitro compounds, azide anions, electrooxidative coupling, mono- and di(α-azido)nitro compounds, electrosynthesis.

Geminal azidonitroalkanes, azidonitrocycloalkanes, and diazidodinitrocycloalkanes are of considerable interest as compounds with a high energy capacity and promising synthons for construction of various polynitrogeneous structures.[1,2] However, only a few compounds of these types have been obtained to date: 1-azido-1-nitroethane, -butane,[2] and -cyclohexane,[3,4] 2-azido-2-nitropropane,[3,4] 1,4-diazido-1,4-dinitrocyclohexane, 2,5-diazido-2,5-dinitronorbornane,[1] and benzyl 6-azido-6-nitropenicillanate.[5] The best results were attained in oxidative coupling of azide anions with salts of nitro compounds with $K_3Fe(CN)_6$ and $(NH_4)_2S_2O_8$ as oxidants.[1,2,4] A significant drawback of these methods is that multiple molar excess of the oxidant and azide anions should be used, which leads to the formation of large amounts of toxic wastes difficult to handle. Until now, the electrolysis of azide anions in the presence of salts of nitro compounds was reported only as a route to 1-azido-1-nitroalkanes, 2-azido-2-nitropropane, and 1-azido-1-nitrocyclohexane,[6,7] without specifying the electrosynthesis conditions or the yields of the products (except for 1-azido-1-nitrocyclohexane (89%)).

In the present study, electrooxidative coupling of azide anions with Na salts of primary and secondary nitroalkanes (**1a—d**), 5-nitroheptan-2-one (**1e**), methyl 4-nitrohexanoate (**1f**), nitrocycloalkanes (**1g,h**), 2-nitronorbornane (**1i**), 1,4-dinitrocyclohexane (**2**), and 2,5-dinitronorbornane (**3**) was successfully carried out to produce geminal azidonitroalkanes **4a—f**, azidonitrocycloalkanes **4g—i**, and diazidodinitrocycloalkanes **5** and **6** (Scheme 1).

Scheme 1



	R^1	R^2		R^1+R^2
a	Me	H	**g**	$(CH_2)_5$
b	Et	H	**h**	$(CH_2)_6$
c	$C_5H_{11}{}^n$	H	**i**	2-Norbornyl
d	Me	Me		
e	$MeCOCH_2CH_2$	Et		
f	$MeO_2CCH_2CH_2$	Et		

Reagents and conditions: CH_2Cl_2—H_2O, NaN_3 (5 equiv.), divided or undivided cell with a platinum anode and a stainless steel cathode, 2—12 F mol^{-1}, 8—10 °C.

Experiments were carried out in a two-phase methylene chloride—water (or aqueous $NaHCO_3$ and Na_2HPO_4) system (2 : 1, v/v) in undivided and divided cells with 0.1 *M* aqueous NaOH and H_2SO_4 as catholytes. In all experiments, platinum served as an anode and stainless steel as a cathode. The quantity of electricity passed was varied from 2 to 12 F mol^{-1} at an anodic current density

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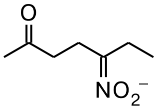
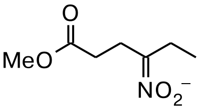
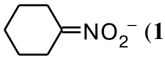
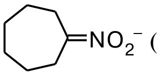
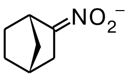
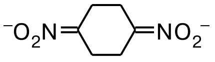
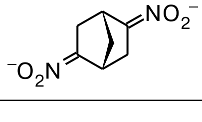
of 50—100 mA cm^{-2}. Electrolysis was performed at 8—10 °C; fivefold (with respect to salts of mononitro compounds) and tenfold molar excesses (with respect to salts of dinitro compounds) of sodium azide were used. The selected results obtained are given in Table 1.

The electrolysis conditions significantly affect the azidation of salts of primary nitroalkanes. For instance, geminal azidonitroethane (**4a**) was not detected among the products obtained by electrolysis of a mixture of nitroethane salt—sodium azide in an undivided cell with a two-phase CH_2Cl_2—water (or aqueous $NaHCO_3$) system, while electrolysis in CH_2Cl_2—aqueous Na_2HPO_4 gave compound **4a** in only 4% yield. The satisfactory yield (44—67%) of nitroazide **4a** was attained only by electrooxidative coupling of NaN_3 with a salt of nitroethane in a divided cell with a two-phase CH_2Cl_2—water (anolyte) system (0.1 *M* H_2SO_4 as a catholyte). In this case, the quantity of electricity passed Q = 2 to 3 F/mol of the salt ensured a 79—94% conversion of the latter (see Table 1, entries *4*, *5*). Under the same conditions, 1-azido-1-

Table 1. Electrooxidative coupling of NaN_3 with salts of nitro compounds **1a**—**g**, **2**, and **3**[a]

Entry	Anion of the salt	Electrolyzer	System	Q /F mol^{-1}	Degree of conversion (%)	Product (yield (%)[b])
1	$MeCH=NO_2^-$ (**1a**)	undivided	CH_2Cl_2—H_2O	2	78	**4a** (0)
2	«	undivided	CH_2Cl_2-aq.$NaHCO_3$	2	86	**4a** (0)
3	«	undivided	CH_2Cl_2-aq.Na_2HPO_4	2	97	**4a** (4)
4	«	divided	CH_2Cl_2—H_2O	2	79	**4a** (67)
5	«	divided	CH_2Cl_2—H_2O	3	94	**4a** (44)
6	$EtCH=NO_2^-$ (**1b**)	divided	CH_2Cl_2—H_2O	2	75	**4b** (50)
7	«	divided	CH_2Cl_2—H_2O	3	95	**4b** (45)
8	n-$C_5H_{11}CH=NO_2^-$ (**1c**)	divided	CH_2Cl_2—H_2O	4	72	**4c** (70)
9	«	divided	CH_2Cl_2—H_2O	6	98	**4c** (67)
10	$Me_2C=NO_2^-$ (**1d**)	undivided	CH_2Cl_2—H_2O	4	100	**4d** (45)[c]
11	 (**1e**)	undivided	CH_2Cl_2—H_2O	4	100	**4e** (78)
12	 (**1f**)	undivided	MeOH	3	95	**4f** (51)[d]
13	 (**1g**)	undivided	CH_2Cl_2—H_2O	4	83	**4g** (92)
14	«	undivided	CH_2Cl_2—H_2O	6	100	**4g** (84)
15	«	divided	CH_2Cl_2—H_2O	4	100	**4g** (84)
16	 (**1h**)	undivided	CH_2Cl_2—H_2O	4	86	**4h** (90)
17	«	undivided	CH_2Cl_2—H_2O	5	100	**4h** (88)
18	 (**1i**)	undivided	CH_2Cl_2—H_2O	6	100	**4i** (76)
19	 (**2**)	undivided	CH_2Cl_2—H_2O	8	100	**5** (75)
20	 (**3**)	undivided	CH_2Cl_2—H_2O	12	100	**6** (68)

[a] The conditions: the salt of the nitro compound (2—5 mmol), NaN_3 (5 equiv. in entries *1—18* and 10 equiv. in entries *19—20*), CH_2Cl_2 (20—30 mL), and water (10—15 mL) were used; 8—10 °C, vigorous stirring; the undivided or divided cell with 0.1 *M* H_2SO_4 as the catholyte; the current density was 100 mA cm^{-2} for the undivided cell and 50 mA cm^{-2} for the divided cell.

[b] The yields are given with respect to the converted salt of the nitro compound.

[c] 2,2-Diazidopropane (**7**) was also obtained in 14% yield.

[d] Methyl 4-oxohexanoate was also obtained in 26% yield.

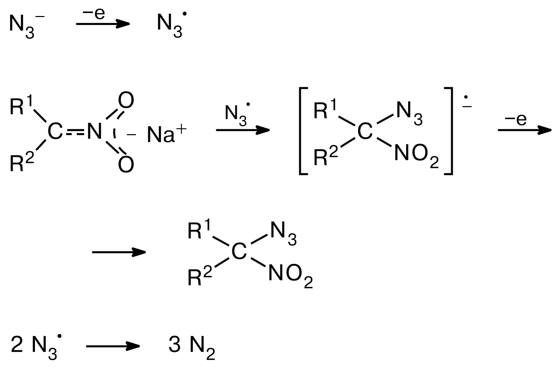
nitropropane (**4b**) was obtained in 45—50% yield. When the salt of 1-nitrohexane and NaN_3 were simultaneously subjected to electrolysis, the yield of 1-azido-1-nitrohexane (**4b**) increased to 67% and the degree of conversion of the starting salt reached 98% since Q was 6 F mol^{-1} (see Table 1, entry *9*). Most probably, the absence of products from electrooxidative coupling of salts of primary nitroalkanes with NaN_3 in an undivided cell with the two-phase CH_2Cl_2—water system is due to electrogeneration of NaOH, which favors deprotonation of 1-azido-1-nitroalkanes. The resulting Na salts of 1-azido-1-nitroalkanes are very unstable; for instance, the half-life period of the Na salt of 1-azido-1-nitroethane at pH 10 is 10 min, nitrogen evolving on its decomposition.[2] This assumption was supported by successful electrooxidative coupling of salts of primary nitroalkanes with NaN_3 in a divided cell with 0.1 M H_2SO_4 as a catholyte (with 0.1 M NaOH as a catholyte, no 1-azido-1-nitroalkanes were obtained).

Unlike salts of primary nitroalkanes **1a—c**, salts of secondary nitro compounds, namely, 2-nitropropane (**1d**), 4-nitroheptan-2-one (**1e**), nitrocyclohexane (**1g**), nitrocycloheptane (**1h**), and 2-nitronorbornane (**1i**), can react with NaN_3 to form the corresponding geminal azidonitro compounds under the conditions of two-phase undivided electrolysis. The moderate yield (45%) of 2-azido-2-nitropropane (**4d**) under these conditions is explained by its further azidation into 2,2-diazidopropane (**7**); a similar transformation occurs when compound **4d** is obtained from salt **1d** in the $K_3Fe(CN)_6$—NaN_3 system.[4] The coupling of salts **1e** and **1g—i** with NaN_3 at Q = 4—6 F/mol of the salt afforded the corresponding geminal azidonitro compounds in 78—92% yields; the degrees of conversion of salts **1e** and **1g—i** were 76—100% (see Table 1, entries *10*, *12—17*). A simultaneous electrolysis of salt **1g** and NaN_3 in a divided cell with a two-phase anolyte allowed Q to be reduced from 6 to 4 F mol^{-1} for the complete conversion of the salt (entry *15*). Undivided electrolysis of methyl 4-nitrohexanoate (**1f**) in the presence of NaN_3 in a CH_2Cl_2—water system gave a mixture of products because of the hydrolysis of the ester group; for this reason, the reaction with compound **1f** was carried out in MeOH (entry *12*).

The electrooxidation of salts of 1,4-dinitrocyclohexane (**2**) and 2,5-dinitronorbornane (**3**) in the undivided cell with NaN_3 in a two-phase system proceeds similarly to that of salts of nitrocyclohexane (**1g**), nitrocycloheptane (**1h**), and 2-nitronorbornane (**1i**). For instance, their electrooxidative coupling with NaN_3 in a molar ratio of 1 : 10 and Q = 8—12 F mol^{-1} gave 1,4-diazido-1,4-dinitrocyclohexane (**5**) in 75% yield as a ~2.5 : 1 mixture of *trans*- (**5a**) and *cis*-isomers (**5b**) and 2,5-diazido-2,5-dinitronorbornane (**6**) in 68% yield as a ~2 : 1 mixture of *exo*-2-azido-*exo*-5-azido (**6a**) and *exo*-2-azido-*endo*-5-azido isomers (**6b**) (see Table 1, entries *19*, *20*). Earlier, compounds **5** and **6** were alternatively synthesized by oxidative azidation of salts **2** and **3** with $K_3Fe(CN)_6$.[1] Our electrochemical method for the synthesis of compounds **5** and **6** has substantial advantages over that known technique: the excess of azide anions is reduced by half, the toxic inorganic oxidant used in a tenfold excess is replaced by ecologically safe electric current, and the target compounds are obtained in good yields.

One can assume that electrooxidative coupling of salts of nitro compounds with NaN_3 and oxidative coupling of these substrates follow the same radical nucleophilic substitution mechanism ($S_{RN}1$).[3,4] First, radicals are generated in the one-electron oxidation of the substrate with the lowest oxidative potential; in our case, this is azide anion with $E_{1/2}$ = 0.20 V[8] (for salt anions of nitro compounds, $E_{1/2} \approx 0.90$ V[9]). Then, azide radicals rapidly add to salts of nitro compounds, which are active radical acceptors,[10] to form stable radical anions. When oxidized, they transform into geminal azidonitro compounds. Some azide radicals undergo recombination to give molecular nitrogen (Scheme 2).

Scheme 2



The evidence for the above mechanism is that the electrolysate contains no vicinal dinitro compounds formed by dimerized α-nitroalkyl and α-nitrocycloalkyl radicals; their formation could be expected as the result of electrooxidation of nitro compound anions under the chosen electrolysis conditions.[9,11]

The geminal azidonitroalkanes and azidonitrocycloalkanes obtained are colorless or slightly yellow mobile liquids, while diazidodinitrocycloalkanes **5a** and **6a** are colorless crystalline substances. Their structures were determined from ^1H and ^{13}C NMR and IR spectra and confirmed by elemental analysis data. All the compounds obtained absorb at 2120—2130 (N_3) and 1540—1560 cm^{-1} (NO_2); the ^{13}C NMR spectra of azidonitroalkanes and azidonitrocycloalkanes show characteristic signals at δ 92—97 and 98—109 for tertiary and quaternary C atoms, respectively. Azidonitroalkanes and azidonitrocycloalkanes remain unchanged when kept in a refrigerator at 5 °C for at least three months, while crystalline dinitrodiazides **5a** and **6a** are stable at room temperature.

Thus, the electrooxidative coupling of salts of nitro compounds with azide anions is an efficient route to geminal azidonitroalkanes, azidonitrocycloalkanes, and diazidodinitrocycloalkanes.

Experimental

Caution! *Azidonitro compounds and possible by-products are toxic and explosive; therefore, respective precautions must be used.*

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200, Bruker WM-250, and Bruker AM-300 spectrometers in $CDCl_3$. IR spectra were recorded on a Specord-80 spectrometer (thin film). Laboratory B5-44 and B5-50 power suppliers with the output current stabilization were used as dc generators. The quantity of passed electricity was measured with a digital electronic coulometer (limiting measurable current 20 A (Special Designing Bureau, Institute of Organic Chemistry, Russian Academy of Sciences)). GLC analysis was performed on a Varian-3700 chromatograph (flame ionization detector, glass columns 2×0.003 m, stationary phases 5% SE-30 and 5% XE-60 on Chromaton N-AW). TLC analysis was carried out on Silufol UV-254 plates. Silica gel L (40/100 μm) was used for flash chromatography. Methanol was dehydrated by distillation over magnesium methoxide. Commercial nitroethane, 1- and 2-nitropropanes, nitrohexane, and nitrocyclohexane were purchased from Aldrich.

Nitrocycloheptane,[12] 2-nitronorbornane,[13] 1,4-dinitrocyclohexane,[13,14] and 2,5-dinitronorbornane[13] were prepared by oxidation of the corresponding ketone and diketone oximes with *m*-chloroperoxybenzoic acid in acetonitrile in the presence of Na_2HPO_4. 5-Nitroheptan-2-one and methyl 4-nitrohexanoate were synthesized according to known procedures.[15—17]

Electrooxidative coupling of Na salts of nitro compounds with NaN_3 in a divided cell with a two-phase system (general procedure). A nitro compound (2—5 mmol) was added to 3 *M* aqueous NaOH (1 equiv.) and the reaction mixture was stirred to a complete conversion of the substrate into its salt (1—2 h). The resulting solution was diluted with water, saturated aqueous $NaHCO_3$, or 1 *M* Na_2HPO_4; NaN_3 (5 equiv.) and methylene dichloride (20—30 mL) were added to prepare an anolyte. Electrolysis was carried out in a cell containing a ceramic cup, a platinum anode (4 cm^2), and a stainless steel cathode (4 cm^2). The anolyte was vigorously stirred under the conditions specified in Table 1 and cooled in an ice bath. The catholyte was 0.1 *M* H_2SO_4. To monitor the course of the reaction, an aliquot of the aqueous phase of the anolyte was acidified with AcOH, organic material was extracted with CH_2Cl_2, and the extract was analyzed by GLC. After the electrolysis was completed, the anolyte was acidified with AcOH (1 mL), the organic layer was separated, and the product from the aqueous layer was extracted with CH_2Cl_2 (2×20 mL). The combined organic phase was washed with water (2×20 mL), dried with $MgSO_4$, and concentrated in a rotary evaporator *in vacuo* at room temperature. Such treatment of the electrolysate gave sufficiently pure nitroazides **4a—c** (quantity of the electricity passed was Q = 3 F mol^{-1} for **1a,b** and 6 F mol^{-1} for **1c**); when a lesser quantity of electricity was passed, the residue (after removal of CH_2Cl_2) was a mixture of compounds **4a—c** with the starting reagents **1a—c**. The mixture was analyzed by ^{1}H NMR spectroscopy with 1,2-dichloroethane as the internal standard to determine the degree of conversion of the starting salt of nitro compound and the yields of the products. The results obtained are summarized in Table 1. Products **4a—c** were identified from ^{1}H and ^{13}C NMR and IR spectra. 1-Azido-1-nitroethane (**4a**) and 1-azido-1-nitropropane (**4b**) were also isolated by vacuum distillation of electrolysis products obtained with the use of a larger membrane electrolyzer. It should be noted that azidonitroalkanes and azidonitrocycloalkanes cannot be isolated or purified by column chromatography because of their decomposition into the corresponding carbonyl compounds in contact with silica gel.[1,4]

Synthesis of 1-azido-1-nitroalkanes 4a,b. Electrolysis was carried out in a 200-mL beaker charged with nitroalkane **1a,b** (40 mmol) and 1 *M* NaOH (40 mL). The reaction mixture was stirred to complete homogenization (~1 h) and then NaN_3 (7.8 g, 120 mmol) and CH_2Cl_2 (40 mL) were added. The beaker was cooled in an ice bath and fitted with a platinum anode (4×2 cm) and a cylindrical flat-bottom ceramic cup (3×15 cm) as a cathode compartment. A stainless steel cathode (4×2 cm) was placed in the cup and conc. H_2SO_4 (2.1 mL) in 20 mL of water was added as a catholyte. The anolyte was vigorously stirred during electrolysis; the anodic current density was 200 mA cm^{-2} and Q = 3 F mol^{-1}. After Q = 2 F mol^{-1} was passed, conc. H_2SO_4 (1 mL) in 10 mL of water was added to the catholyte. After the electrolysis was completed, the anolyte was acidified with conc. HCl (1 mL), the organic layer was separated, and the organic material from the aqueous layer was extracted with CH_2Cl_2 (2×20 mL). The combined organic phase was washed with water (2×20 mL), dried with $MgSO_4$, and concentrated *in vacuo* at room temperature. The residue was distilled *in vacuo* in a water bath heated to 80 °C.

1-Azido-1-nitroethane (4a).[2] Yield 40%, b.p. 56 °C (10 Torr), n_D^{20} 1.4527. ^{1}H NMR, δ: 1.78 (d, 3 H, J = 6.6 Hz); 5.31 (q, 1 H, J = 6.6 Hz). ^{13}C NMR, δ: 18.36 (CH_3); 92.29 (CH).

1-Azido-1-nitropropane (4b). Yield 40%, b.p. 45 °C (1 Torr), n_D^{20} 1.4467. IR, ν/cm^{-1}: 2124 (N_3), 1560 (NO_2). ^{1}H NMR, δ: 1.04 (t, 3 H, J = 7.2 Hz); 1.95—2.27 (m, 2 H); 5.17 (t, 1 H, J = 6.5 Hz). ^{13}C NMR, δ: 8.71 (CH_3); 26.00 (CH_2); 97.03 (CH). Found (%): C, 27.50; H, 4.61; N, 43.18. $C_3H_6N_4O_2$. Calculated (%): C, 27.70; H, 4.65; N, 43.06.

1-Azido-1-nitrohexane (4c). IR, ν/cm^{-1}: 2124 (N_3), 1564 (NO_2). ^{1}H NMR, δ: 0.89 (t, 3 H, J = 7.2 Hz); 1.22—1.50 (m, 6 H); 1.85—2.21 (m, 2 H); 5.19 (t, 1 H, J = 6.6 Hz). ^{13}C NMR, δ: 13.68 (C(6)); 22.15 (C(5)); 24.10 (C(3)); 30.67, 32.34 (C(2), C(4)); 96.00 (C(1)). Found (%): C, 41.62; H, 6.88; N, 32.78. $C_6H_{12}N_4O_2$. Calculated (%): C, 41.85; H, 7.02; N, 32.54.

Electrooxidative coupling of Na salts of nitro compounds with NaN_3 in an undivided cell in a two-phase system (general procedure). A nitro compound (2 mmol) was mixed with CH_2Cl_2 (20 mL) and 0.2 *M* aqueous NaOH (1 equiv., 10 mL). The reaction mixture was stirred to a complete conversion into the corresponding salt (1—3 h; the presence of the nitro compound in the organic phase was monitored by GLC) and then NaN_3 (5 equiv.) was added. The resulting mixture was transferred to an electrolyzer with a platinum anode (4 cm^2) and a stainless steel cathode (4 cm^2) spaced at 10 mm. Direct current was passed under the conditions specified in Table 1. To monitor the course of the reaction, an aliquot of the aqueous phase was acidified with AcOH, organic material was extracted with CH_2Cl_2, and the extract was analyzed by GLC. After the electrolysis was completed, the organic layer was separated and organic material was extracted from the aqueous layer with CH_2Cl_2 (20 mL). The combined organic phase was washed with water (2×20 mL), dried with $MgSO_4$, and concentrated in a rotary evaporator *in vacuo* at room temperature to give virtually pure compounds **4e**, **4g—i**, **5**, and **6**. 2-Azido-2-nitropropane (**4d**) was obtained as a mixture with 2,2-diazidopropane (**7**); attempts to separate the mixture by column chromatography failed because of the decomposition of both components. The aqueous phase was acidified with AcOH (1 mL) to convert the unreacted salt into the starting nitro compound and organic material was extracted with CH_2Cl_2 (3×20 mL). The combined extracts were dried with $MgSO_4$ and concentrated in a rotary evaporator *in vacuo*. The residue was analyzed by GLC with dodecane or hexadecane as the internal standard to determine the degree of conversion of the starting salts of nitro compounds. The results obtained are given in Table 1. Products **4—7** were identified from their ^1H and ^{13}C NMR and IR spectra.

2-Azido-2-nitropropane (4d).[4] ^1H NMR, δ: 1.80 (s, 6 H). ^{13}C NMR, δ: 24.68 (CH_3), 100.0 (s).

1-Azido-1-nitrocyclohexane (4g).[1,4] IR, ν/cm^{-1}: 2122 (N_3), 1550 (NO_2). ^1H NMR, δ: 1.26—1.43 (m, 1 H); 1.45—1.63 (m, 2 H); 1.63—1.85 (m, 3 H); 2.04 (d, 2 H, J = 12.5 Hz); 2.18 (dt, 2 H, J = 3.7 Hz, J = 13.2 Hz). ^{13}C NMR, δ: 22.37 (C(3)); 24.00 (C(4)); 33.16 (C(2)); 103.00 (C(1)).

1-Azido-1-nitrocycloheptane (4h). IR, ν/cm^{-1}: 2124 (N_3), 1552 (NO_2). ^1H NMR, δ: 1.50—1.83 (m, 8 H); 2.06 (dd, 2 H, J = 14.5 Hz, J = 7.8 Hz); 2.38 (dd, 2 H, J = 14.5 Hz, J = 9.9 Hz). ^{13}C NMR, δ: 22.44 (C(4)); 28.44 (C(3)); 37.28 (C(2)); 107.24 (C(1)). Found (%): C, 45.50; H, 6.42; N, 30.70. $C_7H_{12}N_4O_2$. Calculated (%): C, 45.65; H, 6.57; N, 30.42.

2-Azido-2-nitronorbornane (4i). A 5 : 1 mixture of isomers (^1H NMR data). IR, ν/cm^{-1}: 2124 (N_3), 1548 (NO_2). ^1H NMR, δ: 1.08—1.23 (m, 1 H); 1.29—1.43 (m, 1 H); 1.43—1.56 (m, 1 H); 1.56—1.76 (m, 3 H); 1.76—1.87 (m, 1 H); 2.40—2.51 (m, 2 H); 2.82 and 2.94* (both s, total 1 H). ^{13}C NMR, δ: 23.25*, 23.42, 26.85, 27.60*, 36.56, 37.51*, 38.18, 39.93, 40.94*, 46.01, 46.26*, 109.13, 109.69*. Found (%): C, 45.95; H, 5.42; N, 30.90. $C_7H_{10}N_4O_2$. Calculated (%): C, 46.15; H, 5.53; N, 30.75.

5-Azido-5-nitroheptan-2-one (4e). ^1H NMR, δ: 1.03 (t, 3 H, J = 7.2 Hz); 2.15 (s, 3 H); 2.10—2.70 (m, 6 H). ^{13}C NMR, δ: 7.73 (CH_3), 28.73 (CH_2), 29.45 ($\underline{C}H_3CO$); 30.13 (CH_2); 36.75 ($\underline{C}H_2CO$); 105.91 (s); 205.24 (CO). Found (%): C, 41.73; H, 5.82; N, 28.22. $C_7H_{12}N_4O_3$. Calculated (%): C, 42.00; H, 6.04; N, 27.99.

1,4-Diazido-1,4-dinitrocyclohexane (5).[1] A ~2.5 : 1 mixture of *trans*- and *cis*-isomers (NMR data); the *trans*-isomer was isolated by recrystallization from chloroform. ***trans*-1,4-Diazido-1,4-dinitrocyclohexane (5a),**[1] m.p. 135—137 °C (decomp.). IR, ν/cm^{-1}: 2132 (N_3), 1544 (NO_2). ^1H NMR, δ: 2.30, 2.50 (both d, 4 H each, J = 9 Hz). ^{13}C NMR, δ: 17.70 (CH_2); 98.64 (s). ***cis*-1,4-Diazido-1,4-dinitrocyclohexane (5b)** (in a mixture with isomer **5a**). ^1H NMR, δ: 2.08—2.38 (m, 4 H); 2.38—2.68 (m, 4 H). ^{13}C NMR, δ: 17.52 (CH_2).

2,5-Diazido-2,5-dinitronorbornane (6).[1] A ~2 : 1 mixture of *exo*-2-azido-*exo*-5-azido (**6a**) and *exo*-2-azido-*endo*-5-azido isomers (**6b**) (NMR data); isomer **6a** was isolated by recrystallization from chloroform. ***exo*,*exo*-2,5-Diazido-*endo*,*endo*-2,5-dinitronorbornane (6a),**[1] m.p. 92—95 °C. ^1H NMR, δ: 2.05 (dd, 2 H, H_{exo}(3), J = 15.8 Hz, J = 5.5 Hz); 2.16 (t, 2 H, H(7), J = 1.9 Hz); 2.55 (dt, 2 H, H_{endo}(3), J = 15.8 Hz, J = 1.3 Hz); 3.06 (m, 2 H, H(4)). ^{13}C NMR, δ: 34.01 (CH_2); 36.98 (CH_2); 45.60 (CH); 106.00 (s). ***exo*-2-Azido-*endo*-5-azido-*endo*-2-nitro-*exo*-5-nitronorbornane (6b)** (in a mixture with isomer **6a**). ^{13}C NMR, δ: 34.24 (CH_2); 36.90 (CH_2); 45.89 (CH); 106.68 (s).

2,2-Diazidopropane (7).[4] ^1H NMR, δ: 1.52 (s, 6 H). ^{13}C NMR, δ: 25.80 (CH_3); 80.04 (s).

Electrooxidative coupling of the Na salt of methyl 4-nitrohexanoate (1f) with NaN_3 in methanol (see Table 1, entry *12*). Ester **1f** (2 mmol) was mixed with 0.1 *M* MeONa (1 equiv.) in methanol and the mixture was stirred to its complete conversion into the salt (0.5—1 h). Then NaN_3 (5 equiv.) was added and electrolysis was carried out and monitored as described above. After the electrolysis was completed, the reaction mixture was diluted with water (40 mL) and acidified with acetic acid (1 mL) to convert the unreacted salt into the starting nitro compound. Organic material was extracted with CH_2Cl_2 (3×20 mL) and the combined extracts were washed with water (2×20 mL), dried with $MgSO_4$, and concentrated in a rotary evaporator *in vacuo* at room temperature. The residue was analyzed by GLC with dodecane as the internal standard and by NMR spectroscopy with 1,2-dichloroethane as the internal standard to determine the degree of conversion of the starting salt of nitro compound and the yields of the products. The results obtained are given in Table 1. Product (**4f**) was identified from its ^1H and ^{13}C NMR spectra.

Methyl 4-azido-4-nitrohexanoate (4f) (in a mixture with methyl 3-oxohexanoate). ^1H NMR, δ: 1.03 (t, 3 H, J = 7.2 Hz); 2.16 (q, 2 H, J = 7.2 Hz); 2.27—2.55 (m, 4 H), 3.68 (s, 3 H, OCH_3). ^{13}C NMR, δ: 7.74 (CH_3); 27.86, 30.06, 30.14 (CH_2); 51.61 (OCH_3); 105.63 (s), 171.72 (CO).

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References

1. G. K. S. Prakash, J. J. Struckhoff, Jr., K. Weber, A. Schreiber, R. Bau, and G. A. Olah, *J. Org. Chem.*, 1997, **62**, 1872.
2. I. V. Tselinskii, S. F. Mel´nikova, and S. A. Fedotov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 1354 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1466].
3. S. I. Al-Khalil and W. R. Bowman, *Tetrahedron Lett.*, 1982, **43**, 4513.
4. S. I. Al-Khalil and W. R. Bowman, *J. Chem. Soc., Perkin Trans. 1*, 1986, 555.
5. B. G. Christensen and L. D. Cama, *Ger. Offen.*, 2 151 036; *Chem. Abstr.*, 1972, 77:126616.
6. S. M. Wright and G. A. Ward, *J. Electrochem. Soc.*, 1965, **2**, 11.

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* The signals for the minor isomer.

7. N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, 1968, **68**, 489.
8. R. Haul and E. Scholz, *Naturwissenschaften*, 1944, **32**, 294.
9. S. Wawszonek and T.-Y. Su, *J. Electrochem. Soc.*, 1973, **120**, 745.
10. B. C. Gilbert and R. O. C. Norman, *Can. J. Chem.*, 1982, **60**, 1379.
11. V. A. Kokorekina, V. A. Petrosyan, and L. G. Feoktistov, *Elektrosintez monomerov* [*Electrochemical Synthesis of Monomers*], Nauka, Moscow, 1980, 83 (in Russian); S. T. Bahner, *Ind. Eng. Chem.*, 1952, **44**, 317.
12. N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto, and G. E. Graham, *J. Am. Chem. Soc.*, 1956, **78**, 1497.
13. G. A. Olah, P. Ramaiah, G. K. S. Prakash, and R. Gilardi, *J. Org. Chem.*, 1993, **58**, 763.
14. A. T. Nielson, *J. Org. Chem.*, 1962, **27**, 1993.
15. K. Fukunaga and M. Kimura, *J. Chem. Soc. Jpn, Chem. Ind. Chem.*, 1982, 1499.
16. D. W. Chasar, *Synthesis*, 1982, 841.
17. G. Rosini, E. Marotta, R. Ballini, and M. Petrini, *Synthesis*, 1986, 237.

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