Electrooxidative coupling of salts of nitro compounds with halide, nitrite, cyanide, and phenylsulfinate anions

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Electrolysis of salts of primary and secondary nitro compounds (nitroethane, 1- and 2-nitropropanes, nitrocyclohexane, and nitrocycloheptane) in the presence of excess halide, nitrite, cyanide, and phenylsulfinate anions under undivided and divided amperostatic electrolysis conditions in a two-phase medium (CH_2Cl_2/H_2O) produces geminal nitrohalides (35—85% yields), dinitro compounds (15—51%), nitronitriles (6—27%), and nitrosulfones (50—70%). The salts of secondary nitro compounds form the products of oxidative coupling with halide and phenylsulfinate anions under the undivided electrolysis conditions. In all other cases, divided electrolysis is required.

Key words: nitroethane, 1- and 2-nitropropanes, nitrocyclohexane, nitrocycloheptane, halides, nitrites, cyanides, phenylsulfinates, electrolysis, electrooxidative coupling, *gem*-nitrohalides, *gem*-dinitro compounds, *gem*-nitronitriles, *gem*-nitrosulfones.

Oxidative coupling of salts of nitro compounds with inorganic and organic anions is one of the main methods for introducing different functional groups into the α-position of aliphatic and alicyclic nitro compounds.[1,2] This method using predominantly chemical oxidants (Cl_2, Br_2, I_2, $AgNO_3$, $K_3Fe(CN)_6$, *N*-halosuccinimides, $(NH_4)_2S_2O_8$, and others) gave geminal nitrohalides,[3—10] nitroazides,[11—14] dinitro compounds,[15—18] nitronitriles,[17,18] nitrosulfones,[7,17,19] and nitroimidazoles.[20] Only dinitro compounds and nitroazides were synthesized by electrochemical oxidation,[21—25] although, as shown by our work on the electrosynthesis of geminal azidonitro compounds,[25] this variant of preparation of α-substituted nitro compounds have substantial advantages over traditional chemical methods because excess oxidant can be replaced by ecologically pure electric current. Therefore, it is undoubtedly interesting and urgent to study the electrooxidative coupling of salts of nitro compounds with inorganic and organic anions for the development of methods of electrosynthesis of nitro compounds substituted in the α-position by different functional groups.

To solve this problem, we used Na salts of primary and secondary nitroalkanes (nitroethane, 1- and 2-nitropropanes) and nitrocycloalkanes (nitrocyclohexane and nitrocycloheptane), which were subjected to electrooxidation in the presence of excess halide, nitrite, cyanide, and phenylsulfinate anions. As in the previously described case[25] of coupling of nitro compound salts with azide anions, the study was carried out in two-phase media, *viz.*, CH_2Cl_2—aqueous solutions of NaCl, NaBr, NaI, $NaNO_2$, NaCN, and $PhSO_2Na$ in a volume ratio of 2 : 1, under both undivided (UDE) and divided electrolysis (DE) conditions using 0.1 *M* aqueous solutions of NaOH or H_2SO_4 as catholytes. An advantage of the two-phase system is a possibility to extract the coupling products into the organic phase during electrolysis. This decreases the probability of their hydrolysis to carbonyl compounds and (in the case of primary nitro compounds) deprotonation and subsequent side reactions.

Electrooxidative coupling of salts of nitro compounds **1a—e** with halide anions was carried out using tenfold excess of sodium halide. The reaction mainly affords α-nitrohalides **2—4** and α-nitrodihalides **5** and **6** (Scheme 1, Table 1).

Electrolysis of the nitroethane salt (**1a**) in a two-phase system CH_2Cl_2—aqueous solution of NaBr affords 1-bromo-1-nitroethane (**3a**) in a yield of only 5% in UDE and 15% in DE using a 0.1 *M* solution of NaOH as the catholyte. Geminal nitrobromide **3a** was obtained in a satisfactory yield (64%) only by the electrolysis of the nitroethane salt in the presence of bromide anions using DE and 0.1 *M* H_2SO_4 as the catholyte (see Table 1, entries 8—10). We have earlier found a similar effect for electrochemical azidation,[25] which is related, most likely, to the unstable final products in an alkaline medium. For instance, the pH of the aqueous phase for UDE electrolysis increases from 9 to 11 due to cathodic alkalization. When DE is used, the pH of the anolyte decreases from 9 to 7—8 during electrolysis (catholyte 0.1 *M* H_2SO_4) and

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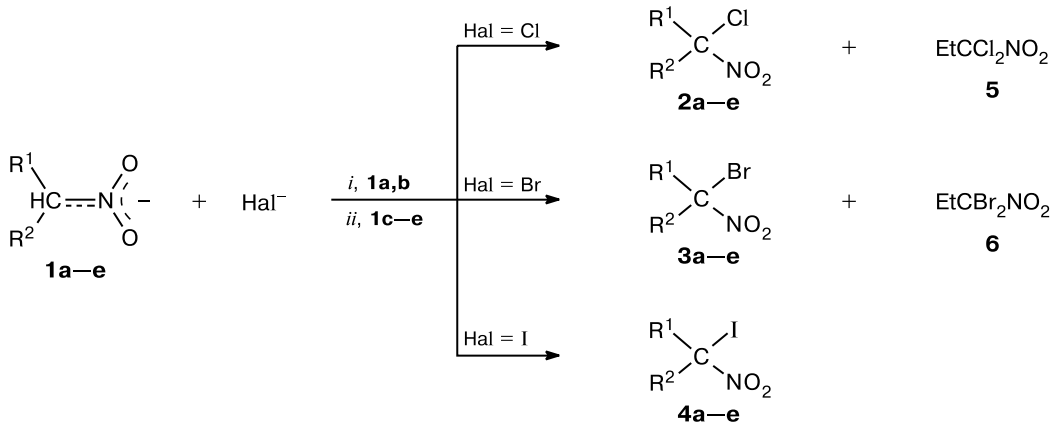
Scheme 1



Compound	R^1	R^2	Compound	R^1R^2
a	H	Me	**d**	$(CH_2)_5$
b	H	Et	**e**	$(CH_2)_6$
c	Me	Me		

Reagents and conditions: *i*, DE, CH_2Cl_2—H_2O (2 : 1), catholyte 0.1 *M* H_2SO_4, NaHal (10 equiv.), 2—5 *F* mol^{-1}, 8—10 °C; *ii*, UDE, CH_2Cl_2—H_2O (2 : 1), NaHal (10 equiv.), 2.5—8 *F* mol^{-1}, 8—10 °C.

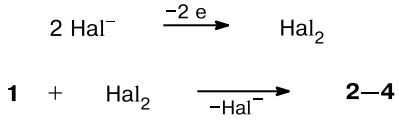
remains almost unchanged in the case of an alkaline or neutral catholyte. Halonitro compounds that formed are sensitive, most likely, to a change in the pH of the aqueous phase, because they have a more acidic α-proton than the starting nitro compounds. Under the optimum conditions, the conversion of salts **1a,b** is 68—95% when 2 *F* electricity is passed per mole of the salt, and the yield of monohalogenation products **2a,b—4a,b** is 55—68%. The electrolysis of salt **1b** in the presence of NaCl and NaBr affords dihalonitropropanes **5** and **6** along with monohalogenation products **2b** and **3b**. When the amount of passed electricity increases to 5 *F* mol^{-1}, compounds **5** and **6** become the main electrolysis products (Table 1, entries 3 and 12). The corresponding diiodonitro compounds are not formed under these conditions.

Salts of secondary nitro compounds (**1c—e**), unlike their primary analogs, can be coupled with halide anions under the undivided electrolysis conditions as well. The yield of the corresponding coupling products changes from 35 to 43% for **2c—e** and from 60 to 85% for **3c—e** and **4c—e** at the 75—100% conversion of salts **1c—e** (see Table 1). It should be mentioned that the conversion of salt **1e** is lower, as a rule, than that of **1d**, and an increase in the amount of electricity passed during their electrolysis gives no effect on the yield of the target products.

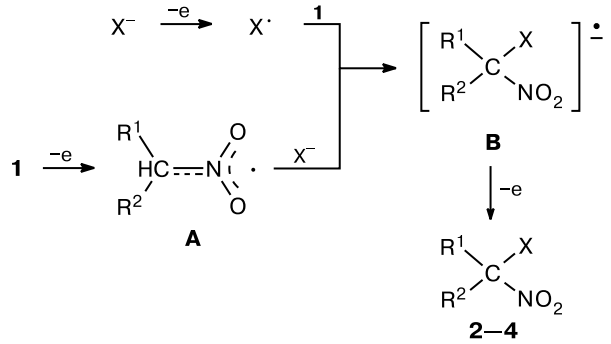
Products **2—4** can be formed by both the reactions of salts **1** with electrogenerated molecular chlorine, bromine, or iodine (Hal_2) (Scheme 2) and oxidative addition[11,12,17,18] (Scheme 3).

These reactions start from radical generation due to the one-electron oxidation of a substrate with the lowest oxidation potential. Then, the generated radicals add to

Scheme 2



Scheme 3



X = Hal, NO_2, CN, $PhSO_2$

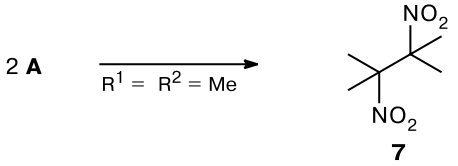
salt **1**, which is an active acceptor of radicals[26], and/or the X^- anions undergo coupling with nitroalkyl radicals **A**. Stable radical anions **B** that formed are transformed into final products **2—4** due to subsequent oxidation (see Scheme 3). Most likely, the mechanism presented in Scheme 3 is correct also for the electrooxidative coupling of nitro compound salts with nitrite, cyanide, and phenylsulfinate anions.

Table 1. Electrooxidative coupling of Na salts of nitroethane (**1a**), 1- and 2-nitropropanes (**1b,c**), nitrocyclohexane (**1d**), and nitrocycloheptane (**1e**) with halide anions using divided and undivided electrolysis conditions[a]

Entry	Salt	Electrolyzer	Q /F mol^{-1}	Conversion (%)	Yield of products **2—6**, **8** (%)[b]
		Coupling of salts **1a—e** with NaCl			
1	**1a**	DE	2	68	**2a** (62)
2	**1b**	DE	2	70	**2b** (68), **5** (2)[c]
3	**1b**	DE	5	100	**2b** (8)[c], **5** (53)
4	**1c**	UDE	4	80	**2c** (43)[d]
5	**1d**	UDE	2.5	90	**2d** (37), **8d** (7)
6	**1e**	UDE	4	52	**2e** (35), **8e** (10)
7	**1e**	UDE	8	95	**2e** (15), **8e** (12)
		Coupling of salts **1a—e** with NaBr			
8	**1a**	UDE	2	90	**3a** (5)[c]
9	**1a**	DE[e]	2	95	**3a** (15)
10	**1a**	DE	2	95	**3a** (64)
11	**1b**	DE	2	93	**3b** (67), **6** (9)[c]
12	**1b**	DE	5	100	**3b** (5)[c], **6** (53)
13	**1c**	UDE	3	100	**3c** (80)[f]
14	**1d**	UDE	2	100	**3d** (85), **8d** (2)[c]
15	**1e**	UDE	4	87	**3e** (60), **8e** (22)
		Coupling of salts **1a—e** with NaI			
16	**1a**	DE	2	82	**4a** (55)
17	**1b**	DE	2	88	**4b** (63)
18	**1c**	UDE	4	93	**4c** (75)
19	**1d**	UDE	4	77	**4d** (80), **8d** (3)[c]
20	**1e**	UDE	4	75	**4e** (62), **8e** (25)

[a] Conditions: 2—5 mmoles of salt **1**, 10 equiv. of NaHal, 20—30 mL of CH_2Cl_2, 10—15 mL of water, vigorous stirring, 8—10 °C, catholyte for DE 0.1 *M* H_2SO_4, current density 100 mA cm^{-2} for UDE and 50 mA cm^{-2} for DE.
[b] Preparative yield calculated to converted salt **1**.
[c] According to the GLC data.
[d] 2,3-Dimethyl-2,3-dinitrobutane (**7**) is also formed in 12% yield.
[e] Catholyte is 0.1 *M* NaOH.
[f] Compound **7** is also formed in 5% yield.

Based on the oxidation potentials of the anions ($2I^-/I_2$ E^0 = 0.536 V, $2Br^-/Br_2$ E^0 = 1.087 V, $2Cl^-/Cl_2$ E^0 = 1.395 V,[27] $RCH{=}NO_2^-$ $E_{1/2}$ = 0.82—0.9 V (SCE)),[28] we can conclude that the reaction proceeds mainly *via* Scheme 2 during electrooxidative bromination and iodination of salts **1**, while anions of salts **1** are also oxidized in the case of chloride anions (see Scheme 3). A relative amount of 2,3-dimethyl-2,3-dinitrobutane (**7**), which is the dimerization product of radicals **A**[21,29] formed by coupling of salt **1c** with halide anions allows one to estimate the participation of α-nitroalkyl radicals **A** in the formation of radical anions **B** (see Scheme 3):



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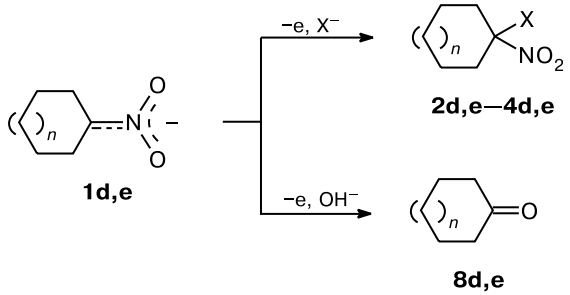
For instance, in the presence of NaI, product **7** is not formed; in the case of NaBr, its amount is not higher than 5%, for tenfold excess NaCl 12%, and for threefold excess NaCl increases up to 45%; the same increase in the yield of dimer **7** is provided by a decrease in the current density from 100 to 20 mA cm^{-2}. Thus, an increase in the sodium chloride concentration and current density favors the predominant oxidation of chloride anions rather than salts of nitro compounds. A similar effect has been observed previously for the electrochemical chlorination of the dinitroethane anion.[30]

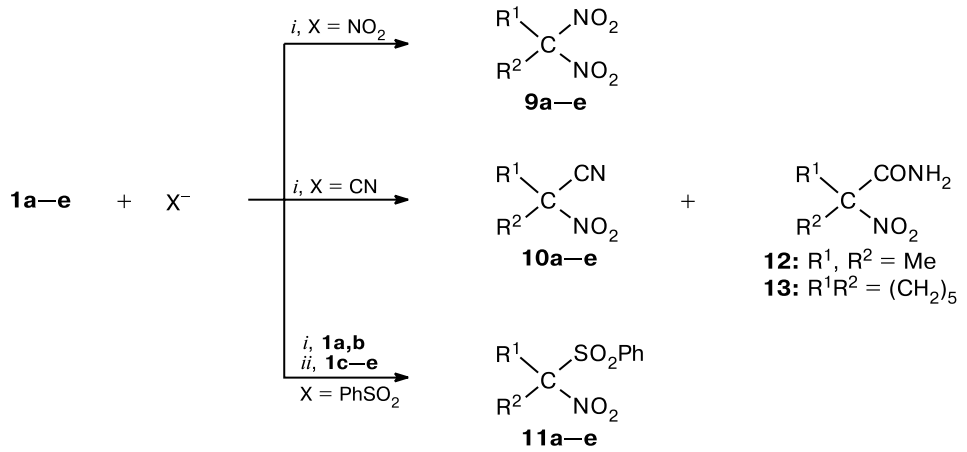
Electrooxidative coupling of salts **1d,e** with halide anions is usually accompanied by the competitive electrooxidative hydrolysis of the starting salts[28,29,31] with the formation of ketones **8d,e**, and the amount of ketone increases substantially on going from salt **1d** to salt **1e**. This fact can be explained by a facilitated change in the hybridization of the reaction center from sp^2 to sp^3 upon the conversion of **1d,e** into products **2—4** (Scheme 4) in the case of the six-membered ring (n = 1), because it is related to a decrease in the internal strain in the ring. In the case of the seven-membered ring (n = 2), by contrast, keeping the planar geometry for the formation of ketone **8** is energetically favorable.[32,33] This rule is also correct for the coupling of salts of nitro compounds with nitrite, cyanide, and phenylsulfinate anions.

Scheme 4



Unlike the reactions with halide anions, the electrooxidative coupling of salts **1a—e** with nitrite, cyanide, and

Scheme 5



Reagents and conditions: *i*, divided cell, CH_2Cl_2—H_2O (2 : 1), catholyte 0.1 *M* NaOH or H_2SO_4, 2 equiv. $NaNO_2$, NaCN, and $PhSO_2Na$, 2—3 *F* mol^{-1}, 8—10 °C; *ii*, undivided cell, CH_2Cl_2—H_2O (2 : 1), 2 equiv. $PhSO_2Na$, 2 *F* mol^{-1}, 8—10 °C.

phenylsulfinate anions (Scheme 5, Table 2) was carried out at a salt—anion ratio of 1 : 2. The further increase in this ratio is unreasonable because of a decrease in the current efficiency for the target products, and the yield also decreased for the geminal dinitro compounds and α-nitronitriles. Most likely, the competitive oxidation of the X^- anions produces undesirable by-products when the oxidation potentials of salts **1** and anions X^- are close (for example, $E_{1/2}(RCH{=}NO_2)$ = 0.82—0.9 V, $E_{1/2}(NO_2^-)$ = 0.87—1.05 V [28] (SCE)); the yield of coupling products is higher for the reactions with phenylsulfinate anions ($E_{1/2}$ ~0.63 V).[34] In turn, a decrease in the concentration of X^- anions increases the degree of competitive electrooxidative hydrolysis of the nitro compound salts.

Coupling of salts **1a—e** with nitrite anions was carried out under the DE conditions using 0.1 *M* NaOH as the catholyte. In this case, *gem*-dinitro compound **9d** is formed in approximately 50% yield (see Scheme 5, Table 2, entries 1—5), while the yields of the *gem*-dinitro compounds are substantially lower for other substrates. When UDE is used, the yield of **9d** does not exceed 5%. The electrochemical coupling of salt **1a** with nitrite anions was earlier carried out with a high yield of 1,1-dinitroethane (>80%) under the divided electrolysis conditions using powdered silver as an anode.[22] The Ag^+ cations that formed act as a mediator (one-electron oxidant).[16,35] The yield of the coupling products on the Pt anode under comparable conditions did not exceed 30%,[22] which agrees with our data. A low yield of the target products is caused, most likely, by the destruction of the *gem*-dinitro compounds and their anions due to side reactions initiated by decomposition products of polynitroalkyl radicals.[36]

Electrooxidative coupling of salts of secondary nitro compounds **1c—e** with cyanide anions occurs under both the UDE and DE conditions. However, the yield of α-nitronitriles does not exceed 20% even for DE (see Table 2, entries 6—11). An attempt to obtain coupling products with salts of primary nitro compounds **1a,b** failed, which is probably related to unstable products formed under the electrolysis conditions. In addition, the process is complicated by the hydrolysis of the nitrile group in the product to the amide group, which occurs (although to a less extent) even when an acidic catholyte is used and is accompanied by the formation of considerable amounts of ketones **8**. Electrolysis in methanol affords a mixture of α-nitronitrile and the corresponding imino ester **14**, and the ketone amount in the reaction mixture decreases substantially (see Table 2, entry 10).

The electrooxidative coupling of salts of primary nitroalkanes **1a**,**b** with phenylsulfinate anions occurs efficiently under DE using an alkaline catholyte (0.1 *M* NaOH). In this case, nitrosulfones **11a**,**b** are formed in 55—58% yield at the 82—85% conversion of salts **1a**,**b** (see Scheme 5, Table 2). Unlike the primary salts, the salts of secondary nitro compounds **1c—e** form the corresponding sulfones under the undivided electrolysis conditions. The yield of nitrosulfones **11c—d** is 54—70%. The low yield of nitrosulfone **11e** (27%) is caused by the competitive electrooxidative hydrolysis of salt **1e** and the formation of 1,1-bis(phenylsulfonyl)cycloheptane (**15**) (yield 23%).

Thus, the study of electrooxidative coupling of salts of primary and secondary nitro compounds with halide, nitrite, cyanide, and phenylsulfinate anions under the undivided and divided amperostatic electrolysis conditions in a two-phase methylene dichloride—water system showed that salts of secondary nitroalkanes form coupling products with halide and phenylsulfinate anions under the undivided electrolysis conditions, while divided electrolysis is required in all other cases.

Table 2. Electrooxidative coupling of Na salts of nitroethane (**1a**), 1- and 2-nitropropanes (**1b,c**), nitrocyclohexane (**1d**), and nitrocycloheptane (**1e**) with nitrite, cyanide, and phenylsulfinate anions using divided and undivided electrolysis conditions[a]

Entry	Salt	Electrolysis (catholyte)	Q /F mol^{-1}	Conversion (%)	Yield (%)[b] of products **8—14**
		Coupling of salts **1a—e** with $NaNO_2$ [c]			
1	**1a**	DE (NaOH)	2	80	**9a** (35)
2	**1b**	DE (NaOH)	2	75	**9b** (30)
3	**1c**	DE (NaOH)	2	90	**9c** (40)
4	**1d**	DE (NaOH)	3	90	**8d** (17), **9d** (51)
5	**1e**	DE (NaOH)	3	95	**8e** (48), **9e** (15)
		Coupling of salts **1c—e** with NaCN			
6	**1c**	DE (H_2SO_4)	2	100	**10c** (12) **12** (4)
7	**1d**	UDE	2	98	**8d** (15), **10d** (7) **13** (5)
8	**1d**	DE (NaOH)	2	98	**8d** (20), **10d** (15), **13** (10)
9	**1d**	DE (H_2SO_4)	2	90	**8d** (18), **10d** (27), **13** (8)
10	**1d**	DE (H_2SO_4)[d]	2	93	**8d** (5), **10d** (20) **14** (15)
11	**1e**	DE (H_2SO_4)	2	95	**8e** (75), **10e** (6)
		Coupling of salts **1a—e** with $PhSO_2Na$			
12	**1a**	DE (NaOH)	2	85	**11a** (55)
13	**1b**	DE (NaOH)	2	82	**11b** (58)
14	**1c**	UDE	2	100	**11c** (70)
15	**1d**	UDE	2	95	**8d** (7), **11d** (54)
16	**1e**	UDE	2	95	**8e** (25), **11e** (27)[e]

[a] Conditions: 2—5 mmoles of salt **1**; 2 equiv. of $NaNO_2$, NaCN, or $PhSO_2Na$; 20—30 mL of CH_2Cl_2; 10—15 mL of water; vigorous stirring; 8—10 °C, catholyte using DE: 0.1 *M* NaOH or 0.1 *M* H_2SO_4; current density 100 mA cm^{-2} for UDE and 50 mA cm^{-2} for DE.
[b] Preparative yield calculated to converted salt **1**.
[c] For syntheses of salts **1**, 1.5-fold excess NaOH was used.
[d] Solvent MeOH, catholyte 0.1 *M* H_2SO_4 in MeOH.
[e] 1,1-Bis(phenylsulfonyl)cycloheptane (**15**) is also formed in 23% yield.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200, Bruker WM-250, and Bruker AM-300 spectrometers using $CDCl_3$ as a solvent. IR spectra were measured on a Specord M-82 spectrometer as KBr pellets. Laboratory power sources (B5-44 and B5-50) with output current stabilization were used as dc generators. The amount of passed electricity was measured using an electron coulometer with digital indication and a current measurement limit of 20 A (Design Bureau of the Institute of Organic Chemistry, Russian Academy of Sciences). Electrode materials were Pt (anode) and stainless steel (cathode). GLC analysis was carried out using a Varian-3700 chromatograph (flame-ionization detector, glass columns 2×0.003 m, stationary phase 5% SE-30 and 5% XE-60 on Chromaton N-AW). TLC analysis was carried out using chromatographic plates Silufol UV-254. Silica gel L 40/100 μm was used for flash chromatography. Petroleum ether (b.p. 40—60 °C), CH_2Cl_2, ethyl acetate, and MeOH were purified by standard methods. Nitroethane, 1- and 2-nitropropanes, and nitrocyclohexane were commercial reagents (Aldrich). Nitrocycloheptane[37] was obtained by the oxidation of cycloheptanone oxime with *m*-chloroperoxybenzoic acid in acetonitrile in the presence of Na_2HPO_4.

Electrooxidative coupling of Na salts of nitro compounds with halide anions in a divided cell in a two-phase system (general procedure). Nitro compound (2—5 mmol) was added to a 3 *M* aqueous solution of NaOH (1 equiv.), and the mixture was stirred until the substrate transformed completely into its salt (1—2 h). The resulting solution was diluted with water, sodium halide (10 equiv.) and CH_2Cl_2 (20—30 mL) were added to prepare the anolyte. Electrolysis was carried out using a ceramic diaphragm, Pt anode (4 cm^2), and stainless steel cathode (4 cm^2) with vigorous stirring of the anolyte under the conditions given in Table 1 and cooling in an ice bath. Catholytes were 0.1 *M* solutions of NaOH or H_2SO_4. To monitor the course of the reaction, an aliquot from the aqueous phase of the anolyte was acidified with AcOH and extracted with CH_2Cl_2, and the extract was analyzed by GLC. After the end of electrolysis, the anolyte was acidified with AcOH (1 mL), the organic layer was separated, and the aqueous solution was extracted with CH_2Cl_2 (2×20 mL). The combined organic layers were washed with water (2×20 mL), dried with $MgSO_4$, analyzed by GLC, and evaporated on a rotary evaporator *in vacuo* without heating. Electrolysis products were isolated by vacuum distilla-

tion or flash chromatography on silica gel (eluent 0.5% AcOEt in petroleum ether) and identified by their ^{1}H and ^{13}C NMR spectra.

1-Chloro-1-nitroethane (2a),[5] b.p. 61 °C (50 Torr), n_D^{16} 1.4245. ^{1}H NMR, δ: 2.02 (d, 3 H, J = 6.6 Hz); 5.93 (q, 1 H, J = 6.6 Hz). ^{13}C NMR, δ: 23.56 (C(2)); 87.65 (C(1)).

1-Chloro-1-nitropropane (2b),[6] b.p. 36 °C (15 Torr), n_D^{20} 1.4250. ^{1}H NMR, δ: 1.07 (t, 3 H, J = 7.2 Hz); 2.15—2.44 (m, 2 H); 5.80 (t, 1 H, J = 6.6 Hz). ^{13}C NMR, δ: 8.86 (C(3)); 30.50 (C(2)); 92.85 (C(1)).

1-Bromo-1-nitroethane (3a),[6] b.p. 50—52 °C (15 Torr), n_D^{16} 1.4780. ^{1}H NMR, δ: 2.17 (d, 3 H, J = 6.6 Hz); 6.04 (q, 1 H, J = 6.6 Hz). ^{13}C NMR, δ: 24.08 (C(2)); 74.60 (C(1)).

1-Bromo-1-nitropropane (3b),[6] b.p. 61 °C (15 Torr), n_D^{20} 1.4710. ^{1}H NMR, δ: 1.08 (t, 3 H, J = 7.2 Hz); 2.20—2.52 (m, 2 H); 5.88 (t, 1 H, J = 6.6 Hz). ^{13}C NMR, δ: 10.14 (C(C(3)); 30.90 (C(2)); 81.21 (C(1)).

1-Iodo-1-nitroethane (4a),[9] b.p. 75—78 °C (20 Torr), n_D^{16} 1.5360. ^{1}H NMR, δ: 2.33 (d, 3 H, J = 6.6 Hz); 6.37 (q, 1 H, J = 6.6 Hz). ^{13}C NMR, δ: 26.29 (C(2)); 45.98 (C(1)).

1-Iodo-1-nitropropane (4b), b.p. 76—80 °C (15 Torr), n_D^{20} 1.5274. ^{1}H NMR, δ: 1.01 (t, 3 H, J = 7.9); 2.18—2.51 (m, 2 H); 6.13 (pseudo-t, 1 H, J = 6.6 Hz). ^{13}C NMR, δ: 12.05 (C(3)); 32.58 (C(2)); 55.29 (C(1)). Found (%): C, 16.33; H, 2.72; N, 6.22. $C_3H_6INO_2$. Calculated (%): C, 16.76; H, 2.81; N, 6.52.

1,1-Dichloro-1-nitropropane (5).[38] ^{1}H NMR, δ: 1.18 (t, 3 H, J = 7.2 Hz); 2.73 (q, 2 H, J = 7.2 Hz). ^{13}C NMR, δ: 10.57 (C(3)); 40.26 (C(2)); 114.90 (C(1)).

1,1-Dibromo-1-nitropropane (6).[39] ^{1}H NMR, δ: 1.21 (t, 3 H, J = 7.2 Hz); 2.89 (q, 2 H, J = 7.2 Hz). ^{13}C NMR, δ: 11.73 (C(3)); 42.96 (C(2)); 89.43 (C(1)).

Electrooxidative coupling of Na salts of nitro compounds with halide anions in an undivided cell (general procedure). Nitro compound (2 mmol) was mixed with CH_2Cl_2 (20 mL) and a 0.2 M aqueous solution of NaOH (1 equiv., 10 mL). The mixture was stirred for 1—3 h until complete transformation of the substrate into the corresponding salt (the presence of the nitro compound in an organic phase was monitored by GLC), and sodium halide (10 equiv.) was added. The resulting mixture was placed in an electrolyzer with a Pt anode (4 cm^2) and a stainless steel cathode (4 cm^2). The distance between the electrodes was 10 mm. Direct current was passed under the conditions given in Table 1. The course of the reaction was monitored and the products were isolated and identified according to the above described procedures.

2-Chloro-2-nitropropane (2c),[7] b.p. 38 °C (20 Torr), n_D^{20} 1.4264. ^{1}H NMR, δ: 2.16 (s, 6 H). ^{13}C NMR, δ: 30.62 (C(1)); 100.05 (C(2)).

1-Chloro-1-nitrocyclohexane (2d).[10] ^{1}H NMR, δ: 1.28—1.46 (m, 1 H); 1.53—1.85 (m, 5 H); 2.31 (dt, 2 H, J = 13.8 Hz, J = 5.3 Hz); 2.42 (ddd, 2 H, J = 13.8 Hz, J = 8.5 Hz, J = 5.3 Hz). ^{13}C NMR, δ: 23.02 (C(3)); 24.02 (C(4)); 38.37 (C(2)); 103.82 (C(1)).

1-Chloro-1-nitrocycloheptane (2e).[40] ^{1}H NMR, δ: 1.69 (m, 8 H); 2.43 (dt, 2 H, J = 15.9 Hz, J = 5.3 Hz); 2.73 (dt, 2 H, J = 15.9 Hz, J = 5.3 Hz). ^{13}C NMR, δ: 22.93, 28.32 (C(3), C(4)); 42.56 (C(2)); 110.71 (C(1)).

2-Bromo-2-nitropropane (3c),[7] b.p. 60 °C (20 Torr), n_D^{16} 1.4720. ^{1}H NMR, δ: 2.25 (s, 6 H). ^{13}C NMR, δ: 32.32 (C(1)); 88.99 (C(2)).

1-Bromo-1-nitrocycloheptane (3d).[41] ^{1}H NMR, δ: 1.28—1.86 (m, 6 H); 2.45 (br.t, 4 H, J = 5.9 Hz). ^{13}C NMR, δ: 23.52 (C(3)); 23.77 (C(4)): 39.23 (C(2)); 94.74 (C(1)).

1-Bromo-1-nitrocycloheptane (3e).[41] ^{1}H NMR, δ: 1.66 (br.s, 8 H); 2.60, 2.84 (both dd, 2 H each, J = 15.5 Hz, J = 7.5 Hz). ^{13}C NMR, δ: 23.33, 28.09 (C(3), C(4)); 43.36 (C(2)); 99.67 (C(1)).

2-Iodo-2-nitropropane (4c),[7] b.p. 73—75 °C (15 Torr), n_D^{16} 1.5320. ^{1}H NMR, δ: 2.38 (s, 6 H). ^{13}C NMR, δ: 35.69 (C(1)); 63.14 (C(2)).

1-Iodo-1-nitrocyclohexane (4d).[42] ^{1}H NMR, δ: 1.38—1.70 (m, 6 H); 2.33 (m, 2 H); 2.53 (dt, 2 H, J = 14.4 Hz, J = 5.9 Hz). ^{13}C NMR, δ: 24.04 (C(4)); 24.64 (C(3)); 42.32 (C(2)); 74.10 (C(1)).

1-Iodo-1-nitrocycloheptane (4e).[7] ^{1}H NMR, δ: 1.56, 1.63 (both m, 4 H each); 2.72, 2.87 (both dt, 2 H each, J = 15.5 Hz, J = 5.3 Hz). ^{13}C NMR, δ: 24.05, 27.77 (C(3), C(4)); 45.88 (C(2)); 77.81 (C1)).

2,3-Dimethyl-2,3-dinitrobutane (8),[43] m.p. 202 °C. ^{1}H NMR, δ: 1.73 (s, 12 H). ^{13}C NMR, δ: 23.06 (C(1), C(4)); 91.51 (C(2), C(3)).

Electrooxidative coupling of Na salts of nitro compounds with cyanide and phenylsulfinate anions in a divided cell in a two-phase system. The reaction was carried out according to the above procedure. Products were isolated by flash chromatography on silica gel (eluent 0.5—2% AcOEt in petroleum ether) and identified by their IR and ^{1}H, ^{13}C NMR spectra (see Table 2).

1,1-Dinitroethane (9a).[16] ^{1}H NMR, δ: 2.14 (d, 3 H, J = 6.6 Hz); 6.30 (q, 1 H, J = 6.6 Hz). ^{13}C NMR, δ: 16.97 (C(2)); 108.18 (C(1)).

1,1-Dinitropropane (9b).[43] ^{1}H NMR, δ: 1.15 (t, 3 H, J = 7.0 Hz); 2.55 (quint, 3 H, J = 6.8 Hz); 6.11 (t, 1 H, J = 6.6 Hz). ^{13}C NMR, δ: 8.54 (C(3)); 24.81 (C(2)); 112.95 (C(1)).

2,2-Dinitropropane (9c).[17] ^{1}H NMR, δ: 2.16 (s, 6 H). ^{13}C NMR, δ: 23.93 (C(1)); 117.67 (C(2)).

1,1-Dinitrocyclohexane (9d).[17,18] ^{1}H NMR, δ: 1.59 (m, 2 H); 1.70, 2.59 (both m, 4 H each). ^{13}C NMR, δ: 22.34 (C(3)); 23.43 (C(4)); 32.87 (C(2)); 120.17 (C(1)).

1,1-Dinitrocycloheptane (9e). ^{1}H NMR, δ: 1.65—1.89 (m, 4 H); 1.69 (s, 4 H); 2.71 (m, 4 H). ^{13}C NMR, δ: 22.92, 29.11 (C(3), C(4)); 36.53 (C(2)); 123.95 (C(1)). Found (%): C, 44.38; H, 6.22; N, 14.70. $C_7H_{12}N_2O_4$. Calculated (%): C, 44.68; H, 6.43; N, 14.88.

2-Methyl-2-nitropropionitrile (10c).[17,18] ^{1}H NMR, δ: 2.00 (s, 6 H). ^{13}C NMR, δ: 26.13 (C(1)); 80.27 (C(2)); 115.86 (CN).

1-Nitrocyclohexylcarbonitrile (10d).[17,18] ^{1}H NMR, δ: 1.21—1.44 (m, 1 H); 1.59—1.87 (m, 3 H); 1.90—2.05 (m, 2 H); 2.20 (td, 2 H, J = 12.5 Hz, J = 3.9 Hz); 2.45 (d, 2 H, J = 13.1 Hz). ^{13}C NMR, δ: 22.78 (C(3)); 23.78 (C(4)); 35.06 (C(2)); 86.17 (C(1)); 114.84 (CN).

1-Nitrocycloheptylcarbonitrile (10e). ^{1}H NMR, δ: 1.56—1.82 (m, 6 H); 1.82—2.02 (m, 2 H); 2.45 (m, 4 H). ^{13}C NMR, δ: 22.75, 27.49 (C(3), C(4)); 38.28 (C(2)); 89.29 (C(1)); 115.89 (CN). Found (%): C, 57.02; H, 7.08; N, 16.35. $C_8H_{12}N_2O_2$. Calculated (%): C, 57.13; H, 7.19; N, 16.65.

2-Methyl-2-nitropropanamide (12),[44] m.p. 117—119 °C. IR, ν/cm^{-1}: 3432, 3188 (NH_2); 1692 (CO); 1548, 1356 (NO_2). ^{1}H NMR, δ: 1.87 (s, 6 H); 5.89 and 6.13 (both br.s, 2 H).

1-Nitrocyclohexylcarboxamide (13),[44] m.p. 118—120 °C. ^{1}H NMR, δ: 1.40 (m, 3 H); 1.63 (m, 1 H); 1.72 (m, 2 H); 2.12

(td, 2 H, J = 12.5 Hz, J = 4 Hz); 2.58 (d, 2 H, J = 13 Hz); 5.90 and 6.05 (both br.s, 2 H).

1-(1-Nitroethyl)phenylsulfone (11a),[45] m.p. 47—48 °C. ^{1}H NMR, δ: 1.90 (d, 3 H, J = 6.6 Hz); 5.63 (q, 1 H, J = 6.6 Hz); 7.62 (t, 2 H, J = 7.2 Hz); 7.77 (t, 1 H, J = 7.2 Hz); 7.89 (d, 2 H, J = 7.6 Hz). ^{13}C NMR, δ: 13.32 (C(2)); 97.47 (C(1)); 129.58, 129.94 (C(2′), C(3′)); 133.93 (C(1′)); 135.53 (C(4′)).

1-(1-Nitropropyl)phenylsulfone (11b),[18] m.p. 55—56 °C. ^{1}H NMR, δ: 1.04 (t, 3 H, J = 7.2 Hz); 2.12—2.42 (m, 2 H); 5.45 (dd, 1 H, J = 10.5 Hz, J = 3.9 Hz); 7.61 (t, 2 H, J = 7.8 Hz); 7.77 (t, 1 H, J = 7.2 Hz); 7.89 (dd, 2 H, J = 7.8 Hz, J = 1.3 Hz). ^{13}C NMR, δ: 9.93 (C(3)); 21.96 (C(2)); 103.65 (C(1)); 129.53, 130.02 (C(2′), C(3′)); 134.10 (C(1′)); 135.50 (C(4′)).

Electrooxidative coupling of Na salts of nitro compounds with phenylsulfinate anions in an undivided cell. The reaction was carried out according to the above procedure. Products were isolated by crystallization from petroleum ether or using flash chromatography on silica gel (eluent 0.5—10% AcOEt in petroleum ether) and identified by the ^{1}H and ^{13}C NMR spectra (see Table 2).

2-(2-Nitropropyl)phenylsulfone (11c),[7,17] m.p. 115—117 °C. ^{1}H NMR, δ: 1.52 (m, 2 H); 1.61 (br.s, 4 H); 1.83 (m, 2 H); 2.53, 2.69 (both dd, 2 H each, J = 15.4 Hz, J = 8.8 Hz); 7.44—8.08 (m, 5 H). ^{13}C NMR, δ: 20.99 (C(1)); 103.50 (C(2)); 129.19, 130.90 (C(2′), C(3′)); 133.93 (C(1′)); 135.30 (C(4′)).

1-(1-Nitrocyclohexyl)phenylsulfone (11d),[7,18] m.p. 102—103 °C. ^{1}H NMR, δ: 1.12—1.37 (m, 3 H); 1.66—1.77 (m, 1 H); 1.87 (m, 2 H); 2.17 (td, 2 H, J = 12.5 Hz, J = 3.9 Hz); 2.69 (d, 2 H, J = 13.8 Hz); 7.59 (t, 2 H, H(3′), J = 7.2 Hz); 7.74 (tt, 1 H, H(4′), J = 7.2 Hz, J = 1.3 Hz); 7.81 (dd, 2 H, H(2′), J = 8.5 Hz, J = 1.3 Hz). ^{13}C NMR, δ: 21.99 (C(3)); 23.71 (C(4)); 28.44 (C(2)); 107.62 (C(1)); 129.17, 130.79 (C(2′), C(3′)); 132.38 (C(1′)); 135.23 (C(4′)).

1-(1-Nitrocycloheptyl)phenylsulfone (11e),[7] m.p. 100—102 °C. ^{1}H NMR, δ: 1.42—1.70 (m, 6 H); 1.83 (m, 2 H); 2.53 (ddd, 2 H, J = 15.1 Hz, J = 9.8 Hz, J = 2.0 Hz); 2.70 (ddd, 2 H, J = 15.1 Hz, J = 7.9 Hz, J = 1.3 Hz); 7.59 (t, 2 H, J = 7.7 Hz); 7.74 (t, 1 H, J = 7.2 Hz); 7.83 (d, 2 H, J = 7.7 Hz). ^{13}C NMR, δ: 22.85 (C(4)); 29.05 (C(3)); 31.79 (C(2)); 110.97 (C(1)); 128.98, 130.83 (C(2′), C(3′)); 132.77 (C(1′)); 135.03 (C(4′)).

1,1-Bis(phenylsulfonyl)cycloheptane (15),[46] m.p. 198—200 °C. ^{1}H NMR, δ: 1.52 (m, 2 H); 1.61 (s, 4 H); 1.83 (m, 2 H); 2.53, 2.69 (both dd, 2 H each, J = 15.4 Hz, J = 8.8 Hz); 7.44—8.08 (m, 5 H). ^{13}C NMR, δ: 23.01 (C(4)); 29.20 (C(3)); 31.96 (C(2)); 99.46 (C(1)); 129.72, 131.45 (C(2′), C(3′)); 133.01 (C(1′)); 136.41 (C(4′)).

Electrooxidative coupling of Na salt of 1-nitrocyclohexane (1d) with NaCN in a divided cell in MeOH. Nitrocyclohexane (2 mmol) was mixed with a 0.1 M methanol solution of MeONa (1 equiv.). The mixture was stirred for 30 min, and NaCN (2 equiv.) was added. Electrolysis of the resulting mixture was carried out and monitored according to the above-described procedure. After the end of electrolysis, an aliquot from the anolyte was diluted with water, acidified with acetic acid to transform the unreacted salt into the starting nitro compound, and analyzed by GLC using an internal standard (dodecane) to determine the conversion of the starting salt of nitro compound. The anolyte was concentrated *in vacuo* on a rotary evaporator without heating, and the residue was dissolved in CH_2Cl_2 and evaporated to dryness with silica gel. Products were isolated by flash chromatography on silica gel (eluent 0.5—2% AcOEt in petroleum ether) and identified by their ^{1}H and ^{13}C NMR spectra. The results of analysis are presented in Table 2, entry 10.

Methyl (1-nitrocyclohexyl)carboxyimidate (14).[47] ^{1}H NMR, δ: 1.50 (m, 6 H); 2.02, 2.45 (both m, 2 H each); 3.68 (s, 3 H); 7.65 (s, 1 H, NH). ^{13}C NMR, δ: 22.18 (C(3)); 24.24 (C(4)); 32.73 (C(2)); 54.28 (OMe); 92.35 (C(1)); 167.28 (C=N).

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