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Electroorganic Synthesis 65.§ Anodic Homocoupling of Carboxylic Acids Derived from Fatty Acids

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Dedicated to Professor Lennart Eberson on the occasion of his 65th birthday

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Fatty acid derived carboxylic acids with double bonds, hydroxy-, amino-, keto-, ester- and epoxy groups are anodically coupled to dimers (Kolbe electrolysis) in 29 to 81% yield and up to a 2.5 mol scale. Problems due to the low conductivity of fatty acid salts were overcome by the use of a flow cell with a narrow electrode gap. Fatty acids with branched alkyl chains gave dimers with interesting emulsifying properties. Dimethyl hexadecanedioate, accessible from methyl azelate, could be cyclized and further converted into homomuscone and muscone in a few steps. A commercial mixture of dimeric fatty acids (C_{36}-dicarboxylic acids) has been coupled to give C_{70}-diesters.

Anodic decarboxylation of carboxylic acids has, since the initial work of Kolbe in 1849,[1] been applied to CC-bond forming reactions by homolytic coupling. The mechanism of this important electrochemical reaction, the preparative scope and numerous synthetic applications have been covered in several reviews. [2]

Advantages of anodic decarboxylation compared with non-electrochemical radical homocoupling reactions[3] are: (1) simple reaction conditions (the potential of the working electrode need not be controlled, an undivided cell can be used, 5 to 10% of the neutralized carboxylic acid in methanol serves in most cases as solvent/supporting electrolyte); (2) the costs for the reagent electricity are low; (3) scale-up is comparatively easy, which also makes the reaction attractive for technical use;[4] (4) the starting compounds, carboxylic acids, are readily available in a wide structural variety.

Anodic decarboxylation converts carboxylates on a preparative scale into radicals that react in non-chain processes by homocoupling, by heterocoupling in the coelectrolysis of two different acids or by inter- and intra-molecular addition to double bonds.[2,5] The intermediate radicals can also be further oxidized to carbocations, when certain reaction condition predominate, so that anodic decarboxylation is both a selective source of free radicals and of carbocations. The radical pathway is supported by a slightly acidic electrolyte, which requires 5–10% neutralization of the acid, a high current density (100–500 mA cm^{-2}), smooth platinum or platinized titanium as anode material, avoidance of additives or supporting electrolyte in the solvent except for the alkali metal carboxylate, and hydrogen atoms or electron-accepting substituents in the α-position of the carboxylic acid.

In the sixties Lennart Eberson contributed strongly to the field of anodic decarboxylation with preparative and mechanistic work. He synthesized a large variety of substituted succinates by homocoupling of alkyl malonates.[6a,b] He showed convincingly that the intermediate radicals are not adsorbed at the electrode. For that purpose he used acids with a stereogenic center in the α-position, that led to racemic coupling products, which strongly support free radicals as intermediates.[6c] Further proof of the presence of free radicals was the behavior of α-cyano radicals, obtained by decarboxylation of cyanoacetic acid; they form the same ratio of CC/CN-coupling products as those generated in homogeneous solution.[6d] The formation of products that originate from carbocationic intermediates has been connected with the ionization potentials of the intermediate radicals.[6e]

Kolbe electrolysis has been applied, in several examples, to the synthesis of natural and unnatural fatty acids.[7] Here we report on radical homocoupling reactions

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that give new oleochemicals, starting from carboxylic acids, derived mostly from fatty acids.

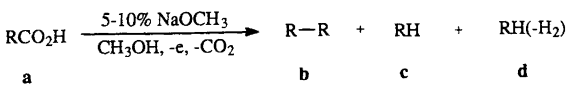
Results

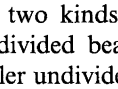
Choice of the electrolysis cell. For Kolbe electrolysis high current densities are needed, which generate high radical concentrations, that favor radical coupling. They furthermore lead to a fast conversion and a very positive anode potential that promotes the oxidation of the negatively charged carboxylate and disfavors the oxidation of the neutral solvent methanol. On the other hand the high resistance of the electrolyte due to the low conductivity of fatty acid salts in methanol and due to the low degree of neutralization necessitates small electrode distances to avoid high cell voltages and the evolution of excessive heat. To meet these conditions two kinds of cell have been used in this work: an undivided beaker-type cell (cell A)[8] and a larger and a smaller undivided circulation cell[8] (cell B, C); all are operated at constant current density of 200 mA cm^{-2}.

The beaker-type cell (cell A) was used for the electrolysis of 1–30 mmol carboxylic acid, dissolved in 30 ml methanol and neutralized to an extent of 5–10% with sodium methoxide. The gap between the electrodes (platinum foils, area 4 cm^2, 0.01 mm thickness, supported on a Teflon frame) was 2–4 mm. Depending on the kind and concentration of acid, cell voltages of 40–110 V had to be applied. For larger-scale electrolyses (100–200 g substrate in 250 ml methanol) the larger circulation cell (cell B) was used. In this case the electrode distance (0.2–1 mm) was very small and allowed electrolyses at cell voltages of 5–15 V. The cell house (V 4 A-steel) served simultaneously as cathode (electrode area: 18 cm^2). A platinum foil anode was pressed by a brass plate as current feeder against a silicon seal. In the narrow gap between the electrodes the electrolyte flow is high, which prevents or retards passivation of the electrodes due to formation of insulating deposits.

Hydrocarbons by dimerization of fatty acids. Kolbe electrolysis can lead selectively and in one step from readily available carboxylic acids to specific long-chain hydrocarbons. Electrolysis of oleic (**1a**), erucic (**2a**), stearic (**3a**) isopalmitic (**4a**) and isostearic acid (**5a**) afforded dimers and disproportionation products (Scheme 1, Table 1). The conversions with **1a**–**3a** were only moderate. The dimers **1b**–**3b**, which are fairly insoluble in methanol, partially precipitated at the electrode (cell A). This led to high cell voltages and made premature interruption of the electrolysis necessary. The use of nonpolar cosolvents such as *n*-hexane, isooctane or petroleum ether to dissolve the hydrocarbons did not solve the problem. An improvement was achieved by continuous extraction with these solvents during electrolysis, which, however, complicated the assembly of the circulation cell.

It was hoped that precipitation would be reduced,



	R
1	(Z)—$CH_3(CH_2)_7CH{=}CH(CH_2)_7$—
2	(Z)—$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}$—
3	$CH_3(CH_2)_{16}$—
4	$CH_3(CH_2)_7[CH_3(CH_2)_5]CH$—
5	$CH_3(CH_2)_{14\text{-}x}CH(CH_3)(CH_2)_x$—
6	$CH_3CONH(CH_2)_{10}$—
7	$HO(CH_2)_{10}$—
8	
9	$CH_3(CH_2)_5CH(OH)(CH_2)_{10}$—
10	$CH_3(CH_2)_5CO(CH_2)_{10}$—
11	*erythro* —$CH_3(CH_2)_7CH(OH)CH(OH)(CH_2)_7$—
12	*erythro* —$CH_3(CH_2)_7CH(OAc)CH(OAc)(CH_2)_7$—
13	$CF_3(CF_2)_7$—
14	$CH_3O_2C(CH_2)_7$—
15	$CH_3O_2C(CH_2)_{10}$—

Scheme 1.

Table 1. Homocoupling of native and synthetic fatty acids[a] by Kolbe electrolysis.

	Yields (%)[b]			
		Disproportionation products		
Acid **a**	Dimer **b**	**c**	**d**	Conversion (%)
1	42 (70)	7.5	7.5	60
2	39 (70)	7	7	56
3	34 (64)	6	6	53
4	22 (42)	11	18	53
4[c]	34 (41)	17	28	82
5	55 (75)	17		73
5[c]	63 (76)	18		83
6	25 (30)	41		84
7	42 (46)	10		91
8	23 (29)	10		80
9	56			
10	81			
11	40 (56)	15		71
12	7 (58)			12
13	41 (61)			67
14	80	10		
15	53	16.5		

[a]Electrolysis conditions: current density 200 mA cm^{-2}, 40–45 °C, 10% neutralization of the acid. [b]Isolated yields, in parentheses yields based on conversion. [c]Conversion of 1 mol **4** or 2.6 mol **5** in the circulation cell.

when liquid, branched carboxylic acids were used. A branched synthetic fatty acid is isopalmitic acid (**4a**), prepared from octanol via guerbet alcohol and subsequent air oxidation.[9] Acid **4a** could indeed be anodically oxidized without severe passivation. The proportion of the dimer, however, is decreased in favor of disproportionation products as expected for the secondary radicals formed here, compared with the primary radicals above.[10] The secondary radical is also easier oxidized to a cation than a primary radical, which explains the higher proportion of olefin **4d** compared with alkane **4c** formed by deprotonation of the intermediate cation. In branched fatty acids, that lead to primary radicals, the portion of disproportionation product should decrease. Isostearic acid (**5a**, Unichema trade name Prisorine® 3505), a side product in the preparation of dimer fatty acid, is a mixture of C_{18}-carboxylic acids with a methyl side chain, which is not in the α-position.[11] Indeed with **5a** the amount of disproportionation product was reduced from 29–45% for **4a** to 17–18%, and the proportion of dimer correspondingly increased from 22–28% for **4b** to 55–63% for **5b**. The conversion of **5a** could be scaled-up by a factor of 50 without problems, namely from 50 mmol in the beaker cell (cell A) to 2.55 mol in the circulation cell (cell B). As the products **5b–d** separated from the solvent during the course of the electrolysis, **5b** was simply obtained by distillation of the separated organic layer.

70 g of **4b** and 390 g of **5b** were prepared and tested by the companies Henkel and Unichema. Both compounds showed qualities that corresponded widely to those of natural squalane, which has many cosmetic applications.[12] **5b** appears to be the more favorable compound as it is simply available in two steps from native fatty acids.

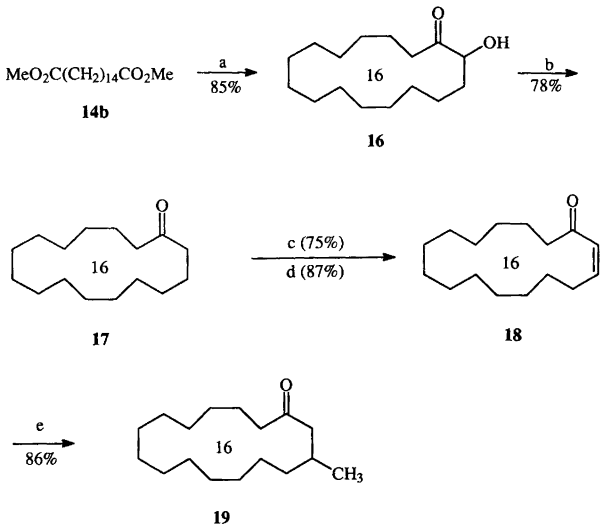
Heteroatom-substituted hydrocarbons. α-Amino acids cannot be subjected to radical coupling by Kolbe electrolysis as further oxidation of the intermediate radical preponderates due to carbocation stabilization by the amino group. Amino acids with more remote amino groups (γ- to ω-position) can be coupled, but it is appropriate to protect the amino group against oxidation by acylation.[13] 11-Aminoundecanoic acid[14] is acetylated in acetic anhydride–acetic acid in 72% yield to **6a**, which leads by anodic decarboxylation in moderate yield (25%) to *N,N'*-diacetyleicosane-1,20-diamine (**6b**); in this electrolysis disproportionation products (41%) are mainly formed, and 16% of the starting compound was recovered as the methyl ester due to partial esterification of **6a** during electrolysis. 11-Hydroxyundecanoic acid (**7a**), prepared by hydroboration–oxidation of methyl 10-undecenoate, could be anodically coupled in 42% yield to the corresponding 1,20-diol, here the yield of disproportionation product dropped to 10%. 10-Undecenoic acid leads immediately from the beginning of the electrolysis to severe passivation of the anode. Use of cosolvents such as cyclohexane, tetrahydrofuran, *tert*-butyl methyl ether or toluene could not prevent passivation. In methanol–pyridine (2:1) electrolysis was possible at 200 mA cm^{-2}, however, no dimer could be detected.

On the other hand 10,11-epoxyundecanoic acid (**8a**), prepared by epoxidation of 10-undecenoic acid, could be dimerized to the 1,2,19,20-bisepoxide **8b** in moderate yield (23%). 12-Hydroxystearic acid (**9a**) and the corresponding oxo acid **10a** afforded good to excellent yields of the corresponding 7,28-dihydroxy- (**9b**, 56%) or 7,28-dioxo-tetratriacontane (**10b**, 81%). **9a** is obtained from ricinoleic acid and **10a** is available from **9a** by oxidation. *erythro*-9,10-Dihydroxystearic acid (**11a**) can be prepared from oleic acid by bishydroxylation with potassium permanganate.[15] With acetic anhydride, and H_2SO_4 as catalyst, **11a** is diacetylated to 90% **12a**. Both **11a** and **12a** afforded moderate yields of the 9,10,25,26-tetrahydroxytetratriacontane (**11b**) and the corresponding tetraacetate **12b**; strangely in the anodic coupling of **12a** the conversion was very low. Perfluorononanoic acid (**13a**) could be coupled to 41% perfluorohexadecane (**13b**) in methanol–acetonitrile[16] with a conversion of 67%.

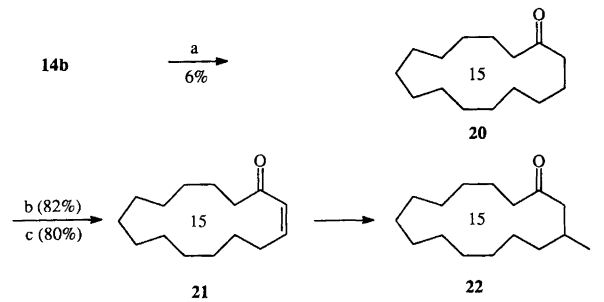
Anodic coupling of methyl hydrogen dioates. Anodic coupling of methyl hydrogen dioates leads to 1,ω-diesters (Brown–Walker coupling).[2,4,7] These are valuable compounds for the preparation of polyesters and polyamides by polycondensation and of macrocyclic ketones by acyloin condensation. The methyl hydrogendioates were obtained by partial hydrolysis of the dimethyl esters with $Ba(OH)_2$ following a procedure by Cason.[17]

Methyl hydrogen azelate (**14a**) accessible from oleic acid by ozonolytic cleavage, and methyl hydrogen dodecanedioate (**15a**) from dodecanedioic acid[18] were coupled in 80% and 53% yield, respectively, to the corresponding C_{16}- (**14b**) and C_{22}- (**15b**) 1,ω-diesters. **14b** has been converted by acyloin condensation, deoxygenation, dehydrogenation and 1,4-addition of a methyl substituent to homomuscone (Schemes 2 and 3).

For that purpose **14b** was reductively cyclized to 85% 2-hydroxycyclohexadecanone (thapsoine, **16**) with sodium in xylene using a described procedure.[19] Dieckmann cyclization of **14b** with potassium *tert*-butoxide in decalin at 190 °C afforded, after acidic work-up, only 6% exaltone (**20**, Scheme 3) with an 80% recovery of **14b**. The low cyclization yield is comparable to those found for corresponding diesters in Dieckmann cyclizations.[20] The hydroxy group in **16** was reductively removed with zinc–HCl in dioxane following a procedure by Stoll[21] to afford cyclohexadecanone (**17**). In order to introduce a methyl group in the β-position of the carbonyl group, **17** was converted into the corresponding enone **18**, following a procedure that Ito[22] has applied to six-membered carbocycles. **17** was converted into the silyl enol ether, which was subsequently oxidized with one equivalent of palladium(II) acetate to afford 87% of the enone **18**. When only 0.5 equiv. of palladium(II) acetate and 0.5 equiv. of benzoquinone as cooxidant



Scheme 2. a, Sodium in xylene; b, Zn, HCl, dioxane; c, 1. LDA, 2. TMSCl; d, $Pd(OAc)_2$ in CH_3CN; e, Me_2CuLi.



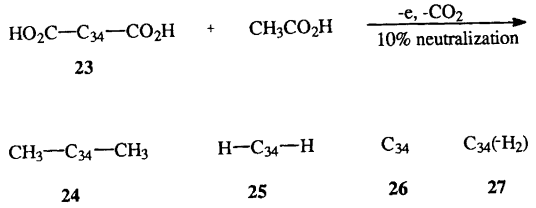
Scheme 3. a, 1. KO Bu^t, decaline, 190 °C; 2. H^+; b,1. LDA; 2. TMSCl; c, $Pd(OAc)_2$ in CH_3CN; d, Me_2CuLi.

were used the yield of **18** dropped from 87% to 70% and full conversion was not achieved after 24 h. Following reported procedures[23] **18** was converted in a 1,4-addition, with $(CH_3)_2CuLi$, in 86% yield, into the homomuscone **19**. Correspondingly exaltone (**20**) was converted into muscone (**22**) (Scheme 3). The perfume qualities of theses compounds have been roughly evaluated:[24] besides **22**, the enones **21** (musk, intensity: medium strong) and **18** (musk, warm, Tonkin intensity: medium strong) were classified as interesting odoriferous compounds.

Anodic coupling of dimer fatty acid monomethyl ester. Properties of polyesters and polyamides such as hardness, toughness, thermostability and mouldability are influenced by the size and flexibility of the methylene chain in the diacid,[25] and for that purpose dimer fatty acid is sometimes used as comonomer.[11a] Dimer fatty acid is prepared on a technical scale by clay-catalyzed, thermal dimerization of a mixture of unsaturated C_{18}-fatty acids from tall oil fatty acids.[26] Thereby one obtains, partly in a thermal ene-reaction, a mixture of isomeric C_{36}-dicacids of complex structure.[27] By way of hydrogenation and distillation the mixture can be purified and made more uniform. With the commercial dimer fatty acid Pripol® 1008 (Unichema), whose isomeric mixture is denoted here as $HO_2C\text{-}C_{34}\text{-}CO_2H$ (**23**), Kolbe electrolysis was attempted to prepare a new diacid with 70 carbon atoms.

At first the direct dimerization of **23** was tried. However, in spite of widely varied experimental conditions, namely the degree of neutralization, the concentration of **23**, current density and temperature, all electrolyses had to be interrupted after short time, because a high degree of passivation occurred at the anode. Probably an insulating polymer film was deposited on the anode by oligomerization of **23**; 94–96% of unchanged **23** could be reisolated in all cases.

To explore whether diacid **23** can be decarboxylated and subsequently undergo radical coupling at all, **23** was subjected to coelectrolysis with a ten-fold excess of acetic acid, to achieve a double heterocoupling at both ends. No passivation occurred, as with **23** alone, and from the electrolysis product by liquid chromatography 40% **23** could be reisolated and 60% of a mixture of **24**–**27** (Scheme 4) was obtained, that could not be further separated. In the IR spectrum of this mixture the carboxy group of **23** was absent. The ^1H NMR spectrum showed olefinic and alkyl protons in a ratio of 0.027. If only the disproportionation of the radical, originating from **23** to form **25**–**27**, had occurred the ratio should have been $3:65 = 0.046$. From the experimental ratio one calculates a portion of 41% **24**, which indicates that **23** can indeed be subjected to Kolbe coupling, when oligomerization is prevented.

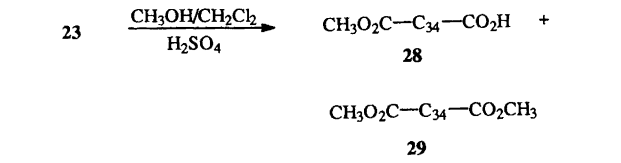


Scheme 4.

As the direct dimerization of **23** was not possible, the common procedure for the coupling of diacids, namely the electrolysis of the half-ester, was applied. Half-esters of long-chain diacids are frequently prepared by partial hydrolysis of the diester.[17] For that purpose diacid **23** was reacted by acid catalysis (H_2SO_4) with different equivalents of methanol in dichloromethane. As the reaction slowed down, when a larger proportion of the half-ester **28** had been formed, it was optimized for the half-ester formation (Table 2, Scheme 5). The purification of **28** by column chromatography, however, was only successful, when most of **23** was converted. Larger amounts of **28** were prepared under the conditions of run No. 3 (Table 2); in this case 174 g of **28** could be obtained per run. An alternative way of preparing **28** is the selective hydrolysis of the diester **29.** This was stirred in several solvents with different bases for 36 h and the products were separated by liquid chromatography

Table 2. Partial esterification of dimer fatty acid **23**.

No.	CH_3OH (equiv.)	Yield (%)		
		28	**29**	**23**
1	4.0	7	92	—
2	2.3	23	75	—
3	1.7	30	65	3
4	1.0	25	35	40
5	0.5	37	16	47



Scheme 5.

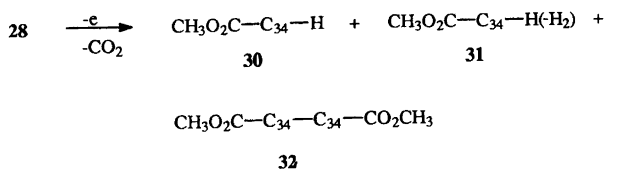
(Table 3). The best conditions were those of run No. 3 (Table 3). The separation of the half-ester **28** from **23**, however, caused problems in larger-scale preparations, therefore the route via partial esterification was found to be more suitable for the preparation of **28**. The IR spectrum showed two absorption bands at $\nu = 1740$ (CO_2CH_3) and 1704 cm^{-1} (CO_2H), **29** only one at 1740 cm^{-1}. In the mass spectrum of **28** and **29** the molecular ions were 14 and 28 mass units, respectively, higher than those of **23**.

The half-ester **28** was electrolyzed in methanol at a current density of 200 mA cm^{-2} to afford after 63% conversion the disproportionation products **30** and **31** (20%) and the dimer **32** (38%) (Scheme 6). The diester **32** was a mixture of isomers with 72 carbon atoms. In spite of its high molecular weight of 1068 g mol^{-1} it was a viscous liquid. The IR spectrum showed only the carbonyl absorption at $\nu = 1740$ cm^{-1} for the ester group. In the mass spectrum obtained by chemical ionization with NH_3 the molecule ions $[C_{72}H_{138}O_4 \cdot NH_4^+]$, $[C_{72}H_{140}O_4 \cdot NH_4^+]$ and $[C_{72}H_{142}O_4 \cdot NH_4^+]$ could be identified. These molecular formulas result from the combination of structures with different unsaturation in diacid **23**. The used commercial dimer fatty acid Pripol® 1008 is, according to the mass spectra of the mono- and the di-ester, a mixture of HO_2C–$C_{34}H_{68}$–CO_2H and HO_2C–$C_{34}H_{66}$–CO_2H. The first compound corresponds to a saturated acyclic diacid, the latter to either an monounsaturated acyclic diacid or a saturated diacid with one alicyclic nucleus.

Table 3. Partial hydrolysis of dimer fatty diester **29**.

No.	Solvent	Base (0.5 equiv.)	Yield (%)	
			23	**28**
1	$MeOH-H_2O$	KOH	—	—[a]
2	Ether	1 M KOH–MeOH	28	17
3	CH_2Cl_2	1 M KOH–MeOH	20	42
4	Ether	1 M $Ba(OH_2)$–MeOH	30	—
5	CH_2Cl_2	1 M $Ba(OH_2)$–MeOH	25	—

[a] No conversion as the solubility of **29** was too low.



Scheme 6.

Discussion

Anodic decarboxylation of carboxylic acids (Kolbe electrolysis) has again demonstrated its versatility and experimental simplicity in the conversion of carboxylic acids derived from fatty acids. The low conductivity of fatty acids salts, being less polar than salts of short-chain carboxylic acids, could be handled by the use of a flow cell with parallel electrodes and a narrow electrode gap. Fatty acids with unbranched chains caused problems in some cases due to the deposition of an insoluble dimer. Mechanical removal of the deposit from the electrode, a fast and turbulent flow of the electrolyte or continuous extraction of the non-polar solid with cosolvents could solve this problem, however, at the expense of simplicity of the experimental set-up. With branched, liquid fatty acids, that also led to liquid dimers, no problems with passivation occurred and in some cases the product separated during the reaction from the polar electrolyte, which simplified the work-up. This way compounds with interesting emulsifying properties could be obtained from commercially available precursors in one step; they might possibly serve as substitutes for natural and more expensive cosmetic basic materials, such as squalane.

A serious and unwanted side reaction to coupling is disproportionation, the extent of which increases when the acid is branched in the α-position. In some cases the acid is converted to the methyl ester during the electrolysis and thus evades conversion into radicals. Double bonds at the terminal position can lead to immediate passivation of the electrode, whilst those in the middle of the alkyl chain mostly have no effect. The anode reaction tolerates many functional groups, such as hydroxy-, amino-, keto-, ester- or even the epoxy group. Electron-donating substituents in the α-position, however, lead to oxidation of the intermediate radical to a carbocation and products derived from that. It is desirable to protect amino groups against oxidation by acylation; in the case of alcohols, however, this has to be tested individually as acylation can both improve and sharply decrease the yield of the conversion.

As already demonstrated in many cases,[2,4,7] the coupling of half-esters to 1,*n*-diesters (Brown–Walker coupling) has a high synthetic potential. The readily accessible diesters afford an easy route to cyclic ketones of medium ring size that are of interest as odoriferous substances. The half-ester of the industrial dimer fatty acid could be

converted into a C_{70}-diacid. The dimerization was again accompanied by disproportionation, but otherwise no problems were encountered due to passivation, as the branched half ester led to a liquid product, that did not deposit at the electrode.

Experimental

Melting points (uncorrected): Kofler hot-stage. Refractive indices: Zeiss refractometer Opton. IR: Shimadzu IR-408. ^1H, ^{13}C NMR: Bruker WM 300, $SiMe_4$ for ^1H NMR, $CDCl_3$ for ^{13}C NMR as internal standards. MS: Varian MAT CH7A, Finnigan MAT 8230, data system SS 300, 70 eV and direct chemical ionization (DCI). Elementary analysis: Mikroanalytisches Laboratorium, M. Beller, Göttingen. GLC: Shimadzu GC-14A with integrator C-R3A, quartz capillary column 0.32 mm × 50 m, 0.25 μm FS-HP1 (Hewlett Packard). Flash chromatography: Silica gel 60 (Merck) 70–230 mesh, glass columns 1–6 cm and 12 cm in diameter. Bulb-to-bulb distillation: Büchi GKR 51.

Electrolysis (small scale, cell A): undivided standard beaker-type cell (150 ml), electrode material: platinum foil (4 cm^2, thickness: 0.01 mm) on Teflon frames, electrode distance: 2–4 mm,[8] current source: galvanostat Heri-TN 250–1250 (Heinzinger). Electrolysis (large scale, cell B): continuous circulation flow reactor (500 ml), centrifugal pump: Type 1022 (Eheim), anode material: platinum foil (18 cm^2, thickness: 0.01 mm), cathodic material: stainless steel, electrode distance: 0.2–1 mm,[8] current source: galvanostat TNS 300–1500 (Heinzinger). Cell C: small continuous circulation flow reactor as cell B, however, smaller electrolyte volume: 50 ml and electrode area: 5.5 cm^2 per electrode. Methyl hydrogen nonanedioate (**14a**) was prepared according to Ref. 17. Isopalmitic acid (**14a**) was a gift from the Henkel company, Prisorine® 3505 and Pripol® 1008 were donated by the Unichema company.

General procedure for the Kolbe-electrolysis. (I) Small scale electrolysis (10–100 mmol): the substrate was dissolved in 30 ml of methanol followed by 10% neutralization with 1 M potassium methoxide. The electrolysis was carried out using the beaker-type cell A at 40–45 °C, applying a current density of 200 mA cm^{-2}. After the required electric charge (1–1.3 F mol^{-1}) had passed the cell, the reaction was terminated and the electrolyte solution removed. The cell was washed with 50 ml of methanol and 50 ml of petroleum ether. The combined organic solutions were diluted with 100 ml of petroleum ether and subsequently washed three times with 50 ml of 0.5 M hydrochloric acid. The organic extracts were dried over magnesium sulfate and evaporated under reduced pressure, and the resulting residue was separated by column filtration using petroleum ether to eluate crude product, and ether to eluate non-converted starting material. The product mixture was further separated by bulb-to-bulb distillation to yield dimer and disproportionation products.

(II) The general procedure for the larger scale electrolyses (0.1–2.6 mol) corresponded essentially to the one described above. The substrate was dissolved in 250 ml of methanol. After the electrolysis the electrolyte was collected and the cell and circulation set-up were rinsed with 150 ml of methanol and petroleum ether, respectively. The organic solutions were combined, the solvent was removed under reduced pressure and the residue was dissolved in 600 ml of petroleum ether. Subsequently this solution was washed with 0.5 M hydrochloric acid (3 × 100 ml). Further work-up followed procedure (I), but instead of bulb-to-bulb distillation, vacuum distillation was used.

(III) The general procedure corresponds to (II), with the exception that a smaller cell and electrolyte volume (20–50 ml methanol) and a smaller amount of acid (16–40 mmol) were used. For work-up the cell was rinsed with organic solvent (cyclohexane or ethyl acetate, 4 × 40 ml), the methanol was evaporated off under reduced pressure to a large extent and the residue was combined with the organic solvent. The organic layer was washed consecutively with saturated sodium bicarbonate solution (3 × 50 ml) and water, and was then dried ($MgSO_4$). The solvent was evaporated off under reduced pressure and the residue distilled or recrystallized. The sodium bicarbonate extracts after acidification to pH 1 with dilute HCl were extracted with diethyl ether (3 × 50 ml), the ether layer was washed and dried ($MgSO_4$) and the product yields determined by isolation or calibrated GLC.

(9Z,25Z)-9,25-Tetratriacontadiene (**1b**). 2.82 g (10 mmol) oleic acid **1a** were electrolyzed (procedure I). Current consumption: 1.3 F mol^{-1}, cell voltage: 60–110 V. Distillation afforded at 90–120 °C/0.01 mbar 0.35 g (15%) of a 1:1 mixture of **1c** and **1d** and 0.99 g (42%) of **1b**. 1.13 g (40%) of the starting material **1a** were recovered. M.p. 21 °C (lit.[28] 15.5–16.5 °C). IR (film): ν = 3000, 2925, 2850, 1460, 1435, 1410, 700 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.86 (t, J = 6.7 Hz, 6 H, 2 × CH_3), 1.20–1.40 (br s, 48 H, 24 × CH_2), 1.97–2.03 (m, 8 H, 4 × CH_2–CH=), 5.33 (t, J = 4.6 Hz, 4 H, 4 × CH_2–CH=). MS (GC–MS, 70 eV): *m/z* (%): 474 (18) [M^+], 376 (4) [$M^+ - C_7H_{14}$], 362 (8) [$M^+ - C_8H_{16}$], 348 (8) [$M^+ - C_9H_{18}$], 334 (4) [$M^+ - C_{10}H_{20}$], 97 (60) [$C_7H_{13}^+$], 96 (74) [$C_7H_{12}^+$], 83 (70) [$C_6H_{11}^+$], 82 (70) [$C_6H_{10}^+$], 69 (74) [$C_5H_9^+$], 55 (100) [$C_4H_7^+$], 43 (52) [$C_3H_7^+$].

(Z)-8-Heptadecene (**1c**). MS (GC–MS, 70 eV): *m/z* (%): 238 (17) [M^+], 210 (2) [$M^+ - C_2H_4$], 154 (4) [$M^+ - C_6H_{12}$], 139 (7) [$C_{10}H_{19}^+$], 97 (76) [$C_7H_{13}^+$], 83 (95) [$C_6H_{11}^+$], 69 (96) [$C_5H_9^+$], 57 (89) [$C_4H_9^+$], 55 (100) [$C_4H_7^+$], 43 (88) [$C_3H_7^+$], 41 (70) [$C_3H_5^+$].

(8Z)-1,8-Heptadecadiene (**1d**). MS (GC–MS, 70 eV): *m/z* (%): 236 (25) [M^+], 208 (5) [$M^+ - C_2H_4$], 166 (4) [$M^+ - C_5H_{10}$], 152 (6) [$M^+ - C_6H_{12}$], 138 (14)

$[M^+ - C_7H_{14}]$, 124 (22) $[C_9H_{16}^+]$, 96 (100) $[C_7H_{12}^+]$, 82 (96) $[C_6H_{10}^+]$, 81 (92) $[C_6H_9^+]$, 67 (86) $[C_5H_7^+]$, 55 (97) $[C_4H_7^+]$, 41 (73) $[C_3H_5^+]$.

(9Z,33Z)-9,33-Dotetracontadiene (**2b**). 3.38 g (10 mmol) erucic acid (**2a**) were electrolyzed as for **1a**. The distillation at 90–150 °C/0.01 mbar, afforded 0.416 g (14%) of a 1 : 1 mixture, identified as **2c** and **2d** by GC–MS analysis and 1.16 g (39%) of **2b**. 1.48 g (44%) of the starting material **2b** were recovered. M.p. 40–41 °C (lit.[29] 33 °C). IR (film): $\nu = 3000$, 2900, 2800, 1450, 1425, 1405, 710 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.86 (t, $J = 6.7$ Hz, 6 H, $2 \times CH_3$), 1.20–1.39 (br s, 64 H, $32 \times CH_2$), 1.95–2.05 (m, 8 H, $4 \times CH_2$–CH=), 5.33 (t, $J = 4.5$ Hz, 4 H, $4 \times CH_2$–CH=). MS (70 eV): *m/z* (%): 586 (100) $[M^+]$, 488 (8) $[M^+ - C_7H_{14}]$, 474 (16) $[M^+ - C_8H_{16}]$, 460 (28) $[M^+ - C_9H_{18}]$, 446 (14) $[M^+ - C_{10}H_{20}]$, 97 (82) $[C_7H_{13}^+]$, 96 (63) $[C_7H_{12}^+]$, 83 (84) $[C_6H_{11}^+]$, 69 (76) $[C_5H_9^+]$, 57 (73) $[C_4H_9^+]$, 55 (67) $[C_4H_7^+]$, 43 (60) $[C_3H_7^+]$. $C_{42}H_{82}$ (586.2): Calcd. C 85.92, H 14.08. Found: C 86.01, H 13.95%.

(Z)-9-Henicosene (**2c**). MS (GC–MS, 70 eV): *m/z* (%): 294 (58) $[M^+]$, 180 (6) $[M^+ - C_8H_{18}]$, 167 (10) $[C_{12}H_{23}^+]$, 154 (12) $[M^+ - C_{10}H_{20}]$, 140 (7) $[C_{10}H_{20}^+]$, 97 (92) $[C_7H_{13}^+]$, 83 (84) $[C_6H_{11}^+]$, 69 (98) $[C_5H_9^+]$, 57 (96) $[C_4H_9^+]$, 55 (100) $[C_4H_7^+]$, 43 (90) $[C_3H_7^+]$.

(12Z)-1,12-Henicosadiene (**2d**). MS (GC–MS, 70 eV): *m/z* (%): 292 (54) $[M^+]$, 193 (8) $[C_{14}H_{25}^+]$, 180 (3) $[M^+ - C_8H_{16}]$, 152 (16) $[M^+ - C_{10}H_{20}]$, 138 (16) $[C_{10}H_{18}^+]$, 96 (53) $[C_7H_{12}^+]$, 82 (100) $[C_6H_{10}^+]$, 69 (79) $[C_5H_9^+]$, 55 (80) $[C_4H_7^+]$, 43 (59) $[C_3H_7^+]$, 41 (76) $[C_3H_5^+]$.

Tetratriacontane (**3b**). 2.84 g (10 mmol) stearic acid **3a** were electrolyzed as for **1a** but with a lower current consumption (0.58 F mol^{-1}). The crude product mixture was recrystallized from *n*-hexane to afford 0.812 g (34%) of **3b** as a colorless solid. 0.287 g (12%) of a 1 : 1 mixture of **3c** and **3d** were isolated from the mother liquor. 1.35 g (47%) of starting material **3a** were recovered.

3b: M.p. 72 °C (lit.[30] 73 °C). MS (GC–MS, 70 eV): *m/z* (%): 478 (4) $[M^+]$, 365 (2) $[C_{26}H_{53}^+]$, 239 (4) $[C_{17}H_{35}^+]$, 183 (6) $[C_{13}H_{27}^+]$, 99 (22) $[C_7H_{15}^+]$, 85 (50) $[C_6H_{13}^+]$, 71 (73) $[C_5H_{11}^+]$, 57 (100) $[C_4H_9^+]$, 43 (58) $[C_3H_7^+]$.

Heptadecane (**3c**). MS (GC–MS, 70 eV):[31] *m/z* (%): 240 (3) $[M^+]$, 169 (2) $[C_{12}H_{25}^+]$, 155 (2) $[C_{11}H_{23}^+]$, 99 (8) $[C_7H_{15}^+]$, 85 (26) $[C_6H_{13}^+]$, 71 (48) $[C_5H_{11}^+]$, 57 (100) $[C_4H_9^+]$, 43 (97) $[C_3H_7^+]$, 41 (38) $[C_3H_5^+]$.

1-Heptadecene (**3d**). MS: (GC–MS, 70 eV):[31] *m/z* (%): 238 (20) $[M^+]$, 210 (6) $[M^+ - C_2H_4]$, 196 (3) $[M^+ - C_3H_6]$, 182 (4) $[M^+ - C_4H_8]$, 154 (8) $[M^+ - C_6H_{12}]$, 97 (93) $[C_7H_{13}^+]$, 83 (100) $[C_6H_{11}^+]$, 69 (79) $[C_5H_9^+]$, 57 (98) $[C_4H_9^+]$, 55 (85) $[C_4H_7^+]$, 43 (87) $[C_3H_7^+]$, 41 (66) $[C_3H_5^+]$.

9,10-Dihexyloctadecane (**4b**). 256 g (1 mol) 2-hexyldecanoic acid (**4a**) were electrolyzed according to procedure (II): cell voltage 11–15 V, current consumption: 1.4 F mol^{-1}. Distillation at 60–95 °C/0.01 mbar afforded 94.3 g (45%) of a 1 : 1.6 mixture of **4c** and **4d** and 71.7 g (34%) of **4b** at 140 °C/0.005 mbar; 46.1 g (18%) of starting material **4a** were recovered.

4b: $n_D^{20} = 1.4517$. B.p. 142–144 °C/0.005 mbar. IR (film): $\nu = 2900$, 2850, 1430, 1370 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0.86$ (t, $J = 6.7$ Hz, 12 H, $4 \times CH_3$), 1.10–1.35 (br s, 50 H, $24 \times CH_2$ and $2 \times >CH$–). ^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (s, CH_3), 22.7 (s), 28.2 (s), 29.4 (s), 29.7 (s), 29.8 (s), 30.1 (s), 30.7 (s), 32.0 (s), 39.6 (s, C-9 and C-10). MS (GC–MS, 70 eV): *m/z* (%): 337 (2) $[M^+ - C_6H_{13}]$, 309 (2) $[M^+ - C_8H_{17}]$, 211 (7) $[C_{15}H_{31}^+]$, 210 (26) $[M^+ - C_{15}H_{32}]$, 99 (17) $[C_7H_{15}^+]$, 97 (18) $[C_7H_{13}^+]$, 85 (44) $[C_6H_{13}^+]$, 71 (65) $[C_5H_{11}^+]$, 57 (100) $[C_4H_9^+]$, 43 (61) $[C_3H_7^+]$. $C_{30}H_{62}$ (422.5): Calcd. C 85.22, H 14.78. Found C 85.18, H 14.87%.

Pentadecane (**4c**). MS (GC–MS, 70 eV): *m/z* (%): 212 (3) $[M^+]$, 183 (1) $[C_{13}H_{27}^+]$, 155 (2) $[C_{11}H_{23}^+]$, 127 (4) $[C_9H_{19}^+]$, 99 (10) $[C_7H_{15}^+]$, 85 (40) $[C_6H_{13}^+]$, 71 (63) $[C_5H_{11}^+]$, 57 (100) $[C_4H_9^+]$, 43 (87) $[C_3H_7^+]$.

7-Pentadecene (**4d**). MS (GC–MS, 70 eV): *m/z* (%): 210 (10) $[M^+]$, 182 (3) $[M^+ - C_2H_4]$, 125 (7) $[C_9H_{17}^+]$, 111 (18) $[C_8H_{15}^+]$, 97 (44) $[C_7H_{13}^+]$, 83 (64) $[C_6H_{11}^+]$, 69 (92) $[C_5H_9^+]$, 55 (100) $[C_4H_7^+]$, 43 (64) $[C_3H_7^+]$, 41 (76) $[C_3H_5^+]$.

$C_{34}H_{70}$ (several isomers). 738 g (2.55 mol) Prisorine® 3505 (**5a**) were electrolyzed as for **4a**. Deviating from this procedure the amount of **5a** was divided into three parts. The first was electrolyzed until one third of the calculated charge had passed. Then the electrolysis was interrupted. The product layer was removed and after addition of the second amount of starting material the electrolysis was continued. This procedure was then repeated with the third portion of the substrate. The reaction was terminated, when altogether a charge of 1.3 F mol^{-1} had passed through the electrolyte. Work-up and separation corresponded to that of **4a**. Distillation at 80–120 °C/0.008 mbar afforded 114 g (18%) of **5c,d** and 393 g (63%) of **5b** as a colorless liquid. 125 g (17%) of the starting material **5a** were recovered.

5b: $n_D^{20} = 1.4591$. IR (film): $\nu = 2950$, 2850, 1455, 1410, 1370 cm^{-1}. $C_{34}H_{70}$ (478.9): Calcd. C 85.27, H 14.73. Found C 85.20, H 14.55%.

$C_{17}H_{36}$ and $C_{17}H_{34}$ (**5c,d**). (Isomeric disproportionation products): $n_D^{20} = 1.4448$. B.p. 80–120 °C/0.008 mbar. IR (film): $\nu = 3050$, 2950, 2850, 1635, 1440, 1370, 980, 955, 895, 710 cm^{-1}.

N,N'-*Diacetylicosane-1,20-diamine* (**6b**). 3.88 g (16 mmol) 11-acetamidoundecanoic acid (**6a**), prepared by treatment of 11-aminoundecanoic acid with acetyl chloride, was electrolyzed according to procedure (I) (cell voltage 60–100 V, current consumption: 2.13 F mol^{-1}). For work-up the methanol was evaporated off, and the residue washed with water and recrystallized from meth-

anol to afford 0.81 g (25%) **6b**. M.p. 136 °C. IR (KBr): ν=3312 (NH), 1631 (amide I), 1538 cm^{-1} (amide II). ^1H NMR (pyridine-d_5): δ 1.3–1.4 (m, 32 H, 6-21 H), 1.58–1.66 (quintet, 4 H, 5-H, 22-H), 2.06 (s, 6 H, CH_3), 3.42–3.47 (quartet, 4 H, 4-H, 23-H). MS (70eV): *m/z* (%)=396 (48) [M^+], 381 (16) [M^+-CH_3], 353 (38) [$M^+-O{=}C{-}CH_3$], 324 (50) [$M^+-CH_2NH{-}COCH_3$], 296 (30) [$324-C_2H_4$], 282 (40), 240 (42) [$H_3CCONH(CH_2)_{15}$], 226 (38) [$H_3CCONH(CH_2)_{12}$]. $C_{24}H_{48}O_2N_2$ (396.7): Calcd. C 72.79, H 12.22, N 7.07. Found C 73.11, H 12.37, N 7.17%.

1,20-Icosanediol (**7b**). 3.23 g (16 mmol) 11-hydroxyundecanoic acid (**7a**) were electrolyzed according to procedure (I) (20 ml methanol, current consumption: 3.03 F mol^{-1}, cell voltage: 50–60 V, T=40 °C, reversal of electrode polarity each 5 s). For work-up the methanol was evaporated off, and the residue was dissolved in dichloromethane–ethyl acetate and extracted with aqueous dilute HCl, saturated with NaCl. After drying ($MgSO_4$), 1.06 g (42% **7b**, 0.24 g (10%) decanol (**7c**), 1-decen-10-ol (**7d**) and 0.292 g (9%) **7a** were isolated from the organic layer by precipitating **7b** from the dichloromethane–ethyl acetate solution with diethyl ether.

7b: M.p. 100–101 °C. IR (KBr): ν=3303 (w, OH), 2903 cm^{-1} (s, CH). ^1H NMR ($CDCl_3$): δ 1.24–1.32 (m, 32 H, 3-H to 18-H), 1.52–1.56 (q, 4 H, 2-H, 19-H, $HOCH_2CH_2$), 3.59–3.63 (t, J=6.6 Hz, 4 H, 1-H, 20-H). MS (70 eV): *m/z* (%)=314 (6) [M^+], 278 (18) [M^+-2H_2O], 250 (15) [$278-C_2H_4$], 222 (16) [$250-C_2H_4$], 208 (14) [$236-C_2H_4$], 194 (14) [$222-C_2H_4$], 180 (13) [$288-C_2H_4$], 166 (14) [$194-C_2H_4$], 152 (14) [$280-C_2H_4$], 138 (19) [$166-C_2H_4$], 124 (23) [$152-C_2H_4$], 110 (27) [$158-C_2H_4$], 96 (85) [$124-C_2H_4$], 82 (93) [$110-C_2H_4$], 69 (84) [$C_5H_9^+$], 68 (66) [$96-C_2H_4$], 57 (70) [$C_5H_9^+$], 54 (100) [$82-C_2H_4$]. $C_{20}H_{42}O_2$ (314.5): Calcd. C 76.49, H 13.48. Found C 76.23, H 13.10%.

7c: GC–MS (as the Me_3Si ether): *m/z* (%)=230 (3) [M^+], 215 (100) [M^+-CH_3], 157 (2) [M^+-SiMe_3], 140 (2) [$M^+-TMSOH$], 103 (12) [$M^+-Me_3SiOCH_2$], 75 (28) [Me_2SiOH^+], 73 (13) [Me_3Si^+, TMS].

7d: GC–MS (as the Me_3Si ether): *m/z* (%)=228 (3) [M^+], 213 (34) [M^+-CH_3], 195 (5), 185 (6) [$213-C_2H_4$], 138 (8) [$M^+-TMSOH$], 129 (6), 103 (18) [$M^+-Me_3SiOCH_2$], 75 (100) [Me_2SiOH^+], 73 (25) [Me_3Si^+].

1,2;19,20-Diepoxyicosane (**8b**). 3.2 g (16 mmol) 10,11-epoxyundecanoic acid (**8a**) were electrolyzed according to procedure (I) (current consumption 2.3 F mol^{-1}, cell voltage 50–70 V, T=40–45 °C). In the work-up dichloromethane was used for extraction, and flash chromatography of the residue (silica gel, dichloromethane) afforded 0.56 g (23%) **8b**, 10% disproportionation products and 20% recovered **8a**.

8b: M.p. 50–53 °C. IR (KBr): ν=3052 (w, epoxy group), 2911 cm^{-1} (CH). ^1H NMR ($CDCl_3$): δ 2.8–2.9 (m, 2 H, 2-H, 19-H), 2.7–2.75 (tt, 2 H, 1-H, 1, 20-H), 2.4–2.47 (tt, 2 H, 1-H, 1; 20-H), 1.2–1.6 (m, 32 H, 3-H_2, 18-H_2, 4–17-H_2). MS (70 eV): *m/z* (%)=310 (1.7) [M^+], 292 (1) [M^+-H_2O], 109 (30), 95 (60), 81 (70), 71 (68) [$C_3H_5O^+$], 57 (35) [$C_2H_3O^+$], 55 (100) [$C_4H_7^+$], 43 (45) [$C_2H_3O^+$], 41 (69). $C_{20}H_{38}O_2$ (310.5): Calcd. C 77.48, H 12.35. Found C 77.16, H 12.35%.

Tetratriacontane-7,28-diol (**9b**). 4.18 g (16 mmol) 12-hydroxyoctadecanoic acid (**6a**) were electrolyzed according to procedure (I) (cell voltage 50–80 V, reversal of electrode polarity every 30 s, current consumption: 1.36 F mol^{-1}, T=40–50 °C). For work-up the residue was filtered off, washed with diethyl ether, dried ($MgSO_4$) and recrystallized from ethanol to afford 2.3 g (56%) **9b**. M.p. 99–100 °C. IR (KBr): ν=3330 (OH), 2916 cm^{-1} (CH). ^1H NMR ($CDCl_3$): δ 3.58 (m, 2 H, 7-H, 28-H), 1.25–1.54 (m, 60 H, 2–6-, 8,27-, 29–33-H), 0.86–0.90 (m, 6 H, CH_3). MS (70eV): *m/z* (%)=4.92 (22) [M^+-H_2O], 474 (90) [M^+-2H_2O], 407 (68) [$M^+-C_6H_{13}-H_2O$], 379 (74) [$407-C_2H_4$], 362 (76), 351 (63) [$379-C_2H_4$], 320 (63), 306 (65), 292 (70), 264 (65) [$292-C_2H_4$], 249 (62), 207 (65), 109 (93), 97 (46) [$C_7H_{13}^+$], 83 (64) [$C_6H_{11}^+$], 69 (97) [$C_5H_9^+$], 55 (100) [$C_4H_7^+$]. $C_{34}H_{70}O_2$ (510.9): Calcd. C 80.06, H 13.83. Found C 80.32, H 13.87%.

Tetratriacontane-7,28-dione (**10b**). 1.00 g (3.35 mmol) 12-oxooctadecanoic acid (**10a**) were electrolyzed according to procedure (I) (current consumption: 5.6 F mol^{-1}, cell voltage: 60–75 V, reversal of electrode polarity every 4 s). Work-up as for **9b** and additional extraction of the acidified electrolyte solution with diethyl ether, drying of the organic layer ($MgSO_4$) and flash chromatography afforded 0.7 g (81%) **10b**. M.p. 101.5–102.5 °C. IR (KBr): ν=2848 (CH), 1705 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 0.85–0.89 (t, J=6.6 Hz, 6 H, CH_3), 1.05–1.24 (m, 44 H, 2,3,4,10–25-H, 31–33-H), 1.53–1.57 (m, 8 H, α-CH_2, $O{=}CCH_2$), 2.35–2.39 (t, 8 H, β-CH_2, $O{=}C{-}CH_2{-}CH_2$). MS (70 eV): *m/z* (%)=506 (17) [M^+], 449 (10) [McLafferty+13], 436 (14) [$M^+-C_5H_{10}$], 421 (23) [$M^+-CH_3(CH_2)_5$], 366 (22), 351 820), 309, 308 (18), 293 (20), 149 (32), 113 (88) [$CH_3(CH_2)_5C{=}O^+$], 55 (100) [$C_4H_9^+$]. $C_{34}H_{66}O_2$ (506.7): Calcd. C 80.7, H 13.14. Found C 80.7, H 13.11%.

10-Undecenoic acid led to severe passivation right from the beginning of the electrolysis. Use of cosolvents such as cyclohexane, tetrahydrofuran, *tert*-butyl methyl ether or toluene did not prevent the passivation. In methanol–pyridine (2:1) electrolysis was possible at 200 mA cm^{-2}, however, no dimer could be detected.

9,10,25,26-Tetrahydroxytetratriacontane (**11b**). 5.05 g (16 mmol) 9,10-dihydroxyoctadecanoic acid (**11a**) were electrolyzed according to procedure (I) (20 ml methanol, addition of **11a** in several portions during the electrolysis, current consumption: 2.7 F mol^{-1}, cell voltage: 50–70 V, T=40–50 °C). For work-up the precipitate in the electrolyte was filtered off (2.45 g). Methanol was removed from the filtrate and the residue partly dissolved in

dichloromethane. The solution was extracted with aqueous 2 M HCl solution to give 0.9 g (15%) disproportionation product **11c,d** (from the dichloromethane layer) and 0.7 g (14%) **11a** (2 M HCl extraction). From the precipitate 1.70 g (40%) **11b** and 0.73 g (15%) estolide of **11a** were obtained.

11b: M.p. 162–164 °C. IR (KBr): ν = 3302 (w, OH), 2914 cm^{-1} (s, CH). ^1H NMR (pyridine-d_5): δ 0.86–0.90 (t, J = 6.7 Hz, 6 H, 1,34-H_3), 1.27–1.48 (m, 44 H, 2–6-, 12–23-, 29–35-H), 1.61–1.65 and 1.86–1.96 (m, 16 H, 7,8,11,12,23,24,27,28-H). MS (70 eV): *m/z* (%) = 506 (10) [$M^+ - 2H_2O$], 381 (65) [$M^+ - CH_3(CH_2)_7CHOH - H_2O$], 363 (55) [381 − H_2O], 284 (45), 255 (45), 155 (57) [$C_{11}H_{23}^+$], 125 (60) [$C_9H_{17}^+$], 111 (63) [$C_8H_{15}^+$], 97 (76) [$C_7H_{13}^+$], 83 (82) [$C_6H_{11}^+$], 71 (90) [$C_5H_{11}^+$], 57 (100) [$C_4H_9^+$]. $C_{34}H_{70}O_4$ (542.9): Calcd. C 75. 34, H 13.02. Found C 75.4, H 12.8%.

9,10,25,26-Tetraacetoxytetratriacontane (**12b**). 5.6 g (14 mmol) 9,10-diacetoxyoctadecanoic acid (**12a**) were electrolyzed according to procedure (I) (20 ml methanol, current consumption: 7.7 F mol^{-1}, cell voltage: 50–60 V). Work-up afforded 4.9 g (88%) **12a** and 0.34 g (7%) **12b**.

12b: IR (KBr): ν = 2926 (s, CH), 1742 cm^{-1} (s, C=O). ^1H NMR ($CDCl_3$): δ 0.82–0.87 (t, 6 H, 1-H, 34-H, J = 6.6 Hz), 1.23–1.57 (m, 56 H, 2–8-, 11–24-, 27–33-H), 2.0–2.2 (m, 12 H, H_3CC=O), 4.92–4.96 (m, 4 H, 9,10,25,26-H). MS (DCI, NH_3): *m/z* (%) = 728 (100, $M^+ + NH_4^+$). $C_{42}H_{78}O_8$ (711.0): Calcd. C 70.95, H 11.1. Found C 70.44, H 11.0%.

Tetratriacontafluorohexadecane (**13b**). 4.27 g (9.2 mmol) perfluorononanoic acid were electrolyzed in 30 ml methanol–acetonitrile (2:1) after neutralization to an extent of 6% (KOH in methanol) according to procedure (I) (cell voltage: 80 V, current consumption: 1 F mol^{-1}). 1.58 g (41%) **13b** were filtered off from the electrolyte as white solid. From the filtrate 1.41 g (33%) **13a** were recovered.

13b: M.p. 125 °C (lit.[32] 125–126 °C). MS (GC–MS, 70 eV): *m/z* (%) = 731 (0.3, $C_{15}F_{29}^+$), 531 (0.3, $C_{11}F_{19}^+$), 519 (0.9, $C_{10}F_{21}^+$), 219 (27, $C_4F_9^+$), 181 (13, $C_4F_7^+$), 169 (41, $C_3F_7^+$), 131 (29, $C_3F_5^+$), 119 (27, $C_2F_5^+$), 100 (6, $C_2F_4^+$), 69 (100, CF_3^+).

Methyl hydrogen azelate (**14a**). 10.0 g (46 mmol) dimethyl azelate were dissolved in 15 ml methanol. At −15 °C a suspension of 7.25 g (23 mmol) barium hydroxide octahydrate in 30 ml methanol were added with stirring. Stirring was continued for 4 days at −10 °C and 10 h at room temperature after which the solvent was evaporated off at room temperature and the residue was washed with tetrachloromethane. After treatment of the barium salt with 100 ml 4 M HCl, **14a** was extracted with diethyl ether (2 × 50 ml), the extract washed with water, and then dried ($MgSO_4$), and the diethyl ether evaporated off to afford after vacuum distillation 7.91 g (85%) **14a**. B.p. 148 °C/1 Torr (lit.[33] 159 °C/3 Torr). n_D^{20} = 1.4468 (lit.[34] 1.4474).

Dimethyl hexadecanedioate (**14b**). 64.2 g (0.311 mol) **14a** dissolved in 350 ml methanol and neutralized to 5% (1 M KOH in methanol) were electrolyzed according to procedure (II) (cell voltage: 20 V, current consumption: 1.4 F mol^{-1} current density 220 mA cm^{-2}, T = 45 °C). The cell was rinsed with methanol (350 ml) and diethyl ether (350 ml) and, after combination with the electrolyte, the solvent was evaporated, the residue was dissolved in 400 ml diethyl ether, washed with sodium hydrogen carbonate (3 × 60 ml) and then with water. After drying ($MgSO_4$), removal of the solvent and vacuum distillation 39.00 g (80%) **14b** were obtained. M.p. 51 °C (lit.[35] 52 °C). B.p. 107–113 °C/0.2 Torr (lit.[35] 105–110 °C/0.2 Torr). IR (KBr): ν = 1735 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.24 (m, 20 H, 10 × CH_2), 1.61 (m, 4 H, 3-H and 14-H), 2.30 (t, J = 7.7 Hz, 4 H, $CH_2CO_2CH_3$), 3.66 (s, 6 H, CO_2CH_3). MS (GC–MS, 70 eV): *m/z* (%) = 314 (1) [M^+], 283 (56) [$M^+ - OMe$], 250 (14) [$M^+ - MeOH$], 241 (45) [McLafferty], 209 (30) [241 − MeOH], 191 (19), 168 (13) [$C_{11}H_{20}O^+$], 154 (14) [$C_{10}H_{18}O^+$], 112 (35) [$C_7H_{12}O^+$], 98 (100) [$C_6H_{10}O^+$], 84 (39) [$C_5H_8O^+$], 74 (47) [McLafferty], 59 (14) [$C_2H_3O^+$], 55 (38) [$C_3H_3O^+$], 43 (23) [$C_2H_3O^+$], 41 (23) [$C_3H_5^+$].

Dimethyl docosanedioate (**15b**). 9.76 g (40 mmol) methyl hydrogen dodecanedioate (**15a**), prepared from dimethyl dodecanedioate as for **14a** from the diester, were electrolyzed according to procedure (III) (current consumption: 1.25 F mol^{-1}, cell voltage 40–70 V). Distillation at 100–160 °C/0.05–0.02 mbar afforded 1.32 g (16.5%) methyl undecanoate and methyl 11-undecenoate and at 160–205 °C/2 × 10^{-4} mbar 4.19 g (53%) **15b**.

15b: IR (KBr): ν = 1742 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.22 (s, 32 H, 4–19-H), 1.58 (m, 4 H, 3-H and 20-H), 2.27 (t, J = 7.17 Hz, 4 H, 2-H, 21-H), 3.63 (s, 6 H, OCH_3). MS (GC–MS, 70 eV): *m/z* (%) = 367 (17) [$M^+ - OCH_3$], 334 (4) [$M^+ - 2\ CH_3OH$], 325 (10) [$M^+ - CH_2COOCH_3$], 293 (7) [325 − CH_3], 275 (6), 252 (5) [$C_{17}H_{32}O^+$], 238 (4) [$C_{16}H_{30}O^+$], 210 (4) [$C_{14}H_{26}O^+$], 182 (4) [$C_{12}H_{22}O^+$], 154 (11) [$C_{10}H_{18}O^+$], 112 (33) [$C_7H_{12}O^+$], 98 (100) [$C_6H_{10}O^+$], 74 (53) [McLafferty], 55 (62) [$C_3H_3O^+$], 43 (50) [$C_2H_3O^+$], 41 (29) [$C_3H_5O^+$].

2-Hydroxycyclohexadecanone (**16**). To 3.0 g (130 mmol) sodium in refluxing dry xylene (350 ml) were continuously added 6.0 g (19 mmol) **14b** in 50 ml of dry xylene over 4 h by means of a motor-driven syringe. The mixture was refluxed for 1 h after which it was cooled in ice. To the ice-cold solution 1 ml methanol and then 5 ml of water were added and then the solution was acidified with 2 M hydrochloric acid to pH 5. The organic layer was extracted with saturated sodium hydrogen carbonate solution (80 ml), washed with brine (2 × 80 ml), and dried ($MgSO_4$) and the solvent evaporated off. Flash

chromatography (petroleum ether–diethyl ether 3:1) of the residue afforded 4.12 g (85%) **16**. B.p. 130 °C/0.05 mbar (lit.[36] 138–140/0.1 Torr). M.p. 58 °C (from pentane) (lit.[37] 58–59 °C). IR (film): $\nu = 1710\ cm^{-1}$ (C=O). ^1H NMR ($CDCl_3$): δ 1.21–1.87 (m, 26 H, 4-H to 15-H), 2.31 (m, 1 H, 3-H), 2.60 (m, 1 H, 3'-H), 3.53 (d, $J = 4.8$ Hz, 1 H, O–H), 4.25 (q, $J = 4.7$ Hz, 1 H, C*H*OHC=O). ^{13}C NMR ($CDCl_3$): δ 22.3 (t, C-4), 22.8 (t, C-14), 27.6–26.5 (10 × t, C-5 to C-13 and C-15), 33.4 (t, C-3), 36.7 (t, C-16), 76.2 (d, *C*HOHCO), 212.0 (s, CHOH*C*O). MS (GC–MS, 70 eV): *m/z* (%) = 254 (18) [M^+], 236 (13) [$M^+ - H_2O$], 210 (4) [236 − CO], 180 (4), 155 (6) [$C_{10}H_{19}O^+$], 55 (100) [$C_3H_3O^+$]. $C_{16}H_{30}O_2$ (254.4): Calcd. C 75.94, H 11.89. Found C 75.52, H 12.04%.

Cyclohexadecanone (**17**). 1.11 g (4.4 mmol) **16** were dissolved in dioxane (30 ml) together with 1.5 g zinc powder and 0.5 ml of conc. hydrochloric acid and heated for 40 h at reflux. Every 8 h, 1 ml of hydrochloric acid and 0.25 g zinc powder were added. Thereafter the mixture was extracted with diethyl ether (3 × 50 ml), the organic layers were neutralized with saturated sodium hydrogen carbonate (20 ml), washed with brine (2 × 20 ml) and dried (calcium chloride) and the solvent evaporated off. Flash chromatography (petroleum ether–diethyl ether) afforded 0.798 g (8%) **17** as a white solid. M.p. 58 °C (lit.[38] 58–60 °C). ^1H NMR ($CDCl_3$): δ 1.29 (m, 22 H, 4-H to 14-H), 1.64 (m, 4 H, 3-H and 15-H9), 2.41 (t, $J = 6.7$ Hz, 4 H, 2-H and 15-H). MS (GC–MS, 70eV): *m/z* (%) = 238 (38) [M^+], 220 (10) [$M^+ - H_2O$], 209 (6) [$M^+ - C_2H_5$], 181 (7) [$M^+ - C_4H_9$], 180 (14) [$M^+ - H_3CCOCH_3$], 71 (100) [$C_4H_7O^+$]. $C_{16}H_{30}O$ (248.4): Calcd. C 80.61, H 12.68. Found C 80.85, H 12.39%.

Cyclohexadec-2-enone (**18**). To 0.97 g (9.6 mmol) of absolute diisopropylamine in 20 ml of dry tetrahydrofuran were added dropwise at −78 °C, 8.5 mmol *n*-butyllithium in hexane, and the solution was subsequently stirred at 0 °C for 30 min. To this solution, over 10 min at −78 °C, 1.9 g (8 mmol) of **17** in 5 ml tetrahydrofuran were added dropwise, after which the solution was stirred at −78 °C for 1 h. After addition of 1.5 g (13.9 mmol) of trimethylsilyl chloride the solution was warmed to room temperature and stirred for 1 h. After addition of 30 ml petroleum ether the precipitated lithium chloride was separated by filtration over silica gel. Flash chromatography afforded 1.88 g (75%) of a mixture of (*E*)- and (*Z*)-1-trimethylsilyloxy-1-cyclohexadecene.

The silyl enol ether (0.914 g, 3.0 mmol) was treated in 5 ml of absolute acetonitrile with 0.661 g (3.0 mmol) palladium(II) acetate. The mixture was stirred under argon for 12 h after which 20 ml of diethyl ether were added and the palladium removed by filtration over silica gel. Flash chromatography of the residue (petroleum ether–diethyl ether 9:1) afforded 0.652 g (87%) of **18**. M.p. 24 °C. The spectroscopic data corresponded to those given in Ref. 38.

3-Methylcyclohexadecanone (**19**). 1.50 g (7.9 mmol) copper(I) iodide were suspended in 20 ml of absolute diethyl ether under argon, and 15.6 mmol methyl lithium were added at 0 °C. The reaction was stirred for 5 min at 0 °C, after which 0.590 g (2.5 mmol) **18** in 10 ml of absolute diethyl ether were added and the solution was stirred for 3 h at room temperature. For work-up the ice-cold reaction mixture was acidified with 1 M HCl, and the organic layer was separated, washed with water (3 × 20 ml) and dried ($MgSO_4$). Flash chromatography (petroleum ether–diethyl ether 9:1) of the residue afforded 0.512 g (86%) of **19** as colorless oil. The spectroscopic data corresponded to those in Ref. 38.

Exaltone (**20**). In a three-necked flask under nitrogen 83.80 g (0.75 mol) potassium *tert*-butoxide were dissolved in 350 ml of absolute decalin and heated. To the refluxing solution (190 °C), over 94 h, a solution of 3.64 g (11.5 mmol) **14b** in 55 ml decalin was added by means of a motor-driven syringe. After the addition the solution was refluxed for an additional 48 h. For work-up the ice-cold solution was acidified with acetic acid and the organic layer was separated. The layer was neutralized with saturated sodium bicarbonate and washed with water (2 × 100 ml). Flash chromatography of the residue following removal of the solvent afforded 0.154 g (6%) **20** . 80% of **14b** were recovered. M.p. 62 °C (lit.[39] 63 °C).

Muscone (**22**). 1.40 g (6.3 mmol) **20** were converted as for **17** into 1.51 g (82%) 1-trimethylsilyloxy-1-cyclopentadecene. The silyl enol ether (0.604 g, 2.0 mmol) was transformed into 0.353 g (80%) cyclopentadec-2-enone (**21**). M.p. 28 °C. The spectroscopic data corresponded to those given in Ref. 40. 0.333 g (1.5 mmol) **21** were converted as for **18** into 0.33 g (87%) **22**. The spectroscopic data corresponded to those in Ref. 40.

Monomethyl ester of Pripol® 1008 (**28**). 566 g (1 mol) Pripol® 1008 (**23**) were dissolved in 2.5 l of dichloromethane and 69 ml (1.7 mol) of methanol were added. The solution was stirred at room temperature, during which 60 g (0.6 mol) of concentrated sulfuric acid were added dropwise. After 72 h the mixture was washed three times with 500 ml portions of water. The organic solution was dried over magnesium sulfate and evaporated under reduced pressure. The residue was separated by flash chromatography. With petroleum ether–ether (5:1) 386 g (65%) of diester **29** were eluted, petroleum ether–ether (3:1) yielded 174 g (30%) of half ester **28** and 16.9 g (3%) of **23** were recovered.

28: R_f 0.2 [petroleum ether–ether (3:1)]. B.p. 230–250 °C/0.005 mbar. IR (film): $\nu = 3600$–2400, 2900, 2830, 1740, 1704, 1450, 1430, 1360, 1240, 1190, 1160, 1100, 1005 cm^{-1}. MS (70 eV): *m/z* (%) = 580, 578 (0.5, 1.5) [M^+], 562, 560 (4, 5) [$M^+ - H_2O$], 548, 546 (1, 2) [$M^+ - MeOH$], 111 (33) [$C_8H_{15}^+$], 97 (57)

$[C_7H_{13}^+]$, 83 (68) $[C_6H_{11}^+]$, 74 (22) [McLafferty], 69 (86) $[C_5H_9^+]$, 57 (90) $[C_4H_9^+]$, 55 (100) $[C_4H_7^+]$, 43 (92) $[C_3H_7^+]$.

29: R_f 0.65 [petroleum ether–ether (3:1)]. B.p. 210–240 °C/0.005 mbar. IR (film): ν = 2900, 2830, 1740, 1450, 1430, 1360, 1240, 1190, 1160, 1110, 1005 cm^{-1}. MS (70 eV): *m/z* (%) = 594, 592 (2, 1.5) $[M^+]$, 562, 560 (2, 4) $[M^+ - MeOH]$, 111 (36) $[C_8H_{15}^+]$, 97 (68) $[C_7H_{13}^+]$, 83 (74) $[C_6H_{11}^+]$, 74 (26) [McLafferty], 69 (92) $[C_5H_9^+]$, 55 (100) $[C_4H_7^+]$, 43 (94) $[C_3H_7^+]$.

Dimethyl heptacontanedioate (**32**). 5.79 g (10 mmol) of the half ester **28** were electrolyzed following general prodecure (I). The reaction was terminated after a charge of 2 F mol^{-1} had passed through the electrolyte. 2.14 g (37%) **28** were recovered after column filtration. The less polar fraction was further separated by bulb-to-bulb distillation to yield 1.07 g (20%) of the disproportionation products **30**, **31** at 210–250 °C/0.005 mbar, and the residue contained 2.04 g (38%) of the desired diester **32** as a colorless oily liquid. IR (film): ν = 2900, 2850, 1740, 1450, 1430, 1355, 1185, 1160 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.84 (m), 1.24 (br s), 1.60 (m) (total = 130 H), 2.28 (t, J = 7.5 Hz, 4 H, $CH_2CH_2CO_2CH_3$), 3.65 (s, 6 H, CO_2CH_3). MS (DCI/NH_3): *m/z* (%) = 1090.5 (52), 1089.4 (75) $[C_{72}H_{142}O_4{}^+NH_4^+]$, 1088.5 (75), 1087.5 (100) $[C_{72}H_{140}O_4{}^+NH_4^+]$, 1086.5 (51), 1085.4 (50) $[C_{72}H_{138}O_4{}^+NH_4^+]$.

$C_{36}H_{72}O_2$, $C_{36}H_{70}O_2$ (**30**, **31**) (*disproportionation products*). B.p. 210–250 °C/0.005 mbar. IR (film): ν = 2900, 2850, 1740, 1450, 1430, 1355, 1235, 1185, 1160 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.85 (m), 1.24 (br s), 1.59 (m), 1.99 (m), 2.29 (t, J = 7.5 Hz, 2 H, $CH_2CH_2CO_2CH_3$), 3.65 (s, 3 H, CO_2CH_3), 4.94 (m), 5.39 (m), 5.80 (m); olefinic protons: alkyl protons = 0.022; the integration ratio proved the mixture to be a 1:1 mixture of **30** and **31**. MS (70 eV): *m/z* (%) = 536, 534 (1, 1) $[M^+]$, 505, 503 (0.5, 0.5) $[M^+ - MeOH]$, 111 (32) $[C_8H_{15}^+]$, 97 (57) $[C_7H_{13}^+]$, 83 (60) $[C_6H_{11}^+]$, 74 (21) [McLafferty], 57 (100) $[C_4H_9^+]$, 55 (80) $[C_4H_7^+]$.

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