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## Influences on the Selectivity of the Kolbe versus the Non-Kolbe Electrolysis in the Anodic Decarboxylation of Carboxylic Acids

Elisabeth Klocke, Agnes Matzeit, Marianne Gockeln and Hans J. Schäfer\*

Organisch-Chemisches Institut der Universität,  
Corrensstraße 40, W-4400 Münster, F. R. G.

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The anodic decarboxylation of 3-oxanonanoic acid (**2a**) and 3-oxapentadecanoic acid (**2b**) in methanol leads exclusively to products of the non-Kolbe electrolysis. The influence of coelectrolysis, solvent, current density, degree of neutralization and chain length of the alkoxy group on the anodic decar-

boxylation of **2a**, **b** have been investigated. An extended alkyl chain in the alkoxy group, coelectrolysis with long-chain fatty acids, ethanol or dimethylformamide as solvent, and a high current density favor the Kolbe coupling against the non-Kolbe electrolysis.

Anodic oxidation of carboxylic acids provides C–C bond-forming reactions and functional interconversion by the Kolbe or non-Kolbe pathway<sup>[2]</sup>. The Kolbe electrolysis produces radicals useful in dimerization or addition to double bonds, the non-Kolbe electrolysis generates carbocations that can react with diverse nucleophiles. The selectivity depends on external and structural parameters of the carboxylic acid. The Kolbe pathway is favored by a platinum electrode, an acidic electrolyte and a high current density, while a low current density, a graphite electrode, salt additives and an alkaline electrolyte support the non-Kolbe pathway. Electron-withdrawing groups in the  $\alpha$ -position of the carboxylic acid assist the Kolbe pathway, whilst electron-donating substituents support the cationic route. This limits the scope of anodic decarboxylations, because carboxylic acids with electron-donating groups lead to no or only unsatisfactory radical coupling.

The present investigation was stimulated by a paper of Muck and Wilson<sup>[3]</sup>, who reported that the non-Kolbe electrolysis of fatty acids at a graphite anode changed to a Kolbe radical pathway with increasing chain length of the fatty acid.

Several reports have previously appeared on the anodic decarboxylation of hydroxy-, alkoxy- or acyloxy-carboxylic acids<sup>[4]</sup>. With an alkoxy group in  $\alpha$ -position no Kolbe dimers, but only products of cationic origin are found<sup>[4h,i,5]</sup>. The ionization potential of the primarily formed radical has been used to decide between the radical and the cationic pathway. If it is above 8 eV Kolbe dimers preponderate, if it is below non-Kolbe products are formed<sup>[6b]</sup>. The ionization potential of the  $\alpha$ -alkoxy radical is below 8 eV<sup>[6]</sup>, it is hence oxidized at the anode to form a stabilized carbocation, which undergoes solvolysis to an acetal or deprotonation to an enol ether.

We transfer the observation by Muck and Wilson to  $\alpha$ -alkoxy-carboxylic acids by extending the alkyl chain of the

alkoxy group. Hexyl and dodecyl groups were used as alkyl substituents. Furthermore, coelectrolysis with long-chain fatty acids such as **1a**, **b** was applied, because radicals derived from coacids, that do not undergo the non-Kolbe electrolysis, can trap Kolbe radicals prior to their oxidation<sup>[7]</sup>. For that purpose, the Kolbe electrolysis of 3-oxanonanoic acid (**2a**) and 3-oxapentadecanoic acid (**2b**) with and without hexanoic acid (**1a**) or dodecanoic acid (**1b**) has been investigated.

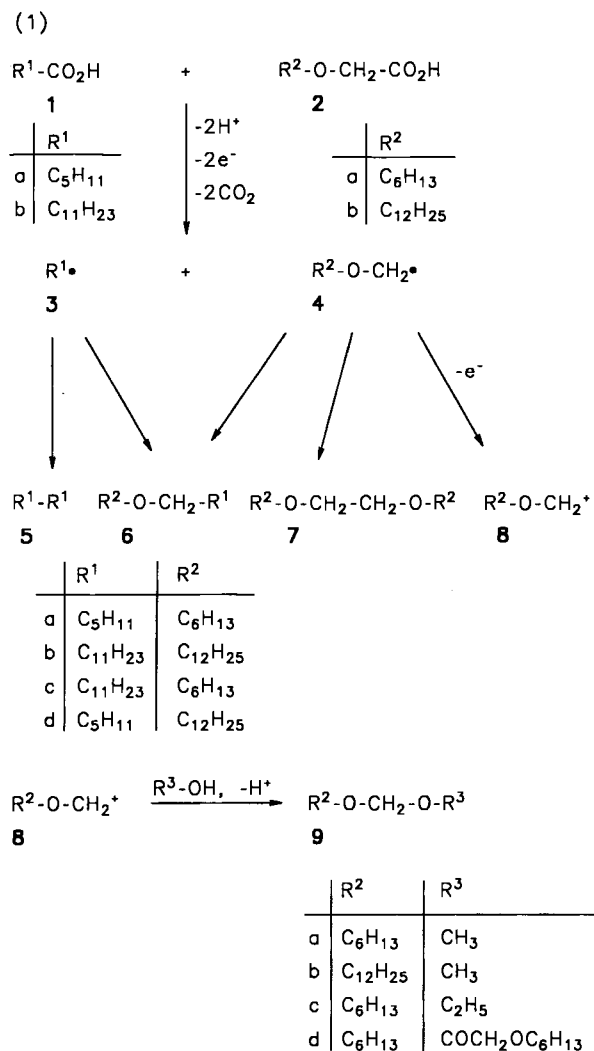
### Results and Discussion

#### A. Coelectrolysis and Variation of Chain Length of **1** and the Alkoxy Group of **2**

**2a**, **b** were prepared by reaction of sodium chloroacetate with sodium hexanolate or dodecanolate. The anodic decarboxylation of the carboxylic acids **1a**, **b** and **2a**, **b** leads to radicals **3** and **4**, which couple to give symmetrical and unsymmetrical Kolbe products **5**, **7** and **6**. Moreover, radical **4** can be oxidized to cation **8**, which undergoes solvolysis to non-Kolbe product **9** (Eq. 1).

Acids **1** and **2** were dissolved in methanol (ratios given in Table 1) and electrolyzed in an undivided beaker-type cell between two platinum electrodes at 5–10% neutralization and a current density of 200 mA cm<sup>-1</sup>. The results are given in Table 1, which shows that no Kolbe dimers of **2a** or **2b** are obtained under the chosen reaction conditions, non-Kolbe products being formed exclusively (entries 1, 2). The mixed coelectrolysis with **1**, however, leads to radical coupling products of **2**, namely **6** and **7**, besides **9**, which is of cationic origin. An influence of the alkyl chain length in **1** and **2** on the selectivity can be clearly seen (entries 3–6). For **2a** and **1a** the ratio of the radical to the cationic pathway for **2** is 0.75:1, for **2b** and **1b** it increases to 2.03:1.

The determination of the conversion rates to **1a** and **2a** (ratio 6.5:1) revealed that **2a** reacts ca. 5 times faster than



**1a.** Correspondingly, the formation of **9** predominates in the first part of the electrolysis, while **5** and **6** are formed to a larger extent later on. The faster conversion of **2a** is possibly due to its lower  $pK_a$  value<sup>[8]</sup> and a better adsorption due to the electron-donating  $\alpha$ -alkoxy group. This leads to a preferential coverage of the electrode surface with **2a** in the first part of the electrolysis and the oxidation of the

intermediate radical **4** to the carbocation **8**. When the concentration of **2a** decreases, alcanoic acid **1a** is adsorbed instead. This enforces a better ordered structure leading to a higher portion of radical products.

To maintain an excess of **1** at the electrode surface small amounts of alkoxyacetic acid **2** were continuously added to an excess of **1** during the course of the electrolysis. The results obtained are shown in Table 2.

In the coelectrolysis of **1a** with **2a** the continuous addition of **2a** increased the ratio of radical coupling to cationic products of **2** by a factor of 2.27 as compared to fixed concentrations of **1a** and **2a** (Table 2, entry 2 and Table 1, entry 3), for **2a** and **1b** to 1.92 (Table 2, entry 4 and Table 1, entry 4), for **2b** and **1a** to 1.61 (Table 2, entry 6 and Table 1, entry 5) and for **2b** and **1b** to 1.15 (Table 2, entry 8 and Table 1, entry 6).

For **2a** and **1a** or **1b** the effect of an ordered carboxylate structure at the electrode surface is most clearly visible, for **1b** and **2b** it is less pronounced, because the yield of radical products is already high with fixed concentrations of the acids. Table 1 (entries 3, 5, 6) shows that an increasing chain length of the fatty acid improves the yield of Kolbe products.

The rate and period of the addition during the electrolysis also influence the ratio of radical to cationic products as shown in Table 3.

In order to obtain a high portion of radical products, acid **2** has to be added at an early stage of the electrolysis, when the concentration of **1** is high. As the concentration of **1** decreases continuously the addition of **2** should be stopped some time before the end of the electrolysis. This consideration is supported by the data in Table 2, entry 2. A faster addition rate at the beginning and a slower one at the end increases the yield of Kolbe dimers as can be seen by comparing entries 1–3 with entry 4 in Table 3.

The electrolysis of **1a** or **1b** leads to radical dimers **5** and disproportionation products (Kolbe products: K). In contrast, **2** exclusively is converted into the acetals **9** (non-Kolbe product: nK), derived from the intermediate cation **8**. Coelectrolysis of **1** and **2**, however, generates to a major extent mixed radical coupling products **6** and minor amounts of the symmetrical dimer **7** apart from the acetal **9**. A rationalization of this result would be that radical **4** is trapped by

Table 1. Anodic decarboxylation of **2** and mixed anodic decarboxylation of the acids **1** and **2**

Entry	Carboxylic acids and ratios <sup>[a]</sup>	Conversion <sup>[b]</sup> (%)	Products and relative yields <sup>[c]</sup>			Ratio radical coupling/cationic product of <b>2</b>
			mixed dimer	symmetrical dimer	non-Kolbe product	
1 <sup>[d]</sup>	<b>2a</b>	89	-	0 ( <b>7a</b> )	100 ( <b>9a</b> )	0
2 <sup>[d]</sup>	<b>2b</b>	83	-	0 ( <b>7b</b> )	100 ( <b>9b</b> )	0
3 <sup>[d]</sup>	<b>2a:1a</b> (1:10)	99	32 ( <b>6c</b> )	7 ( <b>7a</b> )	61 ( <b>9a</b> )	0.75
4 <sup>[e]</sup>	<b>2a:1b</b> (1:10)	100	51 ( <b>6d</b> )	7 ( <b>7a</b> )	42 ( <b>9a</b> )	1.56
5 <sup>[e]</sup>	<b>2b:1a</b> (1:10)	97	30 ( <b>6e</b> )	2 ( <b>7b</b> )	68 ( <b>9b</b> )	0.49
6 <sup>[e]</sup>	<b>2b:1b</b> (1:10)	98	58 ( <b>6f</b> )	7 ( <b>7b</b> )	35 ( <b>9b</b> )	2.03

<sup>[a]</sup> Current density: 200 mA cm<sup>-2</sup>; cell voltage: 50 V; T = 42°C. — <sup>[b]</sup> Conversion of **2** determined by GLC of the methyl ester. — <sup>[c]</sup> Determined by GLC with calibration of the peak areas. — <sup>[d]</sup> Degree of neutralization  $\alpha = 10\%$ ; current consumption  $Q = 3.0 \text{ F mol}^{-1}$ . — <sup>[e]</sup>  $\alpha = 5\%$ ,  $Q = 1.3 \text{ F mol}^{-1}$ .

Table 2. Mixed Kolbe electrolysis of **1** and **2** with continuous addition of small amounts of **2** during the electrolysis

Entry	Carboxylic acids and ratios <sup>[a]</sup>	Conversion <sup>[b]</sup> (%)	Products and relative yields <sup>[c]</sup>			Ratio : radical coupling/ cationic product of <b>2</b>
			mixed dimer	symmetrical dimer	non-Kolbe product	
1	<b>2a</b> : <b>1a</b> (1 : 5)	100	37 ( <b>6c</b> )	12 ( <b>7a</b> )	51 ( <b>9a</b> )	1.17
2	<b>2a</b> : <b>1a</b> (1 : 10)	100	53 ( <b>6c</b> )	7 ( <b>7a</b> )	40 ( <b>9a</b> )	1.70
3	<b>2a</b> : <b>1b</b> (1 : 5)	97	59 ( <b>6d</b> )	8 ( <b>7a</b> )	33 ( <b>9a</b> )	2.33
4	<b>2a</b> : <b>1b</b> (1 : 10)	100	70 ( <b>6d</b> )	4 ( <b>7a</b> )	26 ( <b>9a</b> )	3.00
5	<b>2b</b> : <b>1a</b> (1 : 5)	97	40 ( <b>6e</b> )	3 ( <b>7b</b> )	57 ( <b>9b</b> )	0.82
6	<b>2b</b> : <b>1a</b> (1 : 10)	97	42 ( <b>6e</b> )	1 ( <b>7b</b> )	57 ( <b>9b</b> )	0.79
7	<b>2b</b> : <b>1b</b> (1 : 5)	100	56 ( <b>6f</b> )	8 ( <b>7b</b> )	36 ( <b>9b</b> )	2.03
8	<b>2b</b> : <b>1b</b> (1 : 10)	100	61 ( <b>6f</b> )	7 ( <b>7b</b> )	32 ( <b>9b</b> )	2.33

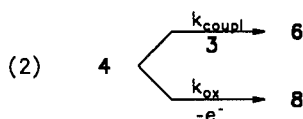
<sup>[a]</sup> Current density: 200 mA cm<sup>-2</sup>; cell voltage: 50 V; *T* = 42 °C; current consumption: 1.3 F mol<sup>-1</sup>; a mixture of 2 mmol of **1** and 2 mmol of **2**, dissolved in methanol, was continuously added to 8 mmol of **1** between 0.05 to 0.8 F mol<sup>-1</sup>. — <sup>[b]</sup> Conversion of **2** determined by GLC. — <sup>[c]</sup> Determined by GLC calibration.

Table 3. Continuous addition of **2** to the electrolyte; influence of the rate and period of addition during the electrolysis

Entry <sup>[a]</sup>	Period of addition from - to F mol <sup>-1</sup> current consumption	Conversion <sup>[b]</sup> (%)	Ratio <sup>[c]</sup> : radical coupling/ cationic product of <b>2</b>
1 <sup>[d]</sup>	0.14 - 0.66	100	1.57
2 <sup>[d]</sup>	0.05 - 0.90	100	1.68
3 <sup>[d]</sup>	0.19 - 1.04	100	1.27
4 <sup>[e]</sup>	0.05 - 0.80	100	3.00

<sup>[a]</sup> Current density: 200 mA cm<sup>-1</sup>; degree of neutralization: 5%; current consumption: 1.3 F mol<sup>-1</sup>; *T* = 42 °C; cell voltage: 50 V; **1b**/**2a** = 10:1. — <sup>[b]</sup> Conversion of **2a** determined by GLC calibration. — <sup>[c]</sup> Determined by GLC calibration. — <sup>[d]</sup> Continuous addition of **2a** at the same rate. — <sup>[e]</sup> Addition of **2a** at the beginning faster than at the end.

**3**, before further oxidation of **4** to **8** occurs. The ratio of Kolbe versus non-Kolbe products (*r<sub>rc</sub>*, ratio of radical- to cation-derived products) of **2**, neglecting the minor portion of the symmetrical dimer, can be expressed according to Eqs. 2, 3.



$$(3) \quad r_{rc} = \frac{K}{nK} = \frac{k_{\text{coupl}}[3][4]}{k_{\text{ox}}[4]} = \frac{k_{\text{coupl}}[3]}{k_{\text{ox}}}$$

Therefore, a higher concentration of radical **3**, which can be set proportional to that of acid **1**, leads to a higher portion of radical-derived mixed Kolbe products.

The ratio of *r<sub>rc</sub>*, however, depends also on the mode of addition of **2** to the electrolyte; *r<sub>rc</sub>* is higher, if **2** is added gradually to an excess of **1** (Table 1, entries 3–6, Table 2, entries 1–8). This indicates a preferential oxidation of **2** in the first period of electrolysis. To our knowledge the oxidation potentials of carboxylates do not differ much, the reaction is more dependent on a critical potential of ca. 2.1 V<sup>[2,10]</sup>, where the electrode surface gets depleted from solvent and is covered by the carboxylate. In the coelectro-

lysis of **1** and **2** the adsorption of **2** seems to be favored at the expense of **1**. This may be due to the lone-pair electrons at the oxygen atom and/or the lower *pK<sub>a</sub>* value of **2** compared to **1**. As only 5–10% of the acid is converted into the carboxylate, **2** is preferentially deprotonated and adsorbed as carboxylate. Thus, without continuous addition of small portions of **2** to keep its concentration comparable to that of **1** at the anode a higher portion of **4** is generated, whose preferential oxidation leads to less radical dimerization. In the later period of the electrolysis less **7** and more **5** is formed, because the amount of **4** has decreased relative to that of **3** due to the depletion of **2**. With continuous addition of **2**, however, the concentration of **2** at the electrode and consequently that of **4** was kept as constant as possible during the entire electrolysis time.

Muck and Wilson<sup>[3]</sup> had observed, that with potassium valerate at graphite electrodes in acetonitrile a substituted acetamide, the product of a non-Kolbe electrolysis, was obtained in 50% yield. The portion of acetamide, however, gradually decreased in favor of the Kolbe dimer by using as carboxylates potassium octanoate and potassium laurate. The authors explained the behavior as follows: short-chain carboxylates are adsorbed more random-like, which decreases the radical concentration and disfavors coupling; carboxylic acids with longer alkyl chains tend to get adsorbed in a stack perpendicular to the electrode surface,

which is favored by enhanced van der Waals attractions of the hydrophobic alkyl groups with increasing chain length. This leads to a high alkyl radical concentration after anodic decarboxylation, which favors the bimolecular coupling reaction in comparison with the monomolecular oxidation.

The data compiled in Table 2 indicate that the portion of radical-derived products increases in the following sequence of coelectrolyses: **2b/1a**: 45%; **2a/1a**: 63%; **2b/1b**: 70%; **2a/1b**: 75%. The behavior shows that the chain length of the carboxylic acids indeed influences the follow-up reaction of the intermediate radical. Two effects can be deduced from the data: the radical pathway is supported (i) by an extended chain length of the alkyl groups and (ii) by a longer alkyl group  $R^1$  of **1** than  $R^2$  of **2**. This is in accordance with the following mechanistic picture: a firm monolayer of alkanates in which the alkoxyacetate is imbedded leads to a high density of radicals **3** and **4** in an apolar matrix of alkyl chains. This favors the radical dimerization and disfavors the oxidation to the cation which prefers a more polar medium. The stability of the monolayer increases with the length of the alkyl chains because of the increased van der Waals attractions of the latter.

Two ways of adsorption of the alkoxyacetate at the electrode are conceivable (Figure 1): (a) the carboxylate group and the lone-pair electron of the alkoxy group interact both with the electrode surface, and (b) only the carboxylate group is adsorbed at the electrode. In mode (a) the hydrophobic attractions of the alkyl chains are smaller and more *gauche* conformations, which are energetically less favorable, occur than in (b). In mode (a), however, energy is gained compared to (b) through the additional interaction of the lone-pair electrons of the ether oxygen atom with the electrode surface.

When  $R^1$  in **1** is longer than  $R^2$  in **2** arrangement (b) of **2** appears to be more favorable because of stronger van der Waals attractions between **2** and **1** than in (a). Furthermore, this combination of **1** and **2** should lead to a better lipophilic apolar wrapping of the polar alkoxy group in **2**. The contrary should prevail in the combination of **1** with a short  $R^1$  and **2** with a long  $R^2$  group, where array (a) should predominate and the coating of **2** should be much less efficient.

The current density offers the possibility of changing the radical concentration at the electrode surface. A high current

density leading to higher radical concentrations should favor the bimolecular coupling of the radicals compared with their monomolecular oxidation to carbocations. The results are shown in Table 4.

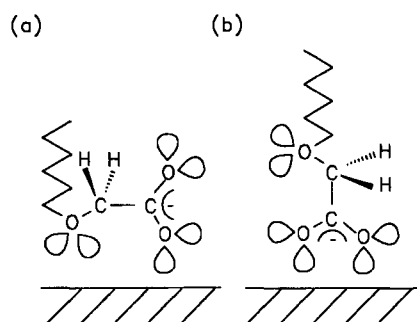


Figure 1. Possible modes of adsorption of the carboxylate **2** at the electrode; (a) carboxylate and alkoxy group interact with the electrode, (b) only the carboxylate group is adsorbed

An increase of the current density from 100 to 200 mA  $\text{cm}^{-2}$  indeed enhances the yield of radical dimers at the expense of cationic products. Above 200 mA  $\text{cm}^{-2}$ , however, the current density seems to have no further significant influence on the ratio of Kolbe to non-Kolbe products.

The current density controls the potential and the radical concentration at the anode. In the Kolbe electrolysis a critical potential has to be reached to achieve a preferential adsorption of the carboxylate and a competitive desorption of the more easily oxidizable solvent. A higher portion of non-Kolbe products was found at a lower current density. This leads to the conclusion that the lower anode potential causes a not yet uniform carboxylate layer with methanol still at the electrode surface, favoring the cationic pathway.

Furthermore,  $r_{rc}$  can be expressed by Eq. (4) for the two competing reactions leading to either a coupling product or monomer cation.

$$(4) \quad r_{rc} = \frac{K}{nK} = \frac{k_{\text{coupl}}[3][4]}{k_{\text{ox}}[4]} = \frac{k_c[3]}{k_{\text{ox}}} \approx \bar{i}$$

That means the portion of Kolbe products increases for kinetic reasons with the current density. A constant value

Table 4. Influence of the current density in the coelectrolysis of **1b** and **2b**

Entry <sup>[a]</sup>	Current density (mA $\text{cm}^{-2}$ )	Conversion <sup>[b]</sup> (%)	Products and relative yields <sup>[c]</sup>			Ratio : radical coupling / cationic product of <b>2</b>
			mixed dimer ( <b>6f</b> )	symmetrical dimer ( <b>7b</b> )	non-Kolbe product ( <b>9b</b> )	
1 <sup>[d]</sup>	100	98	45	5	50	1.08
2 <sup>[e]</sup>	200	100	61	7	32	2.33
3 <sup>[f]</sup>	300	98	61	4	35	1.94
4 <sup>[g]</sup>	400	97	64	4	32	2.23

<sup>[a]</sup> **1b/2b** = 10:1; degree of neutralization: 5%;  $T = 40-45^\circ\text{C}$ ; current consumption: 1.3 F  $\text{mol}^{-1}$ . — <sup>[b]</sup> Conversion of **2b** determined by GLC calibration. — <sup>[c]</sup> Determined by GLC calibration. — <sup>[d]</sup> Cell voltage: 35 V. — <sup>[e]</sup> Cell voltage: 50 V. — <sup>[f]</sup> Cell voltage: 90 V. — <sup>[g]</sup> Cell voltage: 130 V.

Table 5. Mixed Kolbe electrolysis of **1a** and **2a** in methanol<sup>[a]</sup>

Entry	$\alpha$ (%) <sup>[b]</sup>	Conversion <sup>[c]</sup> (%)	Products and relative yields (%) <sup>[d]</sup>			Ratio: radical coupling/ cationic product of <b>2</b>
			mixed dimer ( <b>6a</b> )	symmetrical dimer ( <b>7a</b> )	non-Kolbe product ( <b>9a</b> )	
1	5	98	21	8	71	0.41
2 <sup>[e]</sup>	10	98	32	7	61	0.64
3	20	95	28	7	65	0.54
4	30	96	24	6	70	0.43
5	90	96	22	6	72	0.39

<sup>[a]</sup> **2a/1a** = 1:10; current density: 200 mA cm<sup>-2</sup>; cell voltage: 50 V; *T* = 40 °C; current consumption *Q* = 1.2–1.4 F mol<sup>-1</sup>. — <sup>[b]</sup> Degree of neutralization. — <sup>[c]</sup> Conversion of **2a** determined by GLC. — <sup>[d]</sup> Determined by GLC calibration. — <sup>[e]</sup> Run identical to Table 1, entry 3, deviations are due to experimental error.

Table 6. Mixed Kolbe electrolysis of **1a** and **2a** in ethanol<sup>[a]</sup>

Entry	$\alpha$ (%) <sup>[b]</sup>	Conversion <sup>[c]</sup> (%)	Products and relative yields (%) <sup>[d]</sup>			Ratio: radical coupling/ cationic product of <b>2</b>
			mixed dimer ( <b>6a</b> )	unsymmetrical dimer ( <b>7a</b> )	non-Kolbe product ( <b>9a</b> )	
1	5	89	35	20	44	1.25
2	10	81	42	20	38	1.63
3	20	87	46	11	43	1.33
4	30	83	43	13	44	1.27
5	90	81	44	11	45	1.22

<sup>[a]</sup> **2a/1a** = 1:10; current density: 200 mA cm<sup>-2</sup>; cell voltage: 80 V; *T* = 45 °C; current consumption *Q* = 1.0–1.1 F mol<sup>-1</sup>. — <sup>[b]</sup> Degree of neutralization. — <sup>[c]</sup> Conversion of **2a** determined by GLC. — <sup>[d]</sup> Determined by GLC calibration.

Table 7. Mixed Kolbe electrolysis of **1a** and **2a** in DMF<sup>[a]</sup>

Entry <sup>[a]</sup>	$\alpha$ (%) <sup>[b]</sup>	Conversion <sup>[c]</sup> (%)	Products and relative yields (%) <sup>[d]</sup>	
			mixed dimer ( <b>6a</b> )	symmetrical dimer ( <b>7a</b> )
1	5	82	60	40
2	10	83	64	36
3	20	59	72	28
4	30	77	61	39
5	90	77	64	36

<sup>[a]</sup> **2a/1a** = 1:10; current density: 200 mA cm<sup>-2</sup>; cell voltage: 120 V; *T* = 50 °C; current consumption *Q* = 0.80–1.0 F mol<sup>-1</sup>. — <sup>[b]</sup> Degree of neutralization. — <sup>[c]</sup> Conversion of **2a** determined by GLC. — <sup>[d]</sup> Determined by GLC calibration.

of  $r_{rc}$  above  $\bar{i} = 200$  mA cm<sup>-2</sup> indicates, that the process becomes diffusion-controlled in this case.

In order to investigate the influence of solvent and degree of neutralization ( $\alpha$ ) of the acids, 1:10 mixtures of **2a** and **1a** were coelectrolyzed in methanol, ethanol and DMF (Tables 5–7).

In methanol the acetal **9a** becomes the main electrolysis product. The ratio of Kolbe to non-Kolbe products varies from 0.39 to 0.64:1 (Table 5, entries 1–5). Electrolyses in ethanol or DMF lead to higher portions of Kolbe dimers. Ratios from 1.22 to 1.63:1 are found with ethanol as solvent (Table 6, entries 1–5). Coelectrolyses in DMF even lead to

Kolbe products only (Table 7, entries 1–5). If **2a** is electrolyzed without coacid in DMF, the non-Kolbe product **9d** and the symmetrical Kolbe dimer **7a** are formed in 12% yield, additional products, that account for the poor mass balance could not be identified. A 10% neutralization seems to be necessary for obtaining optimal yields of Kolbe products.

To investigate the influence of the different  $pK_a$  values of the carboxylic acids both **1b** and **2a** were neutralized to 100%. Since an alkaline medium favors the non-Kolbe pathway, mercury was used as cathode<sup>[9]</sup> to keep the electrolyte neutral by the formation of potassium amalgam instead of

potassium methoxide at a platinum cathode. Here, relative yields of 41% of **6c**, 5% of **7a**, and 54% of **9a** were obtained, corresponding to a ratio of Kolbe to non-Kolbe product of 0.94, which is lower than that obtained at 10% neutralization, namely 1.56 (Table 1, entry 4). Also in the coelectrolysis of **1a** and **2a** in methanol or ethanol the portion of radical coupling products is highest at 10% neutralization (Tables 5, 6).

The ratio Kolbe to non-Kolbe products varies with the degree of neutralization. At 10% neutralization the highest portion of Kolbe products is found. The lower portion at 5% neutralization possibly indicates that the carboxylate concentration is not sufficient for the coverage of the electrode surface. The increase of the non-Kolbe products at a higher degree of neutralization can be partly rationalized by an increase of the ionization power of the electrolyte because of its higher ionic strength, which should favor the cation formation at the expense of the radical pathway.

The solvent exerts the largest influence on the ratio of Kolbe versus non-Kolbe products. In the coelectrolysis of **1a** and **2a** at a degree of 10% neutralization  $r_{rc}$  increases from 0.64 in methanol to 1.63 in ethanol. In dimethylformamide only traces of the non-Kolbe product are detectable as ester **9d**.

$k_{ox}$  in Eq. 3 can be separated into a term  $k'_{ox}$  that correlates with the ionization potential of the radical and a term  $k_{sol}$  expressing the cation stabilization by the solvent;  $k_{sol}$  (Eq. 5a) can be connected with the ionization power of the solvent by using the Winstein-Grunwald equation for the solvolysis of alkyl halides or tosylates via carbocations as intermediates<sup>[11]</sup>. This leads to Eq. 5b, and as the radical concentration in these experiments of solvent variation remains constant, one obtains Eq. 5c.

$$(5a) \quad k_{sol} = k_0 10^{mY} \quad m = \text{substrate parameter} \\ Y = \text{Ionization power}$$

$$(5b) \quad \frac{K}{nK} = \frac{k_{coupl}[3]}{k'_{ox} k_0 10^{mY}}$$

$$(5c) \quad \lg \frac{K}{nK} = \lg r_{rc} = fY + C$$

$\lg r_{rc}$  correlates linearly with the Y values  $-1.090$  for methanol,  $-2.033$  for ethanol and  $-3.500$  for dimethylformamide given in ref.<sup>[12]</sup>.

Remarkable is the increase of the symmetrical Kolbe dimer **7** relative to the mixed dimer **6** in passing from methanol (**7/6** = 0.22:1) to ethanol (0.48:1) and dimethylformamide (0.56:1). In these experiments the primary ratio of **1a** and **2a** was not changed by continuous addition of **2a** to an excess of **1a**. The results can possibly be explained by a preferential adsorption of **2a** due to its lower  $pK_a$  value and its additional adsorption by the oxygen atom in the  $\alpha$ -position. Thus, in the first period of the electrolysis **2a** is enriched in the adsorbed monolayer. In the case of methanol this leads to an enhanced formation of the non-Kolbe products, while in the radical-favoring solvents ethanol and dimethylformamide an increased formation of dimer **7** is found.

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## Experimental

**Instrumentation:** <sup>1</sup>H NMR: Bruker WM 300. — MS: Finnigan MAT 312 with Varian MAT data system SS 200; capillary GLC/MS combination Finnigan MAT 8230 with Finnigan MAT data system SS 300. — Capillary GLC: Shimadzu GC-9A, quartz capillary columns: 0.32 mm x 25 m or 50 m, 0.52  $\mu$ m HP1. — Flash chromatography<sup>[13]</sup>: Silica gel 60 (Merck). — Elementary analysis: Universität Münster. — Melting points are not corrected. — Electrolysis: Double-walled, undivided standard beaker-type cell, no potential control, cell volume: 50 ml; electrodes: teflon-supported platinum foils (8 cm<sup>2</sup>). — Power supply for electrolysis: Heri potentiostat TN 250–1600 used as a galvanostat, electronic coulometer (own construction), temperature control by Colora Kryostat MC 15. — All solvents were purified by distillation. — Absolute methanol was purchased from Merck (Darmstadt, F.R.G.), ethanol was dried by distillation from sodium, DMF by distillation from calcium hydride.

**3-Oxanonanoic Acid (2a)** was prepared from hexanol and chloroacetic acid according to ref.<sup>[14]</sup>; b.p. 90–95°C/0.03 mbar (ref.<sup>[14]</sup> 155°C/2 mbar). —  $n_D^{20}$  = 1.4333.

**3-Oxapentadecanoic Acid (2b):** A solution of 18.6 g (0.10 mol) of dodecanol in toluene was added dropwise to a suspension of 8.80 g (0.22 mol, 60%) of sodium hydride in 50 ml of toluene. After 2 h at reflux, a solution of 9.40 g (0.10 mol) of chloroacetic acid in 30 ml of toluene was added, and then the mixture was heated for 4 h at reflux. It was subsequently hydrolyzed with 400 ml of water and 50 ml of methanol. At pH = 2 **2b** was extracted with ether (5 x 100 ml). The combined extracts were washed with brine, and the ether was evaporated. 19.3 g (78%) of **2b** was isolated by distillation; b.p. 135°C/0.025 mbar, m.p. 47°C (ref.<sup>[15]</sup> 46°C).

**2,4-Dioxadecane (9a):** 0.27 g (53%) of **9a** was prepared by non-Kolbe electrolysis of 0.85 g (3.50 mmol) of **2a** in methanol (procedure see below) and isolated by flash chromatography [petroleum ether/ether (10:1, v/v)]; b.p. 156°C (ref.<sup>[16]</sup> 157°C). —  $n_D^{20}$  = 1.4034.

**2,4-Dioxaheptadecane (9b)** was prepared by non-Kolbe electrolysis (procedure see below) of 0.85 g (3.50 mmol) of **2b** in methanol; 0.54 g (66%) was isolated by flash chromatography [petroleum ether/ether (10:1, v/v)],  $n_D^{20}$  = 1.4249. — IR (film):  $\tilde{\nu}$  = 2950 cm<sup>-1</sup>, 2900, 2850, 1145, 1100 (all s). — <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 0.83 (t,  $J$  = 6.9 Hz, 3H, 16-H), 1.18–1.28 (m, 18H), 1.54 (quint, 2H, 6-H), 3.32 (s, 3H, 1-H), 3.47 (t,  $J$  = 6.8 Hz, 2H, 5-H), 4.58 (s, 2H, 3-H). — MS (GC/MS, 70 eV):  $m/z$  (%) = 229 (1) [M<sup>+</sup> – 1], 199 (1) [M<sup>+</sup> – OCH<sub>3</sub>], 75 (24) [C<sub>3</sub>H<sub>7</sub>O<sub>3</sub><sup>+</sup>], 45 (100) [C<sub>2</sub>H<sub>5</sub>O<sup>+</sup>]. — C<sub>14</sub>H<sub>30</sub>O<sub>2</sub> (230.4): calcd. C 72.99, H 13.12; found C 73.21, H 13.02.

**3,5-Dioxaundecane (9c)** was prepared by non-Kolbe electrolysis (procedure see below) of 5.60 g (35.0 mmol) of **2a** in absolute ethanol; 2.15 g (38%) was isolated by flash chromatography [petroleum ether/ether (10:1, v/v)],  $n_D^{20}$  = 1.4000. — IR (film):  $\tilde{\nu}$  = 2925 cm<sup>-1</sup>, 2900, 2810, 1375, 1170 (all s). — <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 0.82 (t,  $J$  = 6.8 Hz, 3H, 11-H), 1.14 (t,  $J$  = 6.8 Hz, 3H, 1-H), 1.21–1.31 (m, 6H, 8-H, 9-H, 10-H), 1.52 (quint,  $J$  = 7.0 Hz, 2H, 7-H), 3.47 (q,  $J$  = 6.7 Hz, 2H, 2-H), 3.47 (t,  $J$  = 6.7 Hz, 2H, OCH<sub>2</sub>), 3.53 (t,  $J$  = 7.0 Hz, 2H, 6-H), 4.60 (s, 2H, 4-H). — MS (GC/MS, 70 eV):  $m/z$  (%) = 159 (3) [M<sup>+</sup> – H], 131 (36) [M<sup>+</sup> – CH<sub>2</sub>CH<sub>3</sub>], 85 (29) [C<sub>6</sub>H<sub>13</sub><sup>+</sup>], 59 (100) [C<sub>2</sub>H<sub>5</sub>OCH<sub>2</sub><sup>+</sup>], 43 (56) [C<sub>3</sub>H<sub>7</sub><sup>+</sup>]. — C<sub>9</sub>H<sub>20</sub>O<sub>2</sub> [M<sup>+</sup> – H]: calcd. 159.1385; found 159.1390.

**2-Oxaocetyl 3-Oxanonanoate (9d):** A solution of 1.60 g (10.0 mmol) of 3-oxanonanoic acid (**2a**), dissolved in 20 ml of DMF, was neu-

tralized with 1.32 ml of triethylamine. The mixture was electrolyzed at 10 °C, a cell voltage of 160 V and a current density of 100 mA cm<sup>-2</sup>. After consumption of 2.1 current equivalents (2033 As), 50 ml water was added. The solution was extracted with ether (3 x 50 ml). The combined extracts were washed with brine and dried (MgSO<sub>4</sub>). After evaporation of the solvent, the ester **9d** was isolated by flash chromatography [petroleum ether/ether (10:1, v/v)] in 12% yield;  $n_D^{20} = 1.4338$ . — IR (film):  $\tilde{\nu} = 2950$  cm<sup>-1</sup>, 2910, 2859, 1760, 1100 (all s). — <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.86$  (t,  $J = 6.8$  Hz, 6H, 1-H, 16-H), 1.28–1.39 (m, 12H, aliphatic H), 1.60 (quint,  $J = 6.8$  Hz, 4H, 5-H, 14-H), 3.52 (t,  $J = 6.7$  Hz, 2H, 13-H), 3.62 (t,  $J = 6.8$  Hz, 2H, 6-H), 4.09 (s, 2H, 11-H), 5.33 (s, 2H, 8-H). — MS (GC/MS, 70 eV):  $m/z$  (%) = 159 (2) [M<sup>+</sup> - C<sub>6</sub>H<sub>13</sub>OCH<sub>2</sub>], 115 (58) [C<sub>6</sub>H<sub>13</sub>OCH<sub>2</sub><sup>+</sup>], 85 (100) [C<sub>6</sub>H<sub>13</sub><sup>+</sup>], 43 (78) [C<sub>3</sub>H<sub>7</sub><sup>+</sup>]. — C<sub>15</sub>H<sub>30</sub>O<sub>4</sub> (274.4): calcd. C 65.69, H 10.95; found C 65.71, H 11.09.

**7-Oxatridecane (6a)**: 2.90 g (0.03 mmol) of hexanoic acid (**1a**) was dissolved in 30 ml of methanol. Then 0.80 g (5.00 mmol) of **2a** was dissolved in 4 ml of this solution. The residual 26 ml was partially neutralized with 1.43 ml of 1N potassium hydroxide in methanol and electrolyzed at 42 °C, a cell voltage of 50 V and a current density of 200 mA cm<sup>-2</sup>. After consumption of 0.05 F mol<sup>-1</sup>, 4 ml of the mixture of **1a** and **2a** was added from a syringe within 0.75 F mol<sup>-1</sup>. The addition was fast at the beginning and became slower towards the end. After consumption of 1.3 current equivalents, 75 ml of water was added to the electrolyte, which was then extracted with ether (3 x 50 ml). The combined extracts were washed (satd. NaCl solution), dried (MgSO<sub>4</sub>), and the ether was evaporated; 0.26 g (28%) of **6a** was isolated by flash chromatography [petroleum ether/ether (50:1, v/v)],  $n_D^{20} = 1.4200$  (ref.<sup>[17]</sup>  $n_D^{20} = 1.4190$ ). — IR (film):  $\tilde{\nu} = 2950$  cm<sup>-1</sup>, 2925, 2850, 1455 (all s), 1370 (m), 1105 (s). — <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.86$  (t,  $J = 6.8$  Hz, 6H, 1-H, 13-H), 1.27 (m, 12H, 2-H, 3-H, 4-H, 10-H, 11-H, 12-H), 1.54 (quint,  $J = 6.7$  Hz, 4H, 5-H, 9-H), 3.36 (t,  $J = 6.7$  Hz, 4H, 6-H, 8-H). — MS (GC/MS, 70 eV):  $m/z$  (%) = 186 (1) [M<sup>+</sup>], 115 (3) [C<sub>6</sub>H<sub>13</sub>OCH<sub>2</sub><sup>+</sup>], 101 (2) [M<sup>+</sup> - C<sub>6</sub>H<sub>13</sub>], 85 (96) [C<sub>6</sub>H<sub>13</sub><sup>+</sup>], 56 (44) [C<sub>4</sub>H<sub>8</sub><sup>+</sup>], 43 (100) [C<sub>3</sub>H<sub>7</sub><sup>+</sup>].

**13-Oxapentacosane (6b)**: 2.50 g (12.5 mmol) of **1b** and 1.22 g (5.00 mmol) of **2b** were electrolyzed as in the case of **6a** to afford after flash chromatography [petroleum ether/ether (70:1, v/v)] 0.62 g (35%) of **6b**; m.p. 32 °C (ref.<sup>[18]</sup> 32–33 °C). — IR (film):  $\tilde{\nu} = 2950$  cm<sup>-1</sup> (s), 2910 (s), 2840 (s), 1455 (s), 1355 (m), 1100 (s). — <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.86$  (t,  $J = 6.7$  Hz, 6H, 1-H, 25-H), 1.18–1.29 (m, 36H, aliphatic H), 1.54 (quint,  $J = 6.7$  Hz, 4H, 11-H, 15-H), 3.37 (t,  $J = 6.7$  Hz, 4H, 12-H, 14-H). — MS (GC/MS, 70 eV):  $m/z$  (%) = 282 (1) [M<sup>+</sup> - C<sub>5</sub>H<sub>11</sub> - H], 199 (2) [C<sub>12</sub>H<sub>25</sub>OCH<sub>2</sub><sup>+</sup>], 169 (21) [C<sub>12</sub>H<sub>25</sub><sup>+</sup>], 168 (20) [C<sub>12</sub>H<sub>24</sub><sup>+</sup>], 111 (36) [C<sub>8</sub>H<sub>15</sub><sup>+</sup>], 99 (32) [C<sub>7</sub>H<sub>15</sub><sup>+</sup>], 97 (50) [C<sub>7</sub>H<sub>13</sub><sup>+</sup>], 85 (60) [C<sub>6</sub>H<sub>13</sub><sup>+</sup>], 71 (78) [C<sub>5</sub>H<sub>11</sub><sup>+</sup>], 57 (100) [C<sub>4</sub>H<sub>9</sub><sup>+</sup>].

**7-Oxanonadecane (6c)**: 2.50 g (12.5 mmol) of **1b** and 0.80 g (5.00 mmol) of **2a** were electrolyzed as in the case of **6a** to afford 0.41 g (30%) of **6c**;  $n_D^{20} = 1.4358$ . — IR (film):  $\tilde{\nu} = 2950$  cm<sup>-1</sup> (s), 2910 (s), 2840 (s), 1455 (s), 1355 (m), 1100 (s). — <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.85$  (t,  $J = 6.7$  Hz, 3H, 1-H), 0.86 (t,  $J = 6.7$  Hz, 3H, 19-H), 1.20–1.28 (m, 24H, aliphatic H), 1.54 (quint,  $J = 6.7$  Hz, 4H, 5-H, 9-H), 3.36 (t,  $J = 6.7$  Hz, 4H, 6-H, 8-H). — MS (GC/MS, 70 eV):  $m/z$  (%) = 241 (1) [M<sup>+</sup> - C<sub>2</sub>H<sub>5</sub>], 199 (1) [C<sub>12</sub>H<sub>25</sub>OCH<sub>2</sub><sup>+</sup>], 168 (6) [M<sup>+</sup> - C<sub>6</sub>H<sub>13</sub>OH], 85 (100) [C<sub>6</sub>H<sub>13</sub><sup>+</sup>], 71 (36) [C<sub>5</sub>H<sub>11</sub><sup>+</sup>], 57 (67) [C<sub>4</sub>H<sub>9</sub><sup>+</sup>], 43 (100) [C<sub>3</sub>H<sub>7</sub><sup>+</sup>]. — C<sub>18</sub>H<sub>38</sub>O (270.5): calcd. C 79.93, H 14.16; found C 79.95, H 14.09.

**7,10-Dioxahexadecane (7a)**: 0.63 g (26.0 mmol) of sodium hydride was suspended in 10 ml of absolute dimethoxyethane and 0.62 g (10.0 mmol) of 1,2-dihydroxyethane in 10 ml of dimethoxyethane added dropwise to the suspension. After 2 h at reflux, 4.29 g (26.0 mmol) of hexyl bromide was added, and the mixture was heated at

reflux for 48 h. Then 50 ml of water was added, the mixture was extracted with ether (3 x 50 ml), the combined ether extracts were washed with brine, dried (MgSO<sub>4</sub>), and the solvent was evaporated. Flash chromatography of the residue [petroleum ether/ether (10:1, v/v)] yielded 0.97 g (42%) of **7a**;  $n_D^{20} = 1.4265$ . — IR (film):  $\tilde{\nu} = 2950$  cm<sup>-1</sup> (s), 2920 (s), 1850 (s), 1455 (s), 1370 (m), 1110 (s). — <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.85$  (t,  $J = 6.7$  Hz, 6H, 1-H, 19-H), 1.25–1.30 (m, 12H, aliphatic H), 1.59 (q,  $J = 6.8$  Hz, 4H, 5-H, 12-H), 3.46 (t,  $J = 6.8$  Hz, 4H, 6-H, 11-H), 3.57 (s, 4H, 8-H, 9-H). — MS (GC/MS, 70 eV):  $m/z$  (%) = 159 (2) [M<sup>+</sup> - C<sub>5</sub>H<sub>11</sub>], 129 (4) [M<sup>+</sup> - C<sub>3</sub>H<sub>11</sub> - CH<sub>2</sub>O], 115 (40) [C<sub>6</sub>H<sub>13</sub>OCH<sub>2</sub><sup>+</sup>], 85 (90) [C<sub>6</sub>H<sub>13</sub><sup>+</sup>], 83 (40) [C<sub>6</sub>H<sub>11</sub><sup>+</sup>], 71 (20) [C<sub>5</sub>H<sub>11</sub><sup>+</sup>], 43 (100) [C<sub>3</sub>H<sub>7</sub><sup>+</sup>]. — C<sub>14</sub>H<sub>30</sub>O<sub>2</sub> (230.3): calcd. C 72.97, H 13.13; found C 73.21, H 13.02.

**13,16-Dioxaoctacosane (7b)**: 0.62 g (10.0 mmol) of 1,2-dihydroxyethane and 7.10 g (24.0 mmol) of *n*-dodecyl iodide were allowed to react as in the case of **7a** to afford after flash chromatography [dichloromethane/petroleum ether (2:1, v/v)] 1.14 g (29%) of **7b**; m.p. 33 °C (ref.<sup>[19]</sup> 33–38 °C). — IR (film):  $\tilde{\nu} = 2950$  cm<sup>-1</sup> (s), 2920 (s), 1850 (s), 1455 (m), 1370 (m), 1110 (s). — <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.86$  (t,  $J = 6.7$  Hz, 6H, 1-H, 28-H), 1.20–1.28 (m, 14H, aliphatic H), 1.54 (quint,  $J = 6.8$  Hz, 4H, 11-H, 18-H), 3.43 (t,  $J = 6.8$  Hz, 4H, 12-H, 17-H), 3.54 (s, 4H, 14-H, 15-H). — MS (GC/MS, 70 eV):  $m/z$  (%) = 243 (4) [M<sup>+</sup> - C<sub>11</sub>H<sub>23</sub>], 199 (3) [C<sub>12</sub>H<sub>25</sub>OCH<sub>2</sub><sup>+</sup>], 169 (16) [C<sub>12</sub>H<sub>25</sub><sup>+</sup>], 140 (19) [C<sub>10</sub>H<sub>20</sub><sup>+</sup>], 111 (31) [C<sub>8</sub>H<sub>15</sub><sup>+</sup>], 85 (54) [C<sub>6</sub>H<sub>13</sub><sup>+</sup>], 71 (68) [C<sub>5</sub>H<sub>11</sub><sup>+</sup>], 57 (100) [C<sub>4</sub>H<sub>9</sub><sup>+</sup>].

**General Procedure for the non-Kolbe Electrolysis of 2a and 2b**: 0.035 mol of **2a** or **2b** was dissolved in 40 ml of absolute methanol or absolute ethanol, and the solution was partially neutralized with 32.7 ml of 1N potassium hydroxide in the corresponding solvent. The two compounds were electrolyzed in an undivided cell at teflon-supported platinum foil electrodes, 0 °C, a cell voltage of 50 V and a current density of 20 mA cm<sup>-2</sup>. After a consumption of 3.0 F mol<sup>-1</sup>, 120 ml of water was added to the electrolyte. The product was extracted several times with ether.

The combined ethereal extracts were washed with brine, dried (MgSO<sub>4</sub>), and the solvent was evaporated.

**General Procedure for the Coelectrolyses of 1a,b with 2a,b**: Both acids were dissolved in methanol, ethanol or DMF, partially neutralized with 1N potassium hydroxide in the corresponding solvent (in the case of DMF: triethylamine) and coelectrolyzed in an undivided cell between two platinum electrodes. Ratios of the acids **1** and **2**, degree of neutralization and reaction conditions are given in Tables 1–7. For workup 40 ml of petroleum ether and 120 ml of water were added, then the mixture was extracted with ether (5 x 50 ml), and the combined extracts were dried (MgSO<sub>4</sub>). After conversion of residual **1a, b** and **2a, b** into their methyl esters by treatment with diazomethane, the mixture was analyzed by GLC. When **2** was continuously added the electrolysis was carried out as in the case of **6a**.

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