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Electrooxidative transformation of unsubstituted and substituted nitro hydrocarbons into carbonyl compounds

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Alkaline salts of *aci*-forms of secondary nitro compounds, *viz.*, β-nitropropylbenzene, nitrocyclohexane, 5-nitroheptan-2-one, and methyl-4-nitrohexanoate, were selectively or predominately oxidized into the corresponding ketones and their ketals under conditions of undivided amperostatic electrolysis in methanol. Mixtures of the corresponding aldehydes, their acetals, and methyl carboxylates were formed under similar conditions from the salts of primary nitro compounds, *viz.*, 1-nitrohexane, nitromethylbenzene, and β-nitroethylbenzene.

Key words: nitrocyclohexane, 1-nitrohexane, nitromethylbenzene, α- and β-nitroethylbenzenes, β-nitropropylbenzene, 5-nitroheptan-2-one, methyl 4-nitrohexanoate, salts of *aci*-nitro compounds, electrolysis, ketones, carboxylates, *vic*-dinitroalkanes.

The present work is devoted to the electrooxidative transformation of unsubstituted and substituted nitro hydrocarbons into carbonyl compounds. This electrochemical process is poorly studied, although, according to available data, can be very useful from the synthetic point of view.[1—3] The chemical prototype of the process is the Nef reaction,[4] which has been known for more than a century, with its numerous modifications[5—19] developed to create more perfect than the Nef reaction methods for the transformation of the nitro group into the carbonyl group. In the most cases, these methods are based on the one- and two-electron oxidation of *aci*-nitro compounds using diaroyl peroxides,[6] $S_2O_8^{2-}$—Ag^+ systems,[7] alkyl nitrites,[8] and ammonium cerium nitrate[9,10] as one-electron oxidants and potassium permanganate,[11,12] sodium chlorite,[13] Caro´s acid (Oxone),[14] dimethyldioxirane,[15] singlet oxygen,[16] ozone,[17] and oxidative systems ruthenate(perruthenate) anions—potassium bromate,[18] tetrapropylammonium perrruthenate—*N*-methylmorpholine-*N*-oxide,[19] and *tert*-butyl hydroxyperoxide—diacetyl complex of vanadium oxide[20] as two-electron oxidants.

It is known that α-nitroalkyl radicals are generated at the initial stage of both the electrochemical and one-electron oxidation of *aci*-nitro hydrocarbons.[21] This is indicated by the formation of dimers of these radicals, *viz.*, α,β-dinitroalkanes, which were obtained in many cases as the main electrolysis product. Therefore, it seems reasonable to assume the intermediate involvement of the α-nitroalkyl radicals in the electrochemical transformation of nitroalkanes into carbonyl compounds.[1—3] However, the question how such radicals are transformed into carbonyl compounds remains unclear, and the choice of electrolysis conditions providing the selective transformation of unsubstituted and functionally substituted nitro hydrocarbons into target products depends on the solution of this problem.

It was assumed until the present study that the electrogenerated nitroalkyl radicals are transformed into carbonyl compounds due to decomposition with nitrogen monoxide elimination.[21,22] Since this reaction is chemical, it should not be affected noticeably by the anodic current density and the material of the anode. However, this contradicts explicitly the later data, which demonstrated an evident interrelation between the conditions and results of electrolysis.[1,2] It is established, for example, that the electrochemical transformation of nitro compounds into carbonyl compounds, similarly to the Kolbe reaction, occurs most efficiently at high anodic current densities and when polished platinum is used as the anode. These facts indicate a mechanism different from that considered previously.[21,22]

The purpose of this work is to establish the general regularities of the electrooxidative transformation of unsubstituted and substituted nitro hydrocarbons into carbonyl compounds, to study the influence of the structure of the initial substrates and electrolysis conditions on the composition of the products, and to reveal some aspects of the mechanism of this process using the results obtained.

We chose 1-nitrohexane (**1a**); nitromethyl- (**1b**), β- and α-nitroethyl- (**1c,d**), and β-nitropropylbenzene (**1e**); nitrocyclohexane (**1f**); 5-nitroheptan-2-one (**1g**); and methyl 4-nitrohexanoate (**1h**) as the initial com-

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pounds. They were electrolyzed as sodium, potassium, or ammonium salts of the corresponding *aci*-nitro compounds **2a—h**. The ammonium salts were prepared by the reactions of compounds **1a**,**g**,**h** with DBU. In the most cases, electrolysis was carried out in methanol using the galvanostatic regime, undivided cells, a platinum anode, and a steel cathode. The electrolysis conditions were varied. Graphite and glassy-carbon were also used as the anodic material. The conversion of the substrates and the composition, structure, and yields of the products were estimated in experiments. The results obtained are presented in Table 1. The structures of the main products are shown in Scheme 1.

The GLC analysis of the electrolyzates showed that the electrolysis under the indicated conditions resulted in the transformation of the salts of secondary *aci*-nitro compounds **2d—h** mainly into the corresponding ketones **3d—h** and their ketals in the ratio from 1 : 1 to 2 : 1, whereas the salts of primary *aci*-nitro compounds **2a—c** are transformed into aldehydes **3a—c**, their acetals (in a ratio of ~1 : 1), methyl carboxylates **4a—c**, and considerable amounts of resinous products. To estimate the overall yield of the carbonyl compounds and their derivatives, the latter were transformed into ketones and aldehydes by the treatment of the electrolyzate with a solution of HCl. Dimers of α-nitroalkyl radicals **5** and **6**

Table 1. Electrolysis of salts of *aci*-nitro compounds **2a—h** in MeOH (a Pt anode and a steel cathode, galvanostatic regime, 10—15 °C)

Entry	Substrate	Source of counterion (equiv.)	Current density /mA cm^{-2}	Conversion (%)	Q /F mol^{-1}	Yield[a] (%) (Product)		
						3	**4**	**5**, **6**
1	**2a**	MeONa (2)	100	95	2	18 (**3a**)	56 (**4a**)	10 (**5**)
2	**2a**	MeONa (2)	100	100	3	10 (**3a**)	58 (**4a**)	3 (**5**)
3[b]	**2a**	KF (2)	100	91	2	8 (**3a**)	74 (**4a**)	5 (**5**)
4[c]	**2a**	MeONa (1)	100	92	2	4 (**3a**)	73 (**4a**)	1 (**5**)
5	**2a**	DBU (1)	100	90	2	29 (**3a**)	43 (**4a**)	3 (**5**)
6	**2b**	MeONa (1)	20[d]	100	2	10 (**3b**)	20 (**4b**)	—
7	PhCH=NOH	MeONa (2)	100	95	2	25 (**3b**)	25 (**4b**)	—
8	PhCHO	MeONa (1)	100	50	2	—	—	60[e]
9	**2c**	MeONa (2)	100	85	2	17 (**3c**)	48 (**4c**)	—
10	**2d**	MeONa (1)	100	87	2	78 (**3d**)	—	—
11	**2e**	MeONa (2)	100	95	2	81 (**3e**)	—	—
12[c]	**2e**	MeONa (2)	50	90	2	62 (**3e**)	—	—
13	**2f**	MeONa (1)	65	95	4	63 (**3f**)	—	2 (**6**)
14	**2f**	MeONa (1)	100	100	3	94 (**3f**)	—	2 (**6**)
15	**2f**	MeONa (1)	100	99	2	95 (**3f**)	—	2 (**6**)
16	**2f**	MeONa (2)	100	100	2	80 (**3f**)	—	2 (**6**)
17	**2f**	MeONa (1)	150	100	2	89 (**3f**)	—	3 (**6**)
18	**2f**	MeONa (1)	200	94	2	82 (**3f**)	—	6 (**6**)
19	**2f**	KOH (2)	100	100	2	86 (**3f**)	—	1.5 (**6**)
20[c]	**2f**	MeONa (1)	100	97	2	52 (**3f**)	—	3 (**6**)
21[f]	**2f**	MeONa (1)	100	100	2	65 (**3f**)	—	3 (**6**)
22[g]	**2f**	MeONa (1)	100	96	2	45 (**3f**)	—	2.5 (**6**)
23	**2g**	DBU (1)	100	80	2	92 (**3g**)	—	—
24	**2g**	MeONa (1)	100	100	2	87 (**3g**)	—	—
25[c]	**2g**	MeONa (1)	100	75	2	90 (**3g**)	—	—
26[f]	**2g**	MeONa (1)	100	100	2	77 (**3g**)	—	—
27	**2h**	MeONa (1)	100	90	2	80 (**3h**)	—	—
28	**2h**	MeONa (2)	100	85	2	78 (**3h**)	—	—
29[f]	**2h**	MeONa (1)	100	85	2	88 (**3h**)	—	—
30	**2h**	DBU (1)	100	82	2	90 (**3h**)	—	—

[a] Calculated per transformed substrate.

[b] Potassium salt.

[c] Graphite anode.

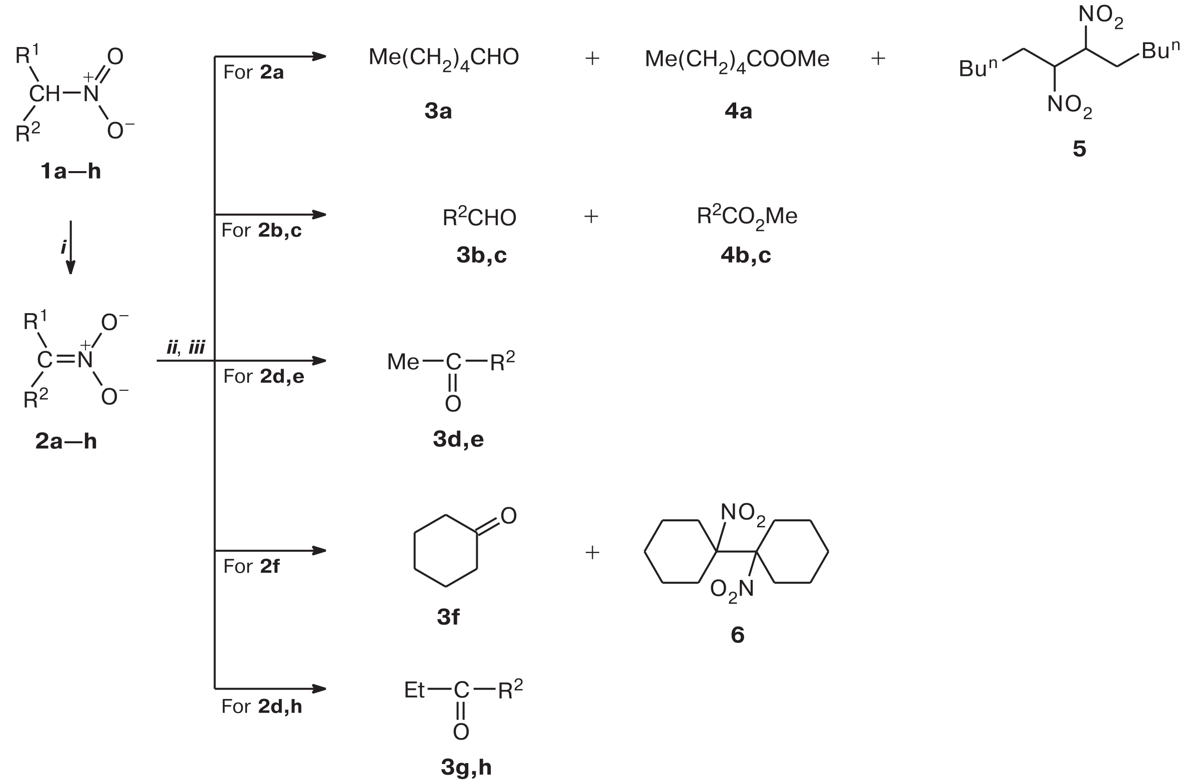
[d] At a current density of 100 mA cm^{-2} only resinous products are formed.

[e] 1,2-Diphenylethanediol.

[f] Glassy-carbon anode.

[g] Electrolysis at 60 °C.

Scheme 1



R^1 = H, R^2 = *n*-C_5H_{11} (**a**); R^1 = H, R^2 = Ph (**b**); R^1 = H, R^2 = Bn (**c**); R^1 = Me, R^2 = Ph (**d**);
R^1 = Me, R^2 = Bn (**e**); R^1 + R^2 = $(CH_2)_5$ (**f**); R^1 = Et, R^2 = CH_2CH_2Ac (**g**); R^1 = Et, R^2 = $CH_2CH_2CO_2Me$ (**h**)

Reagents and conditions: *i.* MeOH, MeONa, KOH, or DBU (1—2 equiv.), ~20 °C; *ii.* MeOH, 2—4 F mol^{-1}, 10—15 °C; *iii.* Acidification of reaction mixture.

were formed only in the case of the electrolysis of substrates **2a** and **2f**, respectively (see Table 1).

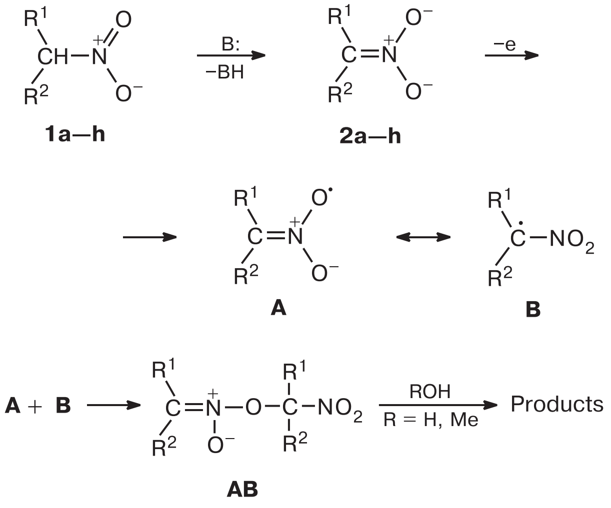
The salt of the *aci*-nitro compound obtained by the preliminary interaction of the initial compound with the equimolar or excessive amount of a solution of MeONa or KOH in MeOH acts simultaneously as the reactant and electrolyte. This feature of the process in combination with the regeneration of the alkaline metal methoxide during electrolysis allows one to avoid the use of other electrolytes and to achieve the ~100% conversion of the salt of the *aci*-nitro compound at anodic current densities of 65—200 mA cm^{-2} even when the theoretical amount of electricity (2 F mol^{-1}) is passed (see Table 1). This conversion to be achieved at lower current densities requires the greater consumption of electricity to 3—4 F mol^{-1}. The anodic current density >150 mA cm^{-2} favors the formation of the dimers of the α-nitroalkyl radicals (see Table 1, entries *14—19*). At the optimum anodic current density (100—150 mA cm^{-2}) the yield of dimers **6** and **5** does not exceed 2% for salt **2f** and achieves 5—10% for salt **2a**, respectively (see Table 1, entries *1* and *2*). The conversion of salts **2** to products **3—6** and their yield decrease when graphite and glassy-carbon are used instead of platinum (the conversion decreases by 3—25% and the yield increases by 10—28%, see Table 1, entries *12*, *20*, *21*, *25*, *26*, and *29*). The yield of carbonyl products decreases when electrolysis is carried out at 60 °C instead of 10—15 °C.

The peculiarities mentioned for the process under study, several common features with the Kolbe reaction (a similar plot of the yields of electrolysis products *vs.* current density at the anode and material of the anode, *etc.*) favor that the electrolysis of salts **2a—h** generates the nitronate (**A**) and α-nitroalkyl radicals (**B**) followed by their transformation through the intermediate formation of esters of nitronic acids into identified products **3a—h** and **4a—c** (Scheme 2).

Evidently, the dimerization of radicals **B** occurs simultaneously to form vicinal dinitro compounds **5** and **6**.

The size of substituents at the C_α atom of the initial nitro compound has a substantial effect on the ratio of radical cross- and homocoupling processes, which determines the formation of the main (see Scheme 2) and by-products of electrolysis: the more bulky the substitu-

Scheme 2

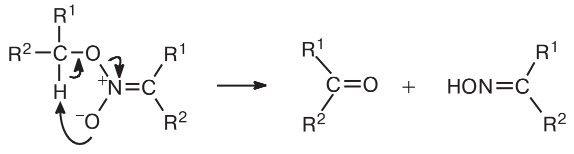


B is base

ents, the lower the contribution of the side reaction. The steric effect hinders, most likely, the transformation of radicals **A** into **B** and, on the contrary, these are the main products upon the electrooxidation of salts of lower *aci*-nitroalkanes.[21]

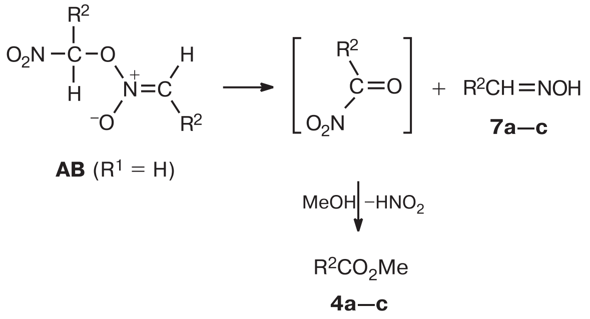
We assume that dimers **AB** are intermediates of the electrochemical transformation of the salts of the *aci*-nitro compounds into the identified products. They are alkyl esters of nitronic acids. It is known[23,24] that esters of this type, especially those obtained from salts of secondary *aci*-nitro compounds, decompose readily. For example, the esters with the C—H bond in the α-position to the ester oxygen disproportionate at room temperature to form ketones and oximes (Scheme 3).

Scheme 3



Taking into account this fact, esters **4a—c** and oximes **7a—c** should be expected as products of the similar reaction of the corresponding dimer **AB** (R^1 = H) upon the electrolysis of salts of primary *aci*-nitro hydrocarbons **2a—c** (Scheme 4). However, they were not found in the electrolysis products.

Scheme 4



This can be reasoned, in particular, by the efficient electrochemical transformation of these compounds into other products. For example, in the model experiment the conversion of benzaldehyde oxime was 95%, and benzaldehyde and methyl benzoate were the main electrolysis products (see Table 1, entry *7*). It was also found experimentally (see Table 1, entry *8*) that methyl benzoate was not formed upon the undivided electrolysis of benzaldehyde in MeOH against the background of MeONa. In this case, PhCHO is transformed into 1,2-diphenylethane-1,2-diol. These observations confirm indirectly that products **3a—c** and **4a—c** can be formed through oximes but only partially because their total yield cannot exceed 50%. The absence of $R^2C(O)NO_2$ in the electrolysis products is due to their transformation into esters **4a—c** by methanol.

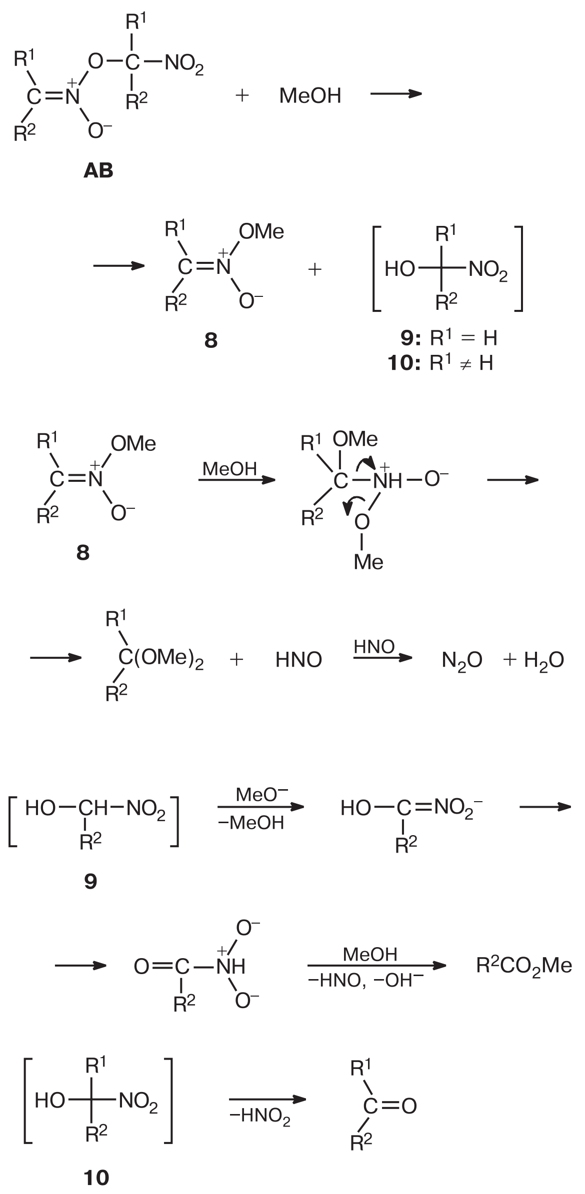
Another possible reason for the absence of oximes in the products of electrolysis of salts **2a—c** is that the decomposition of dimers **AB** can proceed *via* a mechanism different from that presented in Scheme 3. This possibility has also been mentioned previously.[23] Perhaps, the decomposition of dimers **AB** is preceded by ester interchange with methanol and the transformation of methyl nitronates **8** into substituted nitrocarbinols **9** and **10**. The final products, *viz*., ketones, ketals, and esters, are formed in the subsequent transformations of intermediate products **8—10** (Scheme 5).

Esters can be formed in the electrolysis of salts of primary *aci*-nitro compounds also due to the transformations of α-nitroalkyl radicals **B** (R^1 = H) presented in Scheme 6.

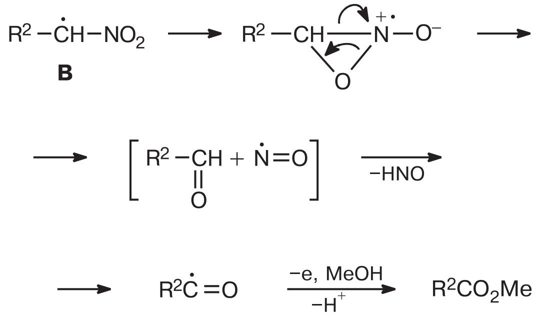
We hope to obtain arguments in favor of the proposed alternative mechanism in our further studies.

The behavior of the radicals generated by the electrolysis of salts **2b,d,f** differs substantially from that of the radicals obtained by the one-electron oxidation of these salts. This difference is resulted by the fact that a much higher concentration of radicals than the average concentration in the solution is created near the electrode due to the electrochemical reaction, while in the chemical reaction the radical concentration is approximately the same and very low in all points of the reaction medium. As a result, the predominant direction of transformation of the radicals generated in the electrochemical process is cross-coupling, while in the chemical pro-

Scheme 5

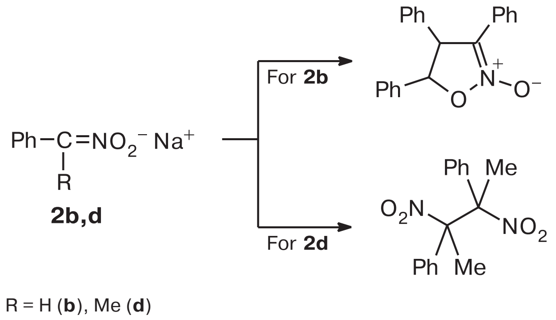


Scheme 6



cess it is homocoupling and the interaction with components of the medium, including one-electron oxidants and intermediate products of their decomposition. The one-electron oxidation of salt **2b** with silver nitrate, peroxydisulfates,[25,26] and the $S_2O_8{}^{2-}$—Ag^+ system[7] in an alkaline medium affords at first dimers of α-nitrobenzyl radicals and dimers of the latter with the corresponding nitronate radicals and sulfate radical anions. Then these dimers are transformed into nitrostilbene and benzaldehyde, which are formed[7] in 58 and 23% yields, respectively, and partially into 1-nitro-2-benzylstilbene (2%) and 3,4,5-triphenylisoxazole (2.4%). If the one-electron oxidation of the salts of α-*aci*-nitroalkylbenzenes, for example, **2b,d**, with silver nitrate is performed in a neutral medium (DMSO), the primary and secondary α-nitrobenzyl radicals generated from these salts are transformed into 3,4,5-triphenyl-4,5-dihydroisoxazole *N*-oxide and 2,3-dinitro-2,3-diphenylbutane,[26] respectively (Scheme 7).

Scheme 7



The oxidation of salt **2f** under these conditions also affords[26] only one product, *viz.*, 1,1´-dinitrobicyclohexane (**6**). Salt **2f** in a weakly alkaline medium is transformed[7] by $K_2S_2O_8$ into cyclohexanone and dimer **6** in 67 and 14—30% yields, respectively.

Thus, the data obtained suggest that the electrolysis of the salts of the *aci*-nitro compounds in methanol generates both the α-nitroalkyl radicals and mesomeric nitronate radicals, and the subsequent transformation of these radicals into the carbonyl compounds proceeds, at least partially, through the intermediate formation of esters of nitronic acids. For the salts of the secondary *aci*-nitro compounds this process is an electrochemical variant of the Nef reaction, providing the yield of ketones up to 95%, which confers it a preparative value.

Experimental

NMR spectra were recorded on a Bruker WM-250 spectrometer (250 MHz) in $CDCl_3$. IR spectra were recorded on a Specord M-80 instrument in CCl_4. GLC analysis was carried out on a Varian-3700 chromatograph (a flame-ionization detector, glass columns, 5% Carbowax 20M on Inerton and 5% XE-60 on Chromaton N-AW). Silufol UV-254 plates were used for TLC. Silica gel L 40/100 μm was used for flash chromatography (eluent hexane—AcOEt (1—5%)).

Commercial 1-nitrohexane (**1a**), nitrocyclohexane (**1f**), and DBU (Aldrich) were used. Methanol was dehydrated by distillation above $Mg(OMe)_2$. Nitromethyl- (**1b**)[5], β- and α-nitroethyl- (**1c,d**)[27], β-nitropropylbenzene (**1e**)[28], 2-nitroheptan-2-one (**1g**)[29], and methyl 4-nitrohexanoate (**1h**)[30] were synthesized using known procedures. *vic*-6,7-Dinitrododecane (**5**) and 1,1´-dinitrobicyclohexane (**6**) used as reference compounds in GLC analysis of electrolysis products were prepared from salts **2a,f** using a previously published procedure.[7]

Electrolysis of salts of *aci*-nitro compounds (general procedure). Nitro compound **1** (2—5 mmol) was dissolved in 20 mL of a solution of MeONa, KOH, or DBU (1—2 equiv.) in MeOH, and the mixture was stirred until the substrate transformed completely into the salt of its *aci*-form (0.5 h). Electrolysis was carried out in a undivided electrolyzer at a constant temperature with a platinum, graphite, or glassy-carbon anode ($S = 3$ cm^2) and a stainless steel cathode ($S = 3$ cm^2), which were remote at a distance of 3—5 mm, with vigorous stirring of the reaction mixture under conditions presented in Table 1. Electrolyzates were diluted with water (20 mL), acidified with AcOH (1 mL) to transform unreacted salt **2** into the initial compound, and extracted with $CHCl_3$ (2×20 mL). An aliquot was taken from the combined extracts, dried above potash, and analyzed by GLC using authentic reference compounds (according to the data of analysis, under these conditions salts **2d—h** are mainly transformed into ketones **3d—h** and their ketals, whereas salts **2a—c** are transformed into aldehydes **3a—c**, their acetals, and esters **4a—c**). To hydrolyze ketals and acetals, the remaining portion of the combined extracts was stirred for 0.5 h with a 2 *M* solution of HCl (10 mL), neutralized with a 5% solution of $NaHCO_3$ (10 mL), and dried above potash. The yield of carbonyl compounds **3a—h**, esters **4a—c**, and dinitroalkanes **5** and **6** was determined by GLC using an internal reference (dodecane, hexadecane). Products **3g** and **3h** were identified by the IR spectra and ^{1}H and ^{13}C NMR spectra of the preparations isolated by flash chromatography on silica gel.

Heptane-2,5-dione (3g).[16,17] IR, ν/cm^{-1}: 1735. ^{1}H NMR, δ: 1.02 (t, 3 H, $J = 7$ Hz); 2.17 (s, 3 H); 2.45 (q, 2 H, $J = 7$ Hz); 2.67 (m, 4 H).

Methyl 4-oxohexanoate (3h).[20] IR, ν/cm^{-1}: 1740. ^{1}H NMR, δ: 1.01 (t, 3 H, $J = 7$ Hz); 2.43 (q, 2 H, $J = 7$ Hz); 2.52 (t, 2 H, $J = 6.5$ Hz); 2.68 (t, 2 H, $J = 6.5$ Hz); 3.61 (s, 3 H). ^{13}C NMR, δ: 7.72 (Me); 27.78, 35.83, and 36.58 (CH_2); 51.64 (OMe); 173.17 (COO); 209.20 (C=O).

Electrolysis of benzaldehyde and benzaldehyde oxime. These experiments were carried out in MeOH in the presence of 1 equiv. of MeONa using the general procedure of electrolysis of nitro compounds. The results are presented in Table 1.

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