Electrosynthesis of esters of mono- and dioxoalkanoic and alkanedioic acids on the basis of nitro-substituted alkyl carboxylates and cycloalkanones*

Yu. N. Ogibin, A. I. Ilovaiskii, V. M. Merkulova, and G. I. Nikishin*

N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5328. E-mail: ogibin@ioc.ac.ru

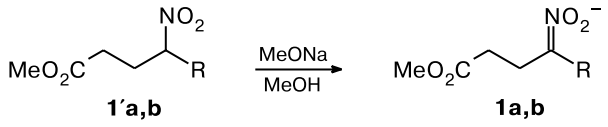
A one-pot electrochemical method for the synthesis of methyl monooxoalkanoates with the carbonyl group in position 4, methyl dioxoalkanoates with the oxo groups in positions 4,7-, 6,9-, 7,10-, and 12,15, and methyl 4-oxoalkanedioates was developed. This method is based on amperostatic electrolysis in an undivided cell of the salts of esters of nitroalkanoic acids and their adducts with CH_2=CHX (X = Ac, CO_2Me).

Key words: methyl 4-oxoalkanoates, dimethyl 4-oxoalkanedioates, methyl 4,7-, 6,9-, 7,10-, and 12,15-dioxoalkanoates, electrolysis, salts of nitro compounds, methyl 4-nitroalkanoates, 2-nitrocycloalkanones.

Previously, we found[1] that salts of nitro compounds (SNC) in methanol can be efficiently transformed with high selectivity into carbonyl compounds by amperostatic electrolysis in an undivided cell. As a development of this study, this work deals with electrochemical transformations of SNC **1—4**, containing acyl and methoxycarbonyl groups (Schemes 1 and 2). The goal was to develop a new route to esters of mono- and dioxoalkanoic and monooxoalkanedioic acids, which are versatile blocks for the construction of heterocyclic systems, cyclopentanoid structures and pheromones.[2]

The starting salts **1** were prepared by the reaction of methyl 4-nitroalkanoates **1′a,b** with 1 equiv. of MeONa, and salts **2**, **3**, and **4** were synthesized from methyl 4-nitrobutanoate (**5**) and 2-nitrocycloalkanones **6b—e** (Schemes 1 and 2).

Scheme 1

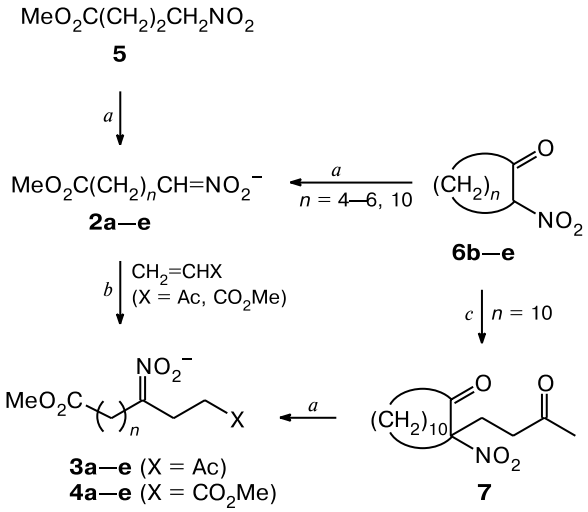


1′a,b **1a,b**

R = Me (**a**), Et (**b**)

The rate of addition of salts **2** to methyl vinyl ketone (MVK) and methyl acrylate (MA) markedly decreases with an increase in the chain length. For this reason and also due to oligomerization of MVK under given conditions, salt **3e** cannot be obtained in this way. This salt was synthesized by the reaction of 2-nitrocyclododecanone (**6e**) with MVK in a THF solution in the presence of a catalytic amount of Ph_3P [2] followed by treatment of adduct **7** with a methanolic solution of MeONa.

Scheme 2



n = 2 (**a**), 4 (**b**), 5 (**c**), 6 (**d**), 10 (**e**)

Reagents and conditions: *a*. MeOH, MeONa (1 equiv.); *b*. MVK or MA (1.5 equiv.); *c*. MVK (1.5 equiv.), THF, Ph_3P.

* Dedicated to Academician I. P. Beletskaya on the occasion of her anniversary.

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Table 1. Preparation of salts **1** and **2** from methyl 4-nitroalkanoates **1´** and **5** and 2-nitrocycloalkanones **6** and electrolysis of the salts[a]

Nitro compound	Salt preparation			Electrolysis			
	T/°C	τ/h	Salt	Anode material	Salt conversion (%)	Product	Yield[b] (%)
1´a	20	0.5	**1a**	Pt	85	**8a**	65
1´b	20	0.5	**1b**	Pt	87	**8b**	76
1´b	20	0.5	**1b**	G	68	**8b**	58
1´b	20	0.5	**1b**	GC	85	**8b**	75
5	20	0.5	**2a**	Pt	100	**11a**	15[c]
6b	60	2	**2b**	Pt	100	**11b**	60
6c	60	2	**2c**	Pt	100	**11c**	49
6e	60	3	**2e**[d]	Pt	90	**11e**	40

[a] Conditions for salt preparation: nitro compound (2 mmol), MeONa (1 equiv.) in MeOH (50 mL). Electrolysis conditions: amperostatic mode, anode current density 100 mA cm^{-2}, quantity of electricity 2 *F* mol^{-1}, 10—15 °C; a platinum (Pt), graphite (G) or glassy carbon (GC) anode and a stainless-steel cathode.
[b] Based on the starting nitro compound according to GLC analysis (for products **8**) or isolated yields (for products **11**).
[c] Methyl 4-oxobutanoate (**12**) is also formed, yield 5%.
[d] Degree of conversion of salt **6e** into salt **2e** is 80%.

Electrolysis of salts **1—4** as 0.1 M solutions in MeOH was carried out at 10—15 °C in an undivided cell with a platinum anode and a steel cathode. The electrolysis was performed in an amperostatic mode at an anodic current density of 100 mA cm^{-1} by passing 2 *F* of electricity per mole of the substrate. In this process, salts **1—4** act simultaneously as reactants and supporting electrolytes. In combination with generation of MeONa during the electrolysis, this eliminates the necessity of using other electrolytes and allows one to reach almost complete conversion of salts **1—4** even when only the theoretical amount of electricity has been passed (2 *F* mol^{-1}). The degree of conversion of salts **1** and **2** and the product yields diminish when platinum is replaced by graphite (Table 1).

Analysis of the electrolysis products after treatment of electrolyzates with dilute HCl shows (Scheme 3, Tables 1

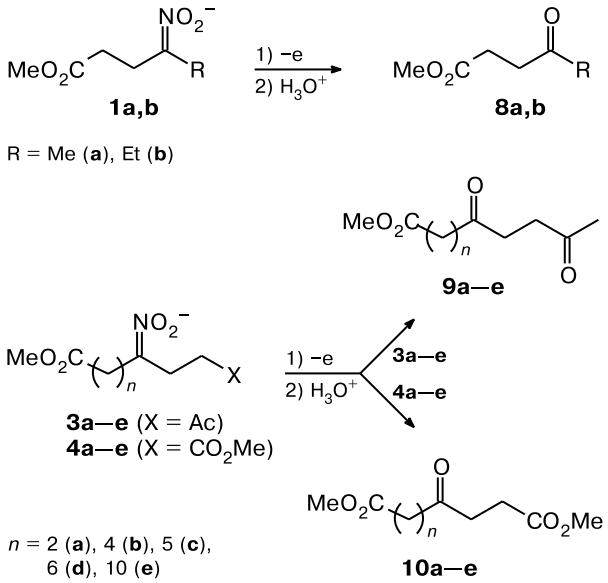
Table 2. Preparation of salts **2—4** and their electrolysis[a]

Starting compounds	Step *a*			Step *b*			Electrolysis		
	T/°C	τ/h	Salt	*T*/°C	τ/h	Salt	Anode material	Product	Yield[b] (%)
5, MVK	20	0.5	**2a**	20	12	**3a**	Pt	**9a**	60
5, MA	20	0.5	**2a**	60	3	**4a**	Pt	**10a**	77
5, MA	20	0.5	**2a**	60	3	**4a**	GC	**10a**	75
6b, MVK	60	2	**2b**	60	2	**3b**	Pt	**9b**	68
6b, MA	60	2	**2b**	60	2	**4b**	GC	**10b**	70
6b, MA	60	2	**2b**	60	2	**4b**	Pt	**10b**	70
6c, MVK	60	2	**2c**	60	3.5	**3c**	Pt	**9c**	50
6c, MA	60	2	**2c**	60	3.5	**4c**	Pt	**10c**	67
6d, MVK	60	2	**2d**	60	3.5	**3d**	Pt	**9d**	78
6d, MA	60	2	**2d**	60	4	**4d**	Pt	**10d**	53
6e, MVK	20	48	**7**[c]	20	5	**3e**	Pt	**9e**	37
6e, MA	60	3.5	**2e**	60	5	**4e**	Pt	**10e**	48[d]

[a] Step *a*: MeONa (1 equiv.) in MeOH (50 mL); step *b*: MVK or MA (1.5 equiv.); electrolysis conditions are given in note *a* to Table 1.
[b] Isolated yield based on the initial nitro compound.
[c] The reaction of 2-nitrocyclododecane (**6e**) with MVK in THF in the presence of 0.1 equiv. of Ph_3P (step *c*, Scheme 2) gave adduct **7**, which was converted into salt **3e** under conditions of step *a*.
[d] The degree of conversion of **6e** was 85%.

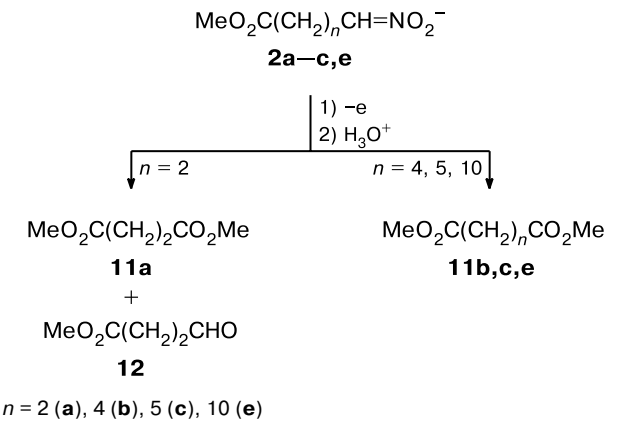
and 2) that salts **1a,b** have been converted into monooxoalkanoates **8a,b** with a 68—87% degree of conversion and a 77—90% selectivity. Salts **3a—e** are transformed into dioxoalkanoates **9a—e**, and salts **4a—e** give rise to monooxoalkanedioates **10a—e**; the selectivities are 37—68% and 48—77%, respectively, based on the starting nitro compound.

Scheme 3



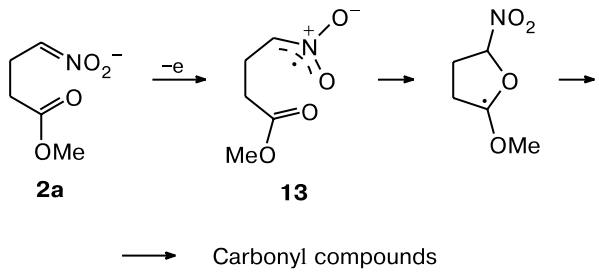
Under similar conditions, salts **2a—c** and **2e** are transformed into esters **11a—c** and **11e** (Scheme 4), which were formed in 15, 60, 49, and 40% yields, respectively (see Table 1); in addition, the reaction gives unidentified resinous products, which remain at the origin during TLC analysis of the electrolyzates (elution with petroleum ether—AcOEt, 100 : 0 to 4 : 1). Apart from the above-mentioned products, electrolysis of salts **2a** gives methyl 4-oxobutanoate (**12**) in ~5% yield.

Scheme 4



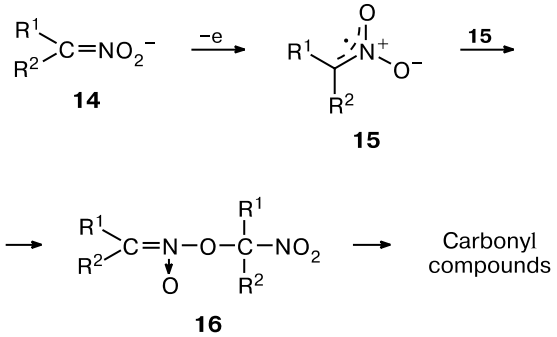
As indicated by the obtained results (low yield of the aldehyde, the formation of side and unidentified resinous products), the transformation of salts **2** into esters **11** and aldehyde **12** is largely complicated by competitive participation of these salts in side reactions. One of these is addition of the salts of primary nitro compounds to formaldehyde formed from MeOH as a side product (Henry reaction). The major identified product obtained in the electrolysis of the salt of 1-nitrohexane, namely, 2-nitroheptan-1-ol, have resulted from this reaction. In the case of salt **2a**, electrogenerated radicals **13** are apparently involved into an intramolecular radical cyclization (Scheme 5), similar to the reaction observed previously during the free-radical addition of dimethyl glutarate to 1-alkenes[3] and in the free-radical cyclization of 3-carboxy- and 2-alkoxycarbonylpropyl radicals.[4]

Scheme 5



When considering the mechanism of electrochemical transformation of SNC into carbonyl compounds,[1] we initially suggested that it includes cross-dimerization of radicals **15**, electrogenerated from SNC of type **14**, to give nitronic esters **16** and the subsequent transformation of esters **16** into carbonyl compounds during the electrolysis and workup of the electrolyzate (Scheme 6).

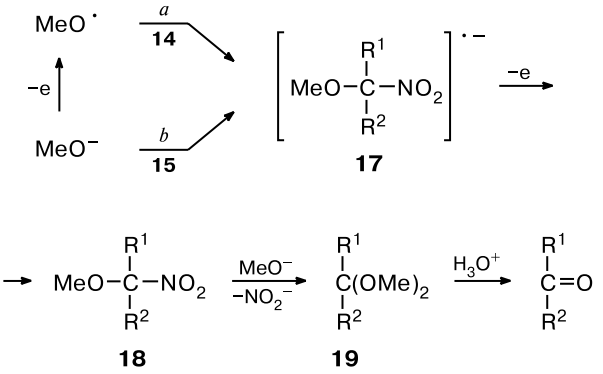
Scheme 6



While proposing this mechanism relying on indirect experimental data reported in a previous study,[1] we overlooked that electrolysis of SNC in MeOH may be accompanied by electrooxidative coupling of these salts with

methoxyl radicals and anions, *i.e.*, by a process similar to that taking place during the known oxidative coupling of these salts with free radicals[5] and nitrite, cyanide, arylsulfonate, and azide anions.[6—9] According to the studies cited, this process consists of two steps: coupling of the free radical generated by single-electron oxidation of the SNC or the anion with either the anion or the SNC and the subsequent oxidation of the resulting radical anions. These data suggest, by analogy, an alternative mechanism for the electrochemical transformation of SNC into carbonyl compounds. As the key intermediate steps, this mechanism may include coupling of methoxyl and nitronate anions **14** with electrogenerated methoxyl and nitronate radicals **15** (Scheme 7, pathways *a* and *b*) and subsequent electrooxidation of the resulting radical anions **17** to give α-methoxynitroalkanes **18**. The transformation of these products into ketals **19** is apparently due to nucleophilic substitution of a methoxy group for the nitro group on treatment with sodium methoxide formed in the electrolysis.

Scheme 7



This alternative mechanism for the electrochemical transformation of SNC into carbonyl compounds is in much better agreement with the experimental results obtained for the electrolysis of SNC in MeOH both previously[1] and in this work than the mechanism proposed earlier (see Scheme 6). In particular, it provides a more substantiated explanation for the fact that the electrolysis of SNC performed under the given conditions virtually does not yield *vic*-dinitroalkanes, the products of oxidative dimerization of SNC. Indeed, according to this mechanism, the transformation of SNC into carbonyl compounds along pathway *a* does not involve the nitronate radicals responsible for the formation of *vic*-dinitroalkanes; judging by the results of this work, this route is almost the only or, at least, the major one. An important argument supporting this assumption is the fact that the transformation of SNC into ketals **19** is promoted by high anodic current densities and the use of platinum as the anode, *i.e.*, by electrolysis conditions favorable for the electrogeneration of methoxyl radicals from MeOH.

Generally, the main outcome of this study is the development of an original electrochemical method for the synthesis of alkyl oxo- and dioxocarboxylates from readily available nitro-substituted alkyl carboxylates and cycloalkanones. An important advantage of this method over the traditional routes for the synthesis of these compounds based on the use of inorganic or organic oxidants is that these reagents are now replaced by electric current and thus the environmental pollution is reduced.

Experimental

NMR spectra were recorded on Bruker AC-200, Bruker WM-250, and Bruker AM-300 spectrometers using $CDCl_3$ as the solvent. IR spectra were measured on a Specord-80 spectrometer in thin films and in CCl_4 solutions. Laboratory power sources B5-44 and B5-50 with output current stabilization were used to generate the direct current. The quantity of electricity passed was measured using an electronic coulometer with a digital display and with a current measurement limit of 20 A (manufactured at the design department, Institute of Organic Chemistry, Russian Academy of Sciences). GLC analysis was carried out using a Varian-3700 chromatograph (flame ionization detector, glass columns, 5% Carbowax 20M on Inerton and 5% XE-60 on Chromaton N-AW). TLC analysis was carried out using Silufol UV-254 plates. Flash chromatography was carried out on silica gel L 40/100 μm. Methanol was dehydrated by distillation over magnesium methoxide. Methyl vinyl ketone, methyl acrylate, nitrohexane, and nitrocyclohexane were commercial preparations (Aldrich).

The initial methyl 4-nitroalkanoates **1´a,b** and **5** were prepared by the reaction of the corresponding primary nitroalkanes with methyl acrylate,[10—12] and 2-nitrocycloalkanones **6b—e** were synthesized by a known procedure[13,14] from appropriate cycloalkanones.

2-Nitrocyclohexanone (6b).[13] M.p. 43 °C (hexane). ^{1}H NMR, δ: 1.65—1.90 (m, 2 H); 1.90—2.22 (m, 2 H); 2.30—2.72 (m, 4 H); 5.24 (dd, 1 H, J = 12.5 Hz, J = 6.5 Hz).

2-Nitrocycloheptanone (6c).[13] M.p. 41—42 °C (hexane). ^{1}H NMR, δ: 1.39—1.56 (m, 1 H); 1.56—1.81 (m, 2 H); 1.81—2.10 (m, 3 H); 2.10—2.51 (m, 2 H); 2.51—2.87 (m, 2 H); 5.42 (dd, 1 H, J = 7.5 Hz, 2.5 Hz).

2-Nitrocycloheptanone (6d).[13] B.p. 62—65 °C (0.1 Torr); n_D^{20} 1.5040. ^{1}H NMR, δ: 1.00—3.00 (m, 12 H); 5.40 (dd, 1 H, J = 6.0 Hz).

2-Nitrocyclododecanone (6e).[13] M.p. 78 °C (hexane). ^{1}H NMR, δ: 1.20—1.45 (m, 14 H); 1.71 (m, 1 H); 1.86 (m, 1 H); 2.13 (m, 1 H); 2.37 (m, 1 H); 2.70 (m, 2 H); 5.16 (dd, 1 H, J = 10.5 Hz, J = 4.5 Hz). ^{13}C NMR, δ: 20.87, 21.52, 22.45, 23.22, 23.47, 23.89, 25.54, 25.76, 27.88 (CH_2); 36.16 ($\underline{C}H_2CO$); 92.08 (C); 199.92 (CO).

Synthesis of 4-oxoalkanoates (8a,b) and alkanedioates (11a—c,e) (general procedure) (see Table 1). Methyl nitroalkanoate **1´** or **5** or 2-nitrocycloalkanone **6** (2 mmol) was mixed with 20 mL of a methanolic solution of MeONa (1 equiv.) and the mixture was stirred until the nitro compound was completely converted into its salt (0.5—3 h at 20—60 °C). Electroly-

sis was carried out with intense stirring in an undivided cell maintained at a constant temperature and equipped with a platinum, graphite, or glassy carbon anode (3 cm^2) and a stainless-steel cathode (3 cm^2) separated by a 3—5 mm distance. The electrolysis was performed under amperostatic conditions, with an anodic current density of 100 mA cm^{-2}; the quantity of electricity was 2 *F* mol^{-1} and the temperature was 10—15 °C. After completion of the electrolysis, the reaction mixture with diluted with water (40 mL), acidified with glacial AcOH (1 mL) to transform the unreacted part of the *aci*-form salt into the initial nitro compound, and extracted with $CHCl_3$ (2×20 mL). An aliquot portion was taken from the combined extracts, dried with K_2CO_3, and analyzed by GLC using an internal standard (dodecane, hexadecane) to estimate the degree of conversion of the starting compound. To hydrolyze the resulting ketals, the rest of the combined extracts was stirred with 2 *M* HCl (10 mL) for 0.5 h, neutralized with a 5% solution of $NaHCO_3$ (10 mL), dried with K_2CO_3, and concentrated using a rotary evaporator. The individual products were isolated by flash chromatography of the residue using 100 : 0 to 90 : 10 petroleum ether—AcOEt mixtures as eluents.

Methyl 4-oxopentanoate (8a).[11] B.p. 65—66 °C (0.3 Torr). IR, ν/cm^{-1}: 1718, 1735. ^{1}H NMR, δ: 2.18 (s, 3 H); 2.57 (t, 2 H, *J* = 7 Hz); 2.73 (t, 2 H, *J* = 7 Hz); 3.66 (s, 3 H, OMe).

Methyl 4-oxohexanoate (8b).[15] ^{1}H NMR, δ: 1.01 (t, 3 H, *J* = 7.2 Hz); 2.42 (q, 2 H, *J* = 7.2 Hz); 2.52 (t, 4 H, *J* = 6.5 Hz); 2.68 (t, 4 H, *J* = 6.5 Hz); 3.62 (s, 3 H, OMe). ^{13}C NMR, δ: 7.72 (Me); 27.77, 35.83 and 36.58 (CH_2); 51.64 (OMe); 173.17 (COO); 209.20 (CO).

Dimethyl succinate (11a).[16] ^{1}H NMR, δ: 2.64 (s, 4 H); 3.71 (s, 6 H, OMe).

Dimethyl adipate (11b).[16] ^{1}H NMR, δ: 1.65 (m, 4 H); 2.32 (m, 4 H); 3.63 (s, 6 H).

Dimethyl pimelate (11c).[16] ^{1}H NMR, δ: 1.40 (m, 2 H); 1.68 (m, 4 H); 2.38 (m, 4 H); 3.68 (s, 6 H).

Dimethyl dodecane-1,12-dioate (11e).[16] ^{1}H NMR, δ: 1.28 (s, 12 H); 1.52 (m, 4 H); 2.30 (t, 4 H, *J* = 7.1 Hz); 3.68 (s, 6 H). ^{13}C NMR, δ: 25.04, 29.22, 29.28, 29.43, 34.19 (CH_2); 51.47 (OMe); 174.35 (COO).

Electrooxidation of Na salt of 1-nitrohexane. 1-Nitrohexane (0.262 g, 2 mmol) was mixed with 20 mL of a methanolic solution of MeONa (1 equiv.) and the mixture was stirred for 0.5 h at 20 °C. Electrolysis and the workup of the electrolyzate were carried out according to the above general procedure. Flash chromatography (gradient elution in 100 : 0 to 1 : 1 hexane—AcOEt systems) afforded 2-nitroheptanol (yield 30%), methyl hexanoate (10%), hexanal (5%), and 5,6-dinitrododecane (3%).

2-Nitroheptan-1-ol.[17] ^{1}H NMR, δ: 0.90 (t, 3 H); 1.33 (m, 8 H); 1.70—2.00 (m, 2 H); 3.35 (br.s, 1 H, OH); 3.90 (dd, 1 H, *J* = 12.4 Hz, *J* = 2.8 Hz); 4.04 (dd, 1 H, *J* = 12.4 Hz, *J* = 8.0 Hz); 4.59 (m, 1 H, CH). ^{13}C NMR, δ: 13.99 (C(7)); 22.38 (C(6)); 25.42 (C(4)); 29.94, 31.22 (C(3), C(5)); 63.32 (C(1)); 89.56 (C(2)).

Methyl hexanoate.[16] ^{1}H NMR, δ: 0.89 (t, 3 H); 1.28 (m, 4 H); 1.53 (m, 2 H); 2.32 (t, 2 H, *J* = 7 Hz); 3.68 (s, 3 H).

Synthesis of methyl 4,7-dioxooctanoate (9a) and methyl 4-oxoheptane-1,7-dioate (10a) (see Table 2). Methyl 4-nitrobutanoate (**5**) (2 mmol) was mixed with 20 mL of a methanolic solution of MeONa (1 equiv.), and the mixture was stirred at ~20 °C until the substrate was completely converted into salt **2a** (30 min). Methyl vinyl ketone or MA (1.5 equiv.) was added and the reaction mixture was stirred for 12 h at 20 °C in the case of MVK or for 3 h at 60 °C in the case of MA until complete conversion of salt **2a** (GLC monitoring). Electrolysis was carried out according to the general procedure.

Methyl 4,7-dioxooctanoate (9a).[18] ^{1}H NMR, δ: 2.16 (s, 3 H, Me); 2.58 (t, 2 H, *J* = 7 Hz); 2.71 (s, 4 H); 2.78 (t, 2 H, *J* = 7 Hz); 3.66 (s, 3 H, OMe). ^{13}C NMR, δ: 27.74, 36.03, 36.94 and 37.08 (CH_2); 29.86 (Me); 51.78 (OMe); 173.15 (COO); 207.03 and 207.39 (CO).

Dimethyl 4-oxoheptane-1,7-dioate (10a).[12,19] IR, ν/cm^{-1}: 1740, 1710. ^{1}H NMR, δ: 2.58 (t, 4 H, *J* = 7 Hz); 2.76 (t, 4 H, *J* = 7 Hz); 3.64 (s, 6 H, OMe).

Synthesis of methyl dioxoalkanoates (9b—d) and monooxoalkanedioates (10b—e) (see Table 2). 2-Nitrocycloalkanone **6b—e** (2 mmol) was mixed with 20 mL of a methanolic solution of MeONa (1 equiv.), the mixture was stirred at 60 °C up to complete transformation of the substrate into sodium salt **2** (2 h), MVK or MA (1.5 equiv.) was added, and the mixture was stirred up to complete conversion of salt **2** (2—5 h, GLC monitoring). The electrolysis and electrolyzate workup were carried out according to the general procedure. The individual products were isolated by flash chromatography (gradient elution in the hexane—AcOEt system, 100 : 0 to 4 : 1).

Methyl 6,9-dioxodecanoate (9b).[2] IR, ν/cm^{-1}: 1730, 1708. ^{1}H NMR, δ: 1.62 (m, 4 H); 2.18 (s, 3 H, Me); 2.32 (m, 2 H); 2.47 (m, 2 H); 2.68 (m, 4 H); 3.66 (s, 3 H, MeO). ^{13}C NMR, δ: 23.25, 24.47, 33.86, 36.12, 36.98 and 42.35 (CH_2); 29.91 (Me); 51.52 (MeO); 173.85 (COO); 207.13 and 208.93 (CO).

Methyl 7,10-dioxoundecanoate (9c).[2] ^{1}H NMR, δ: 1.29 (m, 2 H); 1.58 (m, 4 H); 2.14 (s, 3 H, Me); 2.26 (t, 2 H, *J* = 7.5 Hz); 2.42 (t, 2 H, *J* = 7.5 Hz); 2.65 (m, 4 H); 3.62 (s, 3 H, OMe). ^{13}C NMR, δ: 23.35, 24.67, 28.60, 33.82, 36.05, 36.89 and 42.44 (CH_2); 29.90 (Me); 51.43 (OMe); 173.96 (COO); 207.09 and 209.15 (CO).

Methyl 8,11-dioxododecanoate (9d).[2] ^{1}H NMR, δ: 1.27 (m, 4 H); 1.55 (m, 4 H); 2.14 (s, 3 H, Me); 2.25 (t, 2 H, *J* = 6 Hz); 2.40 (t, 2 H, *J* = 6 Hz); 2.64 (m, 4 H); 3.61 (s, 3 H, OMe). ^{13}C NMR, δ: 23.53, 24.70, 28.72, 28.83, 33.93, 36.02, 36.86 and 42.60 (CH_2); 29.91 (Me); 51.42 (OMe); 174.10 (COO); 207.23 and 209.40 (CO).

Methyl 6-oxononane-1,9-dioate (10b).[2] IR, ν/cm^{-1}: 1732, 1710. ^{1}H NMR, δ: 1.58 (m, 4 H); 2.27 (m, 2 H); 2.43 (m, 2 H); 2.49—2.72 (m, 4 H); 3.61 and 3.62 (both s, 6 H, MeO). ^{13}C NMR, δ: 23.14, 24.39, 27.70, 33.76, 37.01 and 42.24 (CH_2); 51.47 and 51.73 (OMe); 173.15 and 173.70 (COO); 208.33 (CO).

Dimethyl 7-oxodecane-1,10-dioate (10c).[2] ^{1}H NMR, δ: 1.30 (m, 2 H); 1.60 (m, 4 H); 2.29 (t, 2 H, *J* = 7 Hz); 2.43 (t, 2 H, *J* = 7 Hz); 2.56 (t, 2 H, *J* = 6 Hz); 2.69 (t, 2 H, *J* = 6 Hz); 3.64 and 3.66 (both s, 6 H, OMe). ^{13}C NMR, δ: 23.18, 24.52, 27.60, 28.48, 33.68, 36.91 and 42.28 (CH_2); 51.28 and 51.56 (OMe); 173.07 and 173.85 (COO); 208.51 (CO).

Dimethyl 8-oxoundecane-1,11-dioate (10d).[2] IR, ν/cm^{-1}: 1740, 1725. ^{1}H NMR, δ: 1.28 (m, 4 H); 1.56 (m, 4 H); 2.26 (t, 2 H, *J* = 6 Hz); 2.40 (t, 2 H, *J* = 6 Hz); 2.53 (t, 2 H, *J* = 6 Hz); 2.67 (t, 2 H, *J* = 6 Hz); 3.62 and 3.63 (both s, 6 H, MeO). ^{13}C NMR, δ: 23.47, 24.67, 27.65, 28.71, 28.79, 33.90, 36.95 and 42.54 (CH_2); 51.39 and 51.70 (OMe); 173.20 and 174.06 (COO); 208.85 (CO).

Dimethyl 12-oxopentadecane-1,15-dioate (10e).[2] M.p. 57 °C (hexane). ^{1}H NMR, δ: 1.25 (s, 12 H); 1.59 (m, 4 H); 2.28 (t,

2 H, J = 6 Hz); 2.43 (t, 2 H, J = 6 Hz); 2.56 (t, 2 H, J = 6 Hz); 2.70 (t, 2 H, J = 6 Hz); 3.65 and 3.66 (both s, 6 H, OMe). ^{13}C NMR, δ: 23.78, 24.93, 27.74, 29.08—29.33, 34.08, 37.00 and 42.78 (CH_2); 51.34 and 51.67 (OMe); 173.20 and 174.20 (COO); 208.93 (CO).

Methyl 12,15-dioxohexadecanoate (9e).[2] A solution of 2-nitrocyclododecanone (**6e**) (2 mmol), MVK (3 mmol), and Ph_3P (0.1 mmol) in THF (10 mL) was stirred at 20 °C until **6e** was completely converted (48 h, GLC monitoring). A solution was concentrated to dryness and the residue was recrystallized from MeOH to give 2-nitro-2-(3-oxobutyl)cyclododecanone (**7**), yield 80%, m.p. 138—140 °C. ^{1}H NMR, δ: 0.93—1.50 (m, 16 H); 2.05—2.50 (m, 7 H); 2.14 (s, 3 H); 2.75—2.87 (m, 1 H). ^{13}C NMR, δ: 19.13, 21.36, 21.80, 21.94, 22.58, 23.28, 26.21, 26.38, 26.91, 30.51, 32.68 and 37.31 (CH_2); 29.95 (Me); 100.15 (C(12)); 200.82 and 205.86 (CO). The transformation of nitroketone **7** into salt **3e**, its electrolysis, and electrolyzate workup were carried out by the general procedure. Ester **9e** was isolated by flash chromatography (gradient elution in a hexane—AcOEt system, 100 : 0 to 8 : 1). IR, ν/cm^{-1}: 1730, 1700. ^{1}H NMR, δ: 1.28 (s, 12 H); 1.65 (m, 4 H); 2.14 (s, 3 H, Me); 2.25 (t, 2 H, J = 6 Hz); 2.42 (t, 2 H, J = 6 Hz); 2.62 (m, 4 H); 3.62 (s, 3 H, OMe). ^{13}C NMR, δ: 23.63, 24.72, 28.70, 28.87—29.40, 33.93, 36.02, 37.13 and 42.60 (CH_2); 29.93 (Me); 51.41 (OMe); 174.10 (COO); 207.13 and 209.53 (CO).

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