

Recent Contributions of Kolbe Electrolysis to Organic Synthesis

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Carboxylic acids can be decarboxylated by anodic oxidation to radicals (Kolbe-electrolysis) and/or carbocations (non-Kolbe electrolysis). The procedure and necessary equipment is simple, a scale-up easy, the choice of carboxylic acids wide, the selectivity towards radicals or carbocations can be controlled by reaction conditions and the structure of the carboxylic acid, the yields are in general good. The radical pathway can be used for the preparation of e.g. 1,*n*-diesters, pheromones, or rare fatty acids. Electrolysis in the presence of olefins affords additive dimers and monomers or by intramolecular addition five membered carbocycles and heterocycles. By non-Kolbe electrolysis carboxylic acids can be converted into ethers, acetals, olefins or acetamides. Rearrangements and fragmentations lead to stereospecifically substituted cyclopentanoids and one- or four-carbon ring extensions.

2 Reaction Conditions for Kolbe Electrolysis

The yield and selectivity of Kolbe electrolysis is determined by the reaction conditions and the structure of the carboxylate. The latter subject is treated in chaps 3, 4. Experimental factors that influence the outcome of the Kolbe electrolysis are the current density, the temperature, the pH, additives, the solvent, and the electrode material.

High current densities and high carboxylate concentrations favor the formation of dimers. This is due to a high radical concentration at the electrode surface that promotes dimerization. Furthermore, at high current densities the so called critical potential of about 2.4 V (vs NHE) is reached [28] above which Kolbe dimerization proceeds smoothly. At this potential in aqueous solution and nonaqueous solvents the oxygen evolution and solvent oxidation is effectively suppressed [10, 29, 30]. The critical potentials for different carboxylates have been compiled [29], they are in the order of 2.1 to 2.8 V (vs NHE), whereby the structure of the carboxylate and its critical potential do not obviously correlate. There is, however, no need for potential control in Kolbe electrolysis as the critical potential is already exceeded at 1 to 10 mA/cm². This is much below the usually applied current density, which should be as high as possible, normally equal or greater than 250 mA/cm². It is assumed that at the critical potential the carboxylate forms a layer at the electrode surface, whereby the solvent is desorbed, whilst below the critical potential the solvent is preferentially oxidized.

In the anodic decarboxylation of phenylacetic acid benzaldehyde is the major product (80%) at low current density (< 3.2 mA/cm²). Its formation is supposed to occur by reaction of the intermediate benzyl radical with oxygen, which is possibly simultaneously generated at the anode [31].

A neutral, or even better a weakly acidic medium seems to be preferable for the Kolbe reaction. This is achieved by neutralizing the carboxylic acid to an extent of 2 to 5%, in some cases up to 30%, by an alkali metal hydroxide or alkoxide. The concentration of carboxylate remains constant during the electrolysis. When the carboxylate is consumed at the anode, base is continuously formed at the cathode and this way the carboxylate is regenerated from the acid. The endpoint of the electrolysis is indicated by a change of the electrolyte to an alkaline pH. This procedure is denoted as the salt-deficit method. The degree of neutralization can be as low as 0.5%. In spite of the low conductivity in this case, a low cell voltage can be maintained by a small electrode distance (0.1 to 2 mm) and vibrating electrodes [32, 33] or capillary gap electrodes [34, 35]. Sometimes it is necessary to convert the carboxylic acid totally into the carboxylate to improve its solubility in aqueous solution or to suppress discrimination in mixed Kolbe electrolysis due to different acidities of the carboxylic acids. In these cases a mercury cathode is used in the Dinh-Nguyen cell [36]. Here the electrolyte remains neutral, because alkali metals are discharged and bound as amalgams.

In aqueous solution an elevated pressure favors the Kolbe-coupling against non-Kolbe products [37]. A possible explanation is that high pressure aids the formation of a lipophilic medium at the electrode surface that prevents the adsorption of water and thus disfavours the formation of carbenium ions.

Temperature has some effect on Kolbe electrolysis. Higher temperatures seem to support disproportionation against the coupling reaction and intramolecular additions

to double bonds against a competing intermolecular coupling (chap 6). The unwanted conversion of the carboxylic acid into its methyl ester, that rivals to some extent with the decarboxylation, when methanol is used as solvent, can become the main reaction at higher temperatures, e.g. at about 65 °C with 11-bromoundecanoate [38].

Additives can strongly influence the Kolbe-reaction. Foreign anions should be definitively excluded, because they seem to disturb the formation of the necessary carboxylate layer at the anode. Their negative effect increases with the charge of the anion. While fluoride or formate inhibit, in low concentration, only slightly the ethane formation in the electrolysis of acetate, sulfate hinders the Kolbe reaction totally at concentrations as low as 10^{-3} mol/l [39]; even more pronounced, is the effect of $\text{Fe}(\text{CN})_6^{3-}$ [22, 40]. In the anodic decarboxylation of phenylacetate the dimerization can be totally suppressed in favor of the non-Kolbe product, benzylmethylether, when the electrolyte is more than 5.18 mM in NaClO_4 [31]. The inhibition by Cl^- , NO_3^- , NCS^- , Br^- , I^- can be partially counteracted by the addition of cyclohexene or pyridine [41]. The inhibition is attributed to the competitive formation of complexes $\text{Pt.PtO-foreign anion}_{\text{ads}}$ and $\text{Pt.PtO-(RCO}_2^-)_{\text{ads}}$. The former complex does not inhibit the dehydrogenation of the solvent, e.g. MeOH to $\text{H}_2\text{C}=\text{O}$ and $\text{C}\equiv\text{O}$. Unsaturated hydrocarbons are effective, because they trap the halogen from the anode surface. The shift from the radical to the carbenium ion pathway by perchlorate can be explained as due to blocking part of the anode surface by perchlorate adsorption, which lowers the radical concentration at the electrode. This disfavours the bimolecular radical dimerization and aids a second electron transfer to form the carbenium ion.

Foreign cations can increasingly lower the yield in the order Fe^{2+} , $\text{Co}^{2+} < \text{Ca}^{2+} < \text{Mn}^{2+} < \text{Pb}^{2+}$ [22]. This is possibly due to the formation of oxide layers at the anode [42]. Alkali and alkaline earth metal ions, alkylammonium ions and also zinc or nickel cations do not effect the Kolbe reaction [40] and are therefore the counterions of choice in preparative applications. Methanol is the best suited solvent for Kolbe electrolysis [7, 43]. Its oxidation is extensively inhibited by the formation of the carboxylate layer. The following electrolytes with methanol as solvent have been used: MeOH -sodium carboxylate [44], MeOH - MeONa [45, 46], MeOH - NaOH [47], MeOH - Et_3N -pyridine [48]. The yield of the Kolbe dimer decreases in media that contain more than 4% water.

In aqueous solution especially, the current yield is distinctly lower; furthermore, solubility problems can occur when the salt-deficit method is used. In aqueous solution, α -amino- or α -phenyl substituted carboxylates lead mainly to decomposition products, whilst in dry methanol or methanol-pyridine, coupling products were obtained with α -phenyl- and α -acetylamino-carboxylates [49].

Dimethylformamide is also a suitable solvent [50], it has, however, the disadvantage of being oxidized at fairly low potentials to *N*-acyloxy-*N*-methyl formamide [51]. The influence of the composition of the ternary system water/methanol/dimethylformamide on the material and current yield has been systematically studied in the electrolysis of ω -acetoxy or -acetamido substituted carboxylates [32]. Acetonitrile can also be used, when some water is added [52]. The influence of various solvents on the ratio of Kolbe to non-Kolbe products is shown in Table 1 [53].

Other electrolytes, that have been used, are: dimethylsulfoxide- NaH [54], glycol methylether-water (3:7, v, v) [55] or acetic acid [22].

Table 1. [53] Anodic decarboxylation^a of cyclohexanecarboxylic acid in different solvents

Solvent	Bicyclohexyl: Carbeniumion product ^b
H ₂ O-MeOH (30% v/v) ^c	0.97
MeOH ^c	1.76
MeCN ^d	2.26
HCONMe ₂ ^d	4.32

^a Acid (0.78 M), neutralized to 25%; Pt-anode, 0.25 A/cm²

^b Alcohol, ester, ether and acetamide according to solvent

^c Sodium salt

^d Tetrabutylammonium-salt

As anode material, smooth platinum in the form of a foil or net seems to be most universally applicable [32, 33]. In nonaqueous media, platinized titanium, gold, and nonporous graphite can also be used [56]. PbO₂-, MnO₂- or Fe₃O₄-anodes do not lead to Kolbe-dimers [57], except for PbO₂ in acetic acid [58].

To keep the consumption of the valuable platinum low, thin foils have been glued to a graphite support [34] or thin-layers of platinum have been sputtered on to a glass base [59]. Platinum can be used in a particle electrode by plating silica gel with platinum [60], or in a solid polymer electrolyte where platinum is incorporated into a nafion ion exchange membrane [61].

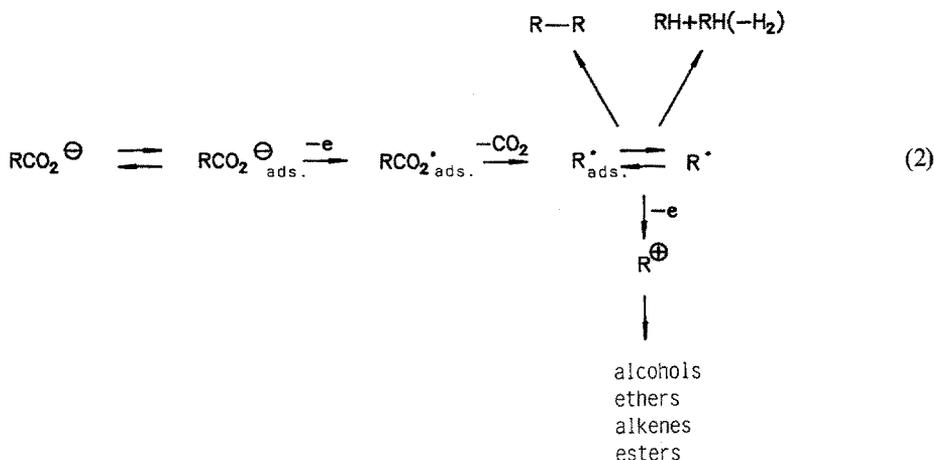
Electrolysis of triethylammonium heptanoate gave, in protic solvents (MeOH, EtOH, H₂O), dodecane as major the product at vitreous carbon (24–53%) or baked carbon (30–39%), compared to 45–62% at platinum; with graphite as anode, esters (non-Kolbe products) were the major products. Additionally, large differences in the product ratios were found by using face or edge surfaces of pyrolytic graphite [48]. In acetonitrile, longer fatty acids form dimers also at graphite anodes. It has been argued that this is possibly due to stacking of the alkyl chain at the electrode surface [52]. In acetonitrile, glassy carbon behaves like platinum in the anodic oxidation of acetate [62]. In non-aqueous media, ruthenium dioxide-titanium anodes have been successfully applied to Kolbe dimerizations [63].

The nature of the cathode material is not critical in the Kolbe reaction. The reduction of protons from the carboxylic acid is the main process, so that the electrolysis can normally be conducted in an undivided cell. For substrates with double or triple bonds, however, a platinum cathode should be avoided, as cathodic hydrogenation can occur there. A steel cathode should be used, instead.

In summary the following general experimental conditions should be applied for a successful dimerization of carboxylic acids: An undivided beaker type cell can be used equipped with a smooth platinum anode and a platinum, steel or nickel cathode in close distance; a current density of 0.25 A/cm² or higher should be provided by a regulated power supply, a slightly acidic or neutral electrolyte, preferable methanol as solvent and a cooling device to maintain temperatures between 10 to 45 °C should be employed. With this simple procedure and equipment yields of coupling product as high as 90% can be obtained, provided the intermediate radical is not easily further oxidized (see chap 7).

3 Mechanism of Kolbe Electrolysis

In the 1930s, very different mechanisms for Kolbe electrolysis were proposed. The discharged ion or free-radical theory was suggested by Crum, Brown and Walker [64], it assumes acyloxy radicals as intermediates. This proposal comes closest to present mechanistic ideas. According to Glasstone's and Hickling's hydrogen peroxide theory [65], Kolbe dimers and Hofer-Moest products (alcohols, esters) are formed by the action of OH^\cdot radicals and H_2O_2 . The acyl peroxide theory by Schall [66] and Fichter [6] proposes that the acyloxy radicals formed by discharge of the carboxylates couple to diacyl peroxides, that decompose. These early mechanistic ideas are covered in refs [67, 68]. More recent mechanistic concepts explain the experimental facts better. However, there is still some dispute between physical and organic chemists on some reaction steps. The recent mechanistic proposals have been critically discussed in refs. [8, 69–72] and from the physical chemists points of view in ref. [10]. The following general scheme is assumed (Eq. 2)



The competing pathways to radical or carbenium ion derived products are determined, apart from experimental factors (see chap. 2), by the ionization potential of the radical. From product ratios and ionization potentials of the intermediate radicals, the conclusion could be drawn that such radicals with ionization potentials above 8 eV lead preferentially to coupling products, whilst those with ionization potentials below 8 eV are further oxidized to carbenium ions [8c].

Pulsed current experiments of aqueous acetate solutions indicate that at least in aqueous solution a platinum oxide layer seems to be prerequisite for the decarboxylation to occur. Only at longer pulse durations ($> 10^{-3}$ s) is ethane produced [73, 74]. These are times known to be necessary for the formation of an oxide film. At a shorter pulse length ($< 10^{-4}$ s) acetate is completely oxidized to carbon dioxide and water possibly at a bare platinum surface [75]. The potentiodynamic response in the electrolysis of potassium acetate in aqueous solution also points to an oxide layer, whose

average thickness is probably equivalent to three monolayers [76]. Other results, however, indicate that platinum oxides formed in the presence of water significantly inhibit the Kolbe reaction. This is assumed from a comparison of reaction rates in anhydrous and aqueous solutions [77] and the fact that the highest yield of dimers are usually obtained in nonaqueous media [78].

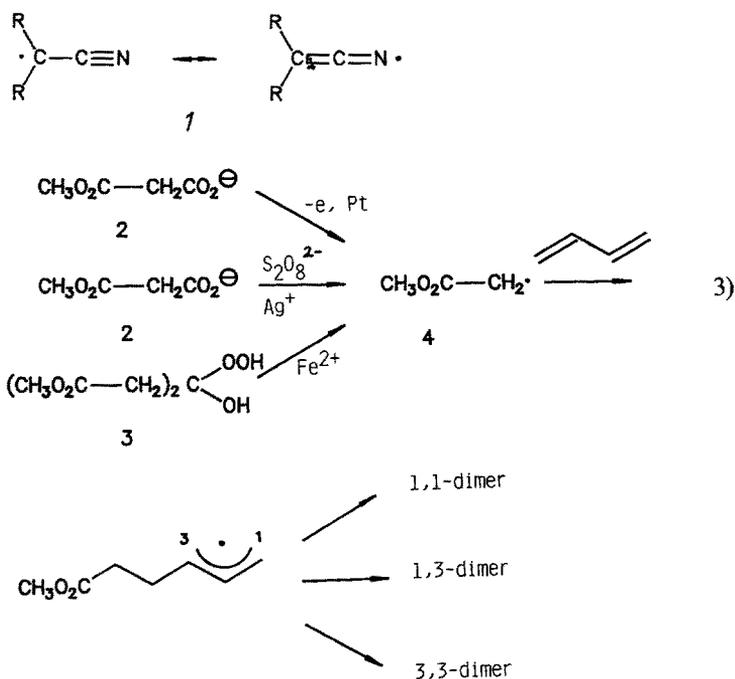
It has been shown by employing the radioactive tracer method with ^{14}C -labeled carboxylic acids [79] and with rotating disc electrode experiments [80] that carboxylates are adsorbed at the anode surface.

Current potential curves exhibit a critical potential at 2.1 to 2.4 V versus NHE. Below this potential in aqueous solution, oxygen is formed preferentially [81], while above it the discharge of oxygen is inhibited and Kolbe dimers are obtained [81–82]. At this critical potential the coverage of the electrode with acetate increases sharply [83]. From an anomalous Tafel slope, from the decrease of the differential capacity in this voltage range [83] and from other electroanalytical data [84] it is deduced that above the critical potential a rigid layer of adsorbed acyloxy or alkyl radicals is formed on top of the metal [8c, 78] or metal oxide [68], which inhibits the oxygen evolution or solvent oxidation and promotes Kolbe electrolysis [8 a, b, 10, 76]. Recent results on the capacitative behaviour of sodium acetate in an aqueous acetic acid solution at platinum indicate that the double layer capacitance is due to adsorption of methyl radicals, while the coverage by acetate radicals is insignificant [85]. The different stages of oxide formation and adsorption of intermediates have been observed by modulated specular reflectance spectroscopy applied to the Kolbe reaction of ethyl malonate in aqueous solution [86]. By polaromicrotribometry it has been shown that at the critical potential a hydrophobic polymer film is formed that apparently inhibits the oxygen discharge [87].

For the tetrabutylammonium salts of substituted acetate the quarter wave potentials have been determined by chronopotentiometry in acetonitrile. The ease of oxidation, as reflected in the $E_{1/4}$ -values, decreases with increasing strength of the acid [88].

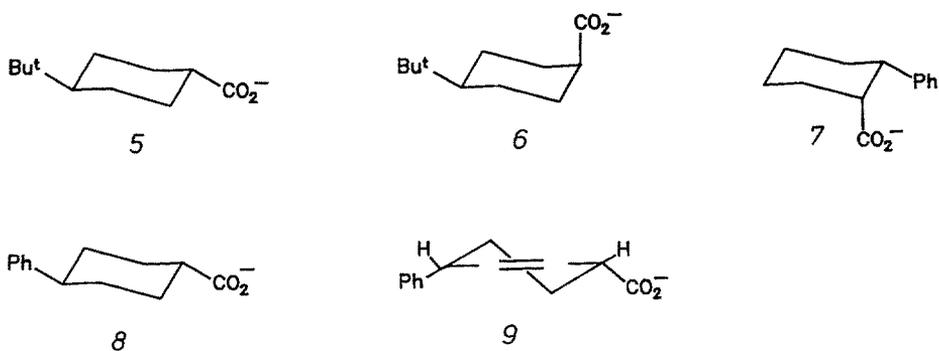
The current-potential relationship indicates that the rate determining step for the Kolbe reaction in aqueous solution is most probably an irreversible 1 e-transfer to the carboxylate with simultaneous bond breaking leading to the alkyl radical and carbon dioxide [8]. However, also other rate determining steps have been proposed [10]. When the acyloxy radical is assumed as intermediate it would be very shortlived and decompose with a half life of $\tau \approx 10^{-8}$ to carbon dioxide and an alkyl radical [89]. From the thermochemical data it has been concluded that the rate of carbon dioxide elimination effects the product distribution. Olefin formation is assumed to be due to reaction of the carboxylate radical with the alkyl radical and the higher olefin ratio for propionate and butyrate is argued to be the result of the slower decarboxylation of these carboxylates [90].

Whilst electroanalytical data have been interpreted in terms of a mechanism involving the coupling of adsorbed radicals [10, 91] the stereochemistry of the products and the regioselectivity of the coupling reaction indicates that adsorption of saturated alkyl radicals seems to be relatively unimportant. Support that non or weakly adsorbed radicals combine, comes from the coupling products of cyanoalkyl radicals **1** [8]. These radicals with two reaction sites produce the same amount of carbon to carbon and carbon to nitrogen coupling product, when generated by photolytic or thermal decomposition of an azonitrile, by persulfate oxidation or by electrolysis



of α -cyanoacetic acid in methanol, acetonitrile or dimethylformamide. In sharp contrast, photolysis of the same azonitrile adsorbed on silica produces only the carbon to carbon coupling product. Similarly the addition of radical 4 to butadiene affords the same ratio of 1,1-, 1,3- and 3,3-additive dimers, irrespective of whether the radical was generated by anodic or persulfate oxidation of methyl malonate 2 or reductive fragmentation of the hydroperoxide 3 (Eq. 3) [92].

Carboxylates, which are chiral in the α -position totally lose their optical activity in mixed Kolbe electrolyses [93, 94]. This racemization supports either a free radical or its fast dynamic desorption-adsorption at the electrode. A clearer distinction can be made by looking at the diastereoselectivity of the coupling reaction. Adsorbed radicals should be stabilized and thus react via a more product like transition state

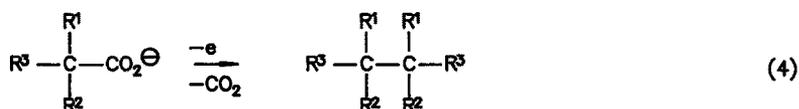


that reflects different stabilities of the products. The free radical on the other side should have a more educt like transition state and should therefore couple more randomly. This has been tested with the carboxylic acids **5** to **9**. The saturated carboxylic acids **5** and **6** coupled randomly, which indicated that these radicals are not significantly adsorbed. The unsaturated carboxylic acids **7** to **9** did not dimerize quite statistically, which agrees with the fact that unsaturation favors adsorption [95, 96].

The intermediate radical (Eq. 2) can be further oxidized to a carbenium ion that undergoes solvolysis, rearrangement and elimination (see chaps 8–12). This oxidation is strongly influenced by experimental factors as for example the presence of foreign anions, or the electrode material (see chap. 2). If one assumes, that the radical is oxidized from an adsorbed state the strong increase of the benzyl cation formation in the phenylacetic acid oxidation by added perchlorate can be explained by the competitive preferential adsorption of the perchlorate anion [31]. With nuclear substituted phenyl acetates the portion of radical coupling products increases with increasing electron withdrawing ability of the substituents, for example with *p*-*tert*-butyl it is 13% (ionization potential of the benzyl radical = 7.4 eV) and for unsubstituted phenyl it is 76% (IP = 7.76 eV). For the oxidation of *p*-methoxyphenylacetic acid a pseudo-Kolbe reaction (see chap. 13) is assumed, which means an electron transfer from the aromatic nucleus [31]. Besides its dimerization or addition to double bonds (chap. 6) the radical can disproportionate or react with oxygen [31, 97]. The ratio of disproportionation to dimerization seems to be higher in Kolbe electrolysis than in an homogeneous reaction [98].

4 Symmetrical Coupling of Carboxylic Acids

Two equal carboxylates can be coupled to symmetrical dimers (Eq. 4). In spite of the high anode potential, that is necessary for Kolbe electrolysis, a fair number of

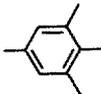
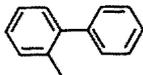


$\text{R}^1, \text{R}^2, \text{R}^3$: H, Alkyl, Arylalkyl

$\text{R}^1, \text{R}^2 = \text{H}$, R^3 : CO_2Me , $(\text{CH}_2)_n\text{X}$ ($\text{X} = \text{COR}$, CO_2R , $n > 1$,
 $\text{X} = \text{OAc}$, NHAc , Hal , $n > 4$)

substituents can be present in the carboxylic acid. As the reaction involves radicals as reactive intermediates, polar substituents can be handled without protection. This saves additional steps for protection and deprotection, that are often necessary in polar reactions, where strong bases, nucleophiles or electrophiles are used as reagents. Furthermore carboxylic acids are readily available in a wide variety of structures. These advantages make Kolbe electrolysis a method of choice for the construction of symmetrical compounds.

Table 2. Symmetrical coupling of selected carboxylic acids

No.	Substituents in $R^1R^2R^3C-CO_2^-$			Yield ^a of coupling product (%)	Ref.
	R^1	R^2	R^3		
1	H	H	H	93	7, 9
2	Alkyl (C_1-C_{17})	H	H	30-90	7, 9
3	Alkyl	Alkyl	H	0-26	9
4	$RO_2C-(CH_2)_n$ $n = 3-15$, R = Me, Et	H	H	40-95	7
5	Alkyl	EtO ₂ C	H	20-85	99, 100
6	Alkyl	Alkyl	EtO ₂ C	15-35	99, 101
7	Alkyl	CN	H, Alkyl	30-60	102
8	Alkyl	CONH ₂	H, Alkyl	5-55	103
9	Alkyl-CO	Alkyl, H	Alkyl, H	32-40	104
10	$CH_3CO(CH_2)_n$ $n = 1$ $n = 5$	H	H	70 63	105 106
11	F, Br, Cl, I, OH, NH ₂	H	H	0	7, 9, 107
12a	F	F	F	93	84b, 108
12b	F	F	Cl	43	109
13	$X(CH_2)_n$ X: F, $n > 3$ X: Cl, $n: 1, 3, 4, 5, 7, 8, 9, 11$ X: Br, $n: 4-11, 14$	H	H	45-70 40-80 54-71	110 110, 111, 112 38a, 110
14	$RO_2C(CF_2)_n$ $n = 0-3$, R = Me, Et	F	F	high yield	113
15	$H(CF_2)_n$ $n = 3, 5$	F	F	40-86	114
16	$CF_3(C_2F_5)_2C$	H	H	75	115
17	$CH_3CO_2(CH_2)_n$ $n: 2-5$	H	H	70-83	32
18	$CH_3CONH-(CH_2)_4$	H	H	24-39	32, 116
19	Phthaloyl-N-CHCH ₂ CO ₂ H	H	H		32, 117
20	 X: <i>p</i> -OMe to X: F ₅	H	H	> 1-74	31
21	Ph	Ph	H	25	118
22	 	H	H	45 39	118 119

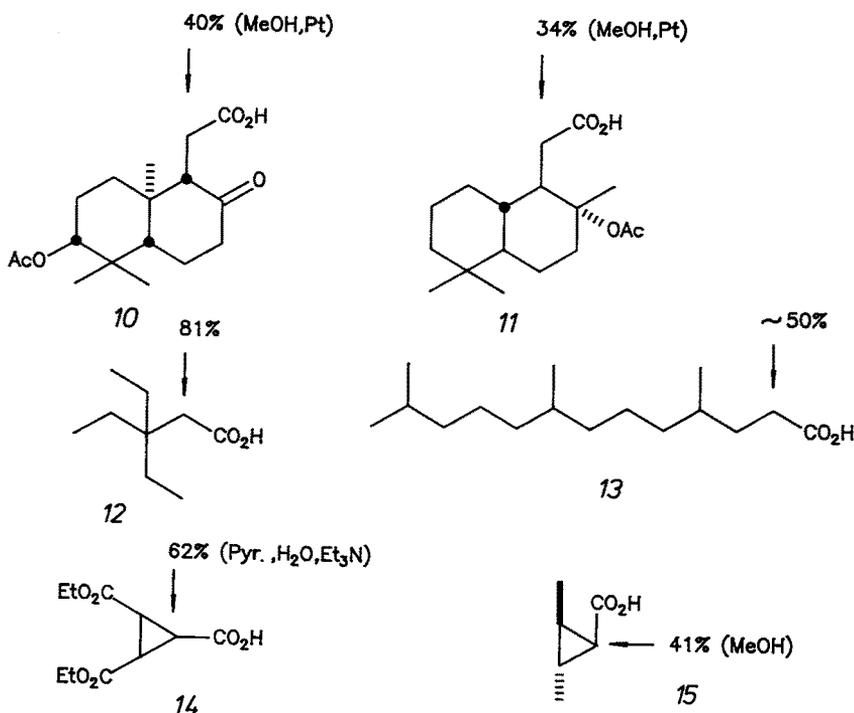
^a Electrolyses are normally performed at a platinum anode in water, methanol, ethanol or ethanol/water

A great number of Kolbe dimerizations have been tabulated in refs. [9, 17–19]. Here no comprehensive coverage is intended, but to demonstrate with selected examples the range and limitations of Kolbe dimerization. In the following discussion and in Table 2 the carboxylates are arranged according to their functional groups in the order alkyl-, ester-, keto-, halo- and olefinic substituents.

In general, only the kind of substituent in the α -position is critical for the yield of the coupling product. Electron donating groups (more than one alkyl group, phenyl, vinyl, halo or amino substituents) more or less shift the reaction towards products that originate from carbenium ions (non-Kolbe products, see chap. 7). Electron attracting groups (cyano, ester or carbonyl substituents) or hydrogen, on the other side, favor the radical dimerization.

The reaction conditions, normally applied, are those described in chap. 2 for the radical pathway. These are a platinum anode, high current densities, no additives and a slightly acidic medium. However, the dimerizations shown in Table 2, No. 2, also gave in some cases good yields at a carbon anode in acetonitrile-water [52] or at a baked carbon anode in methanol [48]. With propionic and butyric acid an unusually high portion of alkene is formed at the cost of the dimer.

The coupling of carboxylic acids has been profitably used in natural product synthesis. Kolbe electrolysis of **10** is part of a (+)- α -onocerin synthesis [120], the dimerization of **11** leads to a pentacyclosqualene [121], the electrolysis of **12** afforded a dimer with two quaternary carbon atoms [122], and 2,6,10,15,19,23-hexamethyltetracontane has been synthesized from **13** [123].



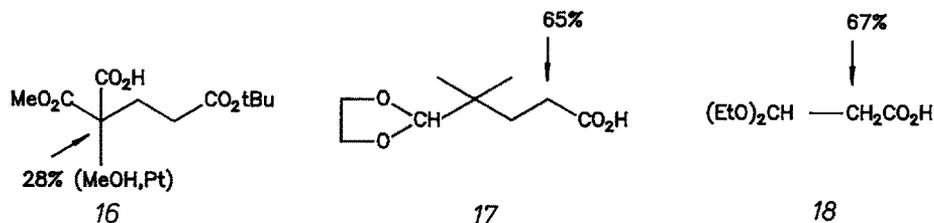
For the preparation of long-chain alkanes it proved useful to extract the electrolyte continuously with a high boiling point nonpolar solvent. This way the alkanes: $C_{34}H_{70}$, $C_{38}H_{78}$ and $C_{42}H_{86}$ were prepared with high yields (70, 75 and 87%, respectively) [124].

Some cyclopropylcarboxylic acids, namely **14** [125] and **15** [46] could be coupled to bicyclopropyl compounds, others led to allylic compounds via ring opening of an intermediate carbenium ion (see chap. 7). Tertiary alkanoates yield predominantly non-Kolbe products (see chap. 8).

The Brown-Walker version of Kolbe electrolysis namely the dimerization of half-esters to diesters of diacids, is of industrial interest, because using this method, sebacates can be prepared from adipic half esters [126]. This process appears to have reached the pilot stage in Germany [11], Japan [13], and Russia [12]. In Russia, the behaviour of other half esters has also been studied in detail [12]. From China, too, activities concerning this coupling reaction have recently been reported [127]. Yields as high as 93% have been obtained [128]. Bis(2-ethylhexyl)sebacate, a plasticizer, has been prepared from the corresponding adipate in 85% yield [128]. In sebacate production, platinum can be replaced by a special carbon anode, which gives nearly the same yields as platinum and is highly resistant to the electrolyte [129].

Efficient syntheses of substituted succinic acids (Table 2, Nos. 5, 6) have been developed in the past; a more recent application is the coupling of **16** as part of a semi-bullvalene synthesis [130].

α,ω -Dicarboxylated polyethylene or polydifluormethylene is reported to be obtained by electrolysis of azelaic acid [131] or perfluoroglutaric acid [132].



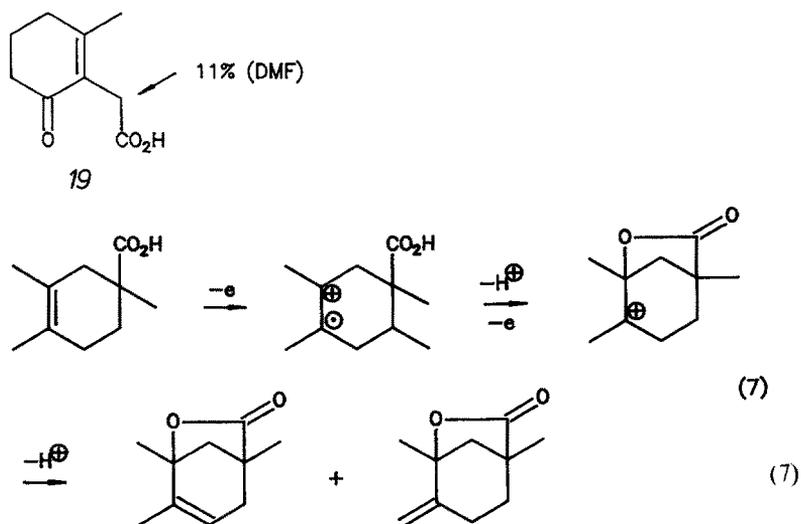
Whilst ketocarboxylic acids can be dimerized satisfactorily (Table 2, No. 9, 10), the corresponding aldehydes couple poorly. Good yields can be obtained in these cases when the acetals, e.g. **17** [133], **18** [134], are electrolyzed instead.

Carboxylic acids with a halide, hydroxy or amino group in the α -position form no dimers (Table 2, No. 11), except when two or three fluorine atoms are present there (Table 2, No. 12). A large amount of work has been devoted to the coupling of fluorocarboxylic acids (Table 2, Nos. 13–16) due to interesting properties of the produced fluorohydrocarbons. By statistical analysis optimal conditions for Kolbe electrolysis of perfluorinated acids have been calculated [135].

Hydroxy- and amino carboxylic acids can be dimerized in good to moderate yields, when the substituents are not in the α - or β -position and when they are additionally protected against oxidation by acylation (Table 2, No. 17–19). 2-Alkenoic acids cannot be dimerized but lead to more or less extensive passivation of the anode due to the formation of polymer films [136]. 3- and 4-Alkenoic acids give moderate yields when they are neutralized with Bu_3N or Et_3N [136]. 3-Alkenoic acids with the structure

With 6-alkenoic acids the intermediate radical partially cyclizes to a cyclopentyl-methyl radical in a 5-*exo-trig* cyclization [139] (Eq. 6) [138a, 140] (see also chap. 6). To prevent double bond migration with enoic acids the electrolyte has to be hindered to become alkaline by using a mercury cathode. *Z*-4-Enoic acids partially isomerize to *E*-configured products. Results from methyl and deuterium labelled carboxylic acids support an isomerization by way of a reversible ring closure to cyclopropyl-carbinyl radicals. The double bonds of *Z*-*N*-enoic acids with $N > 5$ fully retain their configuration [140].

The acid **19** has been dimerized, although in low yield, in the course of a perhydro-phenanthrene synthesis [141]. When the oxidation potential of the double bond is sufficiently lowered by alkyl substituents, lactone formation by oxidation of the double bond rather than of the carboxyl group occurs (Eq. 7) [142] (see also chap. 15).

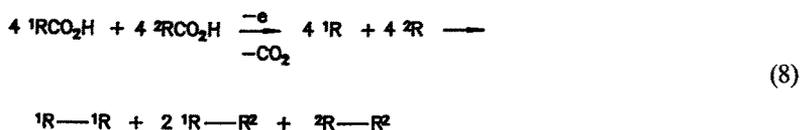


Other alkenoic acids that have been dimerized with retention of configuration at the double bond are oleic acid (23% dimer yield), elaidic acid (44%) [143], and erucic acid (40%) [144].

Substituted phenylacetic acids form Kolbe dimers when the phenyl substituents are hydrogen or are electron attracting (Table 2, Nos. 20–23); they yield methyl ethers (non-Kolbe products), when the substituents are electron donating (see also chap. 8). Benzoic acid does not decarboxylate to diphenyl. Here the aromatic nucleus is rather oxidized to a radical cation, that undergoes aromatic substitution with the solvent [145].

5 Cross-Coupling of Different Carboxylates

Cross coupling of two different carboxylates (= mixed Kolbe electrolysis) is a method for synthesizing unsymmetrical compounds (Eq. 8). As, however, the intermediate radicals combine statistically, the mixed coupling product



is always accompanied by two symmetrical dimers as major side products. To make this coupling more attractive for synthesis the less costly acid is taken in excess. This way the number of major products is diminished to two, which facilitates the isolation of the mixed dimer. Furthermore the more costly acid is incorporated to a large extent into the mixed dimer. Some calculated yields are listed in Table 4. Some experimental yields obtained for cross-coupling of methyl adipate with hexanoate are compiled in Table 5.

When one of the two acids is used in excess and the $\text{p}K_a$ -values of the two acids differ strongly, the salt deficit method should be used with caution. Formic acid, acetic acid, propionic acid, and trifluoroacetic acid have been electrolyzed competitively in mixtures of pairs. Formic acid and trifluoroacetic acid are comparable in case of electrolysis, both are more readily electrolyzed than acetic and propionic acids. Deviations are rationalized on the basis of differences in ionization [147]. It might be useful in such cases to neutralize both acids completely. Sometimes one of the two acids, although being the minor component, is more favorably oxidized possibly due to preferential adsorption or its higher acidity [148]. In this case the continuous addition of the more acidic acid to an excess of the weaker acid may lead to successful cross-coupling [149]. The chain length of the two acids should be chosen in such a

Table 4. Calculated theoretical yields for mixed coupling products $\text{}^1\text{R}-\text{}^2\text{R}$

$\text{}^1\text{RCO}_2\text{H}$:	$\text{}^2\text{RCO}_2\text{H}$	Yield of $\text{}^1\text{R}-\text{}^2\text{R}$ (%) ^a
1	:	1	50
1	:	2	66
1	:	4	80
1	:	6	86
1	:	10	91

^a Calculated according to %-Yield = $n \cdot 100 / (1 + n)$
with 1:n as ratio of $\text{}^1\text{RCO}_2\text{H}:\text{}^2\text{RCO}_2\text{H}$

Table 5. Yield of methyl decanoate in the cross-coupling of methyl adipate and hexanoate [146]

Ratio of $\text{HO}_2\text{C}(\text{CH}_2)_4\text{CO}_2\text{CH}_3$:	$\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}$	%Yield of $\text{MeO}_2\text{C}(\text{CH}_2)_8\text{CH}_3$ (%)	
			in MeOH	in H_2O
1	:	1	36	12
1	:	2	49	39
1	:	6	58	48

way that the symmetrical dimer formed in excess can be separated from the cross-coupling product either by distillation or crystallization. For smaller scale reactions the selective coupling of two different alkyl groups can be achieved by photolysis of unsymmetrical peroxides at low temperatures in the solid state [150].

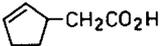
Problems due to passivation that lead to an increase of the cell voltage or due to competition by non-Kolbe electrolysis [179] are often less pronounced in mixed coupling.

Despite of the disadvantage that at least one symmetrical dimer is formed as a major side product, mixed Kolbe electrolysis has turned out to be a powerful synthetic method. It enables the efficient synthesis of rare fatty acids, pheromones, chiral building blocks or non proteinogenic amino acids. The starting compounds are either accessible from the large pool of fatty acids or can be easily prepared via the potent methodologies for the construction of carboxylic acids.

Another advantage of the synthesis by mixed Kolbe electrolysis is that polar groups in the carboxylic acid are tolerated in radical coupling. This makes additional protection-deprotection steps unnecessary, which are often needed in polar CC-bond forming reactions and can make these approaches less attractive in such cases.

Selected examples of the large number of compounds synthesized since the pioneering work of Weedon are subsequently arranged either in Tables 6, 7 or in formulas. At first the coupling products between unsubstituted alkyl groups and substituted

Table 6. Cross-coupling by Kolbe electrolysis of unsubstituted (A) with substituted carboxylic acids (B)

Carboxylic acids		Crosscoupling product (A-B) Yield (%)	Ref.
A—CO ₂ H	B—CO ₂ H		
CH ₃ (CH ₂) ₆ CO ₂ H	CH ₃ O ₂ C(CH ₂) ₄ C≡C(CH ₂) ₄ CO ₂ H	23	151
CH ₃ (CH ₂) ₁₄ CO ₂ H	(CH ₃) ₂ CHCO ₂ H	40	152
CH ₃ (CH ₂) ₅ CO ₂ H	(E)—CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ CO ₂ H	37	152
CD ₃ CO ₂ H	CF ₃ CO ₂ H	68	149
CD ₃ CO ₂ H	CF ₃ CF ₂ CO ₂ H	75	149
CH ₃ CO ₂ H	HC≡C—(CH ₂) ₈ CO ₂ H	36	153
CH ₃ CH ₂ CO ₂ H	C ₆ H ₅ —(CH ₂) ₂ CO ₂ H	44	154
CH ₃ (CH ₂) ₃ CO ₂ H	CH ₃ O ₂ C(CH ₂) ₇ CO ₂ H	69	144
CH ₃ (CH ₂) ₅ CO ₂ H	CH ₃ O ₂ C(CH ₂) ₇ CO ₂ H	61	144
CH ₃ (CH ₂) ₂ CO ₂ H	CH ₃ O ₂ CCH(OCOCH ₃)CO ₂ H	29	155
CH ₃ (CH ₂) ₂ CO ₂ H	CH ₃ CO(CH ₂) ₄ CO ₂ H	62	156
Methylhexadecanoic acid	CH ₃ O ₂ C(CH ₂) ₄ CO ₂ H	42	157
CH ₃ (CH ₂) ₈ CO ₂ H	CH ₃ O ₂ C(CH ₂) ₄ CO ₂ H	38	146
CH ₃ (CH ₂) ₂ CO ₂ H	CH ₃ O ₂ CCH ₂ CH(CH ₃)CH ₂ CO ₂ H	30	158
 —CH ₂ CO ₂ H	CH ₃ O ₂ C(CH ₂) ₁₁ CO ₂ H	30	159
(CH ₃) ₃ C(CH ₂) ₂ CH(CH ₃)—CH ₂ CO ₂ H	CH ₃ O ₂ CCH ₂ CH(C ₂ H ₅)—CH ₂ CO ₂ H	15	160
CH ₃ (CH ₂) ₁₀ CO ₂ H	CH ₃ O ₂ CCH(OCH ₃)CH ₂ CO ₂ H	21	161
CH ₃ (CH ₂) ₇ CH(CH ₃)CH ₂ CO ₂ H	CH ₃ O ₂ C(CH ₂) ₇ CO ₂ H	30	162
Me(CH ₂) _m CO ₂ H m = 8–16, 18	CH ₃ O ₂ C(CH ₂) _n CO ₂ H n = 4, 7, 8, 12–20	—	163
i-C ₄ H ₉ CO ₂ H	(C ₂ H ₅) ₂ C(CO ₂ Et)CO ₂ H	38	164

alkyl groups are described, whereby the latter are ordered according to the presence of double and triple bonds, hydroxy groups, halides, carbonyl, carboxyl, ester, amino groups and other heterosubstituents. These examples are then followed by cross-coupling products between two substituted alkyl groups in the same order. In the formulas often the product of subsequent transformations is shown, the coupling site is marked by an arrow and the yield in mixed Kolbe electrolysis is indicated. Further examples are given in references [9, 23].

A large number of trialkylacetic acid esters have been prepared by mixed Kolbe electrolysis of ethyl malonates [164]. Crossed-coupling is also used for chain extension. Extension by two carbon atoms is achieved with benzyl succinates [153, 180–182], whereby the purification of the chain extended fatty acid is simplified by using the benzyl half ester [181 a].

Extension by three carbon atoms is possible with methyl glutarate [183], by the isoprene unit with ethyl 3-methyl adipate [184], by four carbon atoms with methyl adipate [143], by five carbon atoms with methyl pimelate [185] and by six carbon atoms with methyl suberate [186]. A series of branched ω -fluorocarboxylic acids were prepared by cross-coupling with ω -fluorocarboxylic acids [187]. For further examples see Tables 6, 7.

Table 7. Cross-coupling by Kolbe electrolysis of substituted carboxylic acids (A) with substituted carboxylic acids (B)

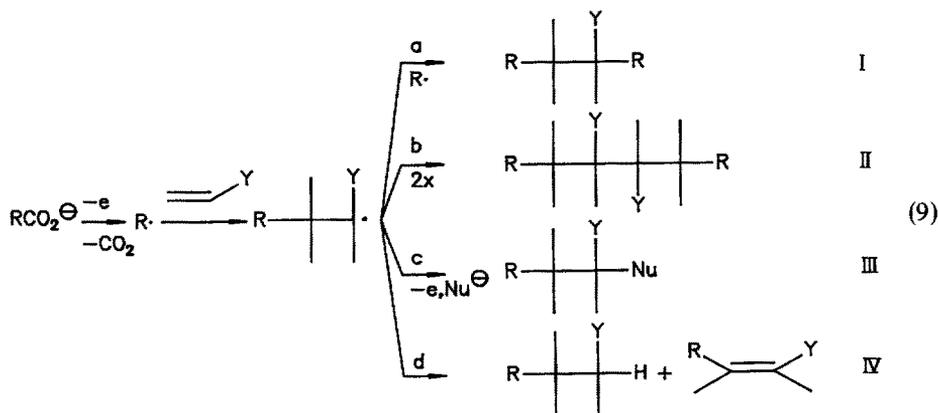
Carboxylic acids		Crosscoupling product (A-B)	Ref.
A—CO ₂ H	B—CO ₂ H	Yield (%)	
CH ₂ =CH(CH ₂) ₂ CO ₂ H	CH ₃ O ₂ C(CH ₂) ₁₀ CO ₂ H	68	165
(CH ₃) ₂ CHCH=CHCH ₂ CO ₂ H	CH ₃ O ₂ C(CH ₂) _n CO ₂ H	good	166 a
	n = 1, 2, 4		
(Z)—CH ₃ O ₂ C(CH ₂) ₂ CH=CH(CH ₂) ₂ CO ₂ H	CH ₃ (CH ₂) ₂ CO ₂ H	30	166 b
CH ₂ =CH(CH ₂) ₈ CO ₂ H	CH ₃ O ₂ C(CH ₂) ₂ CO ₂ H	52	166 c
R—C≡C—(CH ₂) ₃ CO ₂ H	CH ₃ O ₂ C(CH ₂) _n CO ₂ H	45–59	167
R: C ₂ H ₅ , C ₃ H ₇ , C ₄ H ₉	n = 2, 3, 4, 6		
(Z)—CH ₃ (CH ₂) ₇ CH=CH—(CH ₂) ₇ CO ₂ H	CH ₃ O ₂ C(CH ₂) ₂ CO ₂ H	15–20	168
CF ₃ CF ₂ OCF ₂ CO ₂ H	MeO ₂ C(CF ₂) _n CO ₂ H	24–34	169
	n = 1–3		
CF ₃ OCF ₂ CF ₂ CO ₂ H	MeO ₂ C(CF ₂) _n CO ₂ H	24–34	169
	n = 1–3		
CF ₃ CO ₂ H	CH ₃ O ₂ CCH ₂ CO ₂ H	46	170
Br(CH ₂) ₁₀ CO ₂ H	CH ₃ O ₂ C(CH ₂) ₇ CO ₂ H	50	144
Br(CH ₂) ₁₀ CO ₂ H	EtO ₂ C(CH ₂) ₈ CO ₂ H	54	171
Br(CH ₂) ₁₀ CO ₂ H	MeO ₂ C(CH ₂) ₄ CO ₂ H	37	38 b
AcO(CH ₂) ₄ CO ₂ H	EtO ₂ C(CH ₂) ₁₀ CO ₂ H	27–32	172, 178
Me ₃ SiCH ₂ CO ₂ H	MeO ₂ C(CH ₂) _n CO ₂ H	71–76	173
	n = 4, 7		
CH ₃ O ₂ C(CH ₂) ₁₁ CO ₂ H	CH ₃ O ₂ C(CH ₂) ₄ CO ₂ H	—	174
CH ₃ O ₂ C(CH ₂) ₁₀ CO ₂ H	CH ₃ O ₂ C(CH ₂) ₄ CO ₂ H	—	175
CH ₃ O ₂ C(CF ₂) _n CO ₂ H	CH ₃ O ₂ C(CF ₂) _m CO ₂ H	25–38	113
n = m = 1–4			
CH ₃ CO(CH ₂) ₂ CO ₂ H	CH ₃ CO(CH ₂) ₄ CO ₂ H	31	176
CH ₃ CO(CH ₂) ₈ CO ₂ H	CH ₃ O ₂ C(CH ₂) ₄ CO ₂ H	32	177

obtained in two successive electrolyses from methyl 2-methyl-succinate [195]. 10,16-Dimethyleicosanoic acid **28** was synthesized by three successive electrolyses [180]. The bromide **29**, a key intermediate in the synthesis of natural α -tocopherol has been prepared starting from (*R*)-(+)-citronellic acid [196]. The alkane **30** with three quaternary carbon atoms has been obtained by two successive cross-couplings [122]. In an alternative approach looplure **31**, the pheromone of the Cabbage Looper was made available by Kolbe electrolysis of (*Z*)-4-nonenic acid with methyl glutarate [197]. Similarly the pheromone of the fruit pest insect *Dacus cucurbitae* **32** [198] and of the false codling moth **33** [199] have been prepared. Cross-coupling of (*E*)-3-hexenoic acid and levulinic acid provided a shorter route to brevicomin **34** [200], the sex attractant of the western pine beetle. Pure (*E*)- or (*Z*)-configured unsaturated pheromones can be prepared by cross-coupling with 5-alkynoic acids and subsequent selective hydrogenation (Table 7) [167]. In the cross-coupling of perfluorinated acids with unsubstituted acids an excess of the weaker acid and a solvent with alkaline properties, e.g. pyridine, seems to be profitable [201]. The attempted cross coupling between trifluoroacetate and propionate does not lead to a mixed dimer but to the addition product of the CF_3 -radical to ethylene formed from propionate [43 b]. Useful intermediates for the synthesis of dicarba analogues of cystine peptides **35** have been prepared by mixed Kolbe-electrolysis of protected L- or D-glutamic acids [202]. Chiral building blocks **36–38** for synthesis have been obtained by cross-coupling with enantiomerically pure β -hydroxybutyric acid derivatives [203]. Chiral γ -lactones **39** have been prepared from (*R*)-3-cyclohexene-1-carboxylic acid [204].

By coelectrolysis of polymethacrylic acid with ϵ -acetaminocaproic acid or cyanoacetic acid the alkylacetamido- or cyanomethyl group can be grafted on to the main chain of the polymer [205].

6 Addition of Kolbe Radicals to Double Bonds

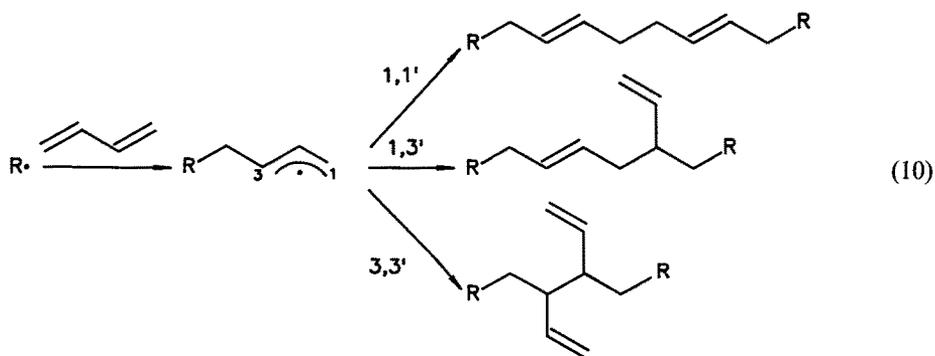
Kolbe radicals can be added to olefins that are present in the electrolyte. The primary adduct, a new radical, can further react by coupling with the Kolbe radical to an additive monomer I (Eq. 9, path a), it can dimerize to an additive dimer II (path b), it can be further oxidized to a cation, that reacts with a nucleophile to III (path c), or it can disproportionate (path d).



Oligomerization and polymerization of the olefin by addition of the primary adduct to further monomers occurs only in a few cases (see below). The radical concentration in the reaction layer in front of the electrode is so high, that the termination step and not the propagation step of the polymerization predominates. On the other hand as a result of the high radical concentration the dimerization of the Kolbe radical can compete strongly with the addition. With reactive olefins, e.g. butadiene, isoprene or styrene, generally good yields of adduct are obtained (Table 8, Nos. 1–10). With unreactive olefins, however, like cyclohexene, isobutene (Table 8, No. 11) the yields of addition product are low and Kolbe dimers predominate. However, for ethylene good yields have also been claimed (No. 12). The yields can be increased, when nucleophilic radicals, as alkyl radicals, are added to electrophilic olefins, as α,β -unsaturated carbonyl compounds or nitriles (Nos. 17–22). The same seems to be valid for the reaction of electrophilic radicals (CF_3 , MeO_2CCH_2) with nucleophilic olefins, as enols or enolacetates (Nos. 23–27). With the trifluoromethyl radical, obtained from trifluoroacetic acid, also with electrophilic olefins fair yields of adduct have been found.

To some degree the ratio of additive monomer to additive dimer can be influenced by the current density. High current densities favor the formation of additive monomers, low ones these of additive dimers (Table 8, Nos. 4, 5). This result can be rationalized according to Eq. 9: At high current densities, which corresponds to a high radical concentration in front of the electrode, the olefin can trap only part of the Kolbe radicals formed. This leads to a preferred coupling to the Kolbe dimer and a combination of the Kolbe radical with the primary adduct to the additive monomer. At low current densities the majority of the Kolbe radicals are scavenged by the olefin, which leads to a preferential formation of the additive dimer.

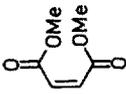
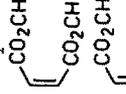
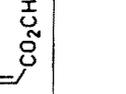
In the addition to 1,3-dienes, e.g. butadiene, an intermediate allyl radical is formed, that couples to 1,1'-, 1,3'- and 3,3'-dimers (Eq. 10). The reactivity of the intermediate allyl radical is about 2.4 to 2.7 higher in the C1- than in the C3-position leading to a preferred formation of the 1,1'-dimer [206].

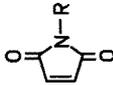
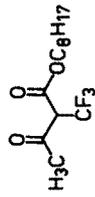
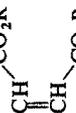


The ratio of C1- to C3-coupling is not influenced by the solvent but to some extent by the electrode material [227].

Additions of Kolbe radicals to dienes are reported in refs. [45, 215, 228] and in the reviews named in chap. 1.

Table 8. Addition of Kolbe-radicals to olefins

No.	Carboxylic acid	Olefin	Additive monomer (% α -yield)	Additive dimer (% α -yield)	Ref.
1	$\text{CH}_3\text{O}_2\text{CCH}_2\text{CO}_2\text{H}$	styrene	4	38 ^a	206
2	$\text{CH}_3\text{O}_2\text{CCH}_2\text{CO}_2\text{H}$	butadiene	17	18	206
3	$\text{CH}_3\text{O}_2\text{CCH}_2\text{CO}_2\text{H}$	isoprene	1	43	206
4	$\text{EtO}_2\text{CCO}_2\text{H}$	butadiene ($i = 0.025 \text{ A/cm}^2$)	4	66	206, 207
5	$\text{EtO}_2\text{CCO}_2\text{H}$	butadiene ($i = 0.66 \text{ A/cm}^2$)	15	8	206
6	$\text{EtO}_2\text{CCO}_2\text{H}$	isoprene	8	59	206
7	$\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2\text{H}$	butadiene	48	48	208, 209
8a	$\text{HO}_2\text{CCO}_2\text{H}$	butadiene	—	20	210
8b	$\text{HO}_2\text{CCO}_2\text{H}$		62	34	211
9	$\text{CH}_3\text{O}_2\text{CCH}_2\text{CO}_2\text{H}$	α -methyl-styrene	—	46 ^b	138 b
10	$\text{CH}_3\text{CO}_2\text{H}$	styrene	—	15	212
11	$\text{EtO}_2\text{CCO}_2\text{H}$	isobutene	9	—	206
12	$\text{CH}_3\text{CO}_2\text{H}$	$\text{CH}_2 = \text{CH}_2$	~ 70	—	213
13	$\text{Cl}_3\text{CCO}_2\text{H}$	$\text{CH}_2 = \text{CH}_2$	—	—	214
14	$\text{HO}_2\text{CCO}_2\text{H}$	$\text{CH}_2 = \text{CH}_2$	25	46	213
15	$\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2\text{H}$	$\text{CH}_2 = \text{CH}_2$	15	—	213
16	$\text{CH}_3\text{CO}_2\text{H}$	$\text{Me}_3\text{CCH} = \text{CH}_2$	46	—	215
17	$\text{CH}_3\text{CO}_2\text{H}$	$\text{CH}_2 = \text{C}(\text{CH}_3)\text{CHO}$	—	80	216
18	$\text{CH}_3\text{CO}_2\text{H}$	$\text{CH}_2 = \text{CH}-\text{CO}_2\text{Et}$	—	70	216
19	$\text{CH}_3\text{CO}_2\text{H}$		21-high	—	217, 218
20	$\text{PhCH}_2\text{CO}_2\text{H}$		24	—	219

21	CH ₃ CO ₂ H		80-88	—	219, 218
22	RCO ₂ H R: CH ₃ , C ₂ H ₅ , i-C ₄ H ₉	R: Et, Ph Ph-SO ₂ -CH=CH ₂	37-69	—	220
23	CF ₃ CO ₂ H	CH ₃ C(OAc)=CH-CO ₂ C ₈ H ₁₇		—	221
24	CH ₃ O ₂ CCH ₂ CO ₂ H	CH ₂ =CHOEt	64	35	222
25	CF ₃ CO ₂ H	1-pentene	—	40	223
26	CF ₃ CO ₂ H	CH ₂ =C(CH ₃)OAc	18 ^a	—	224
27	CF ₃ CO ₂ H		31	—	225
28	CF ₃ CO ₂ H	CH ₂ =CHCO ₂ CH ₃	5	50	223
29	CF ₃ CO ₂ H	CH ₂ =CHCO ₂ H	17	28	170
30	CF ₃ CO ₂ H	CH ₂ =CHCF ₃	—	40	213
31	CF ₃ CO ₂ H	CHF=CF ₂	—	30	213
32	CF ₃ CO ₂ H		30	10	213
			41	27	225
33	CF ₃ CO ₂ H	R = Me, Et 	4-42	—	226
		n = 0-3			

^a Additional 16% disproportionation product, ^b 6% Product-type IV, Eq. 9

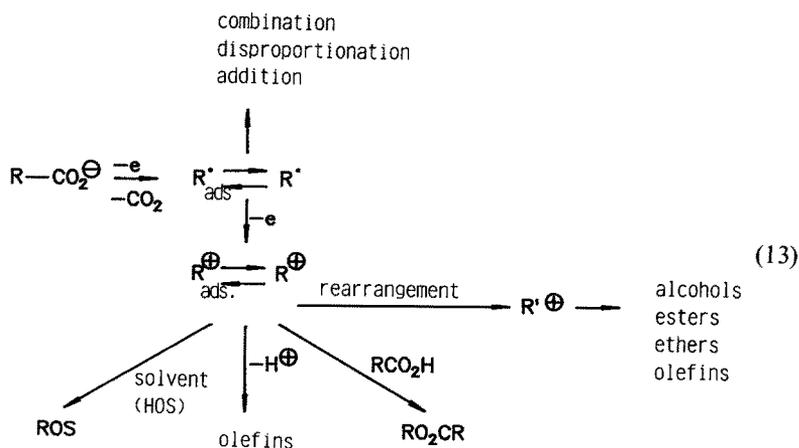
acrylonitrile [212], vinyl acetate [231], methyl acrylate [231], vinylchloride [232], acrylic acid [232] and acrylamide [233].

Kolbe radicals can also be trapped by oxygen to yield dialkylperoxides, aldehydes, and ketones [97]. Furthermore methyl and trifluoromethyl radicals from acetic acid and trifluoroacetic acid are trapped, although inefficiently, by pyridine (3–20%) [234], benzotrifluoride and benzonitrile [235].

Alkyl radicals that add only in low yield to nucleophilic alkenes can be more efficiently trapped, if they react intramolecularly. Kolbe electrolysis of $\Delta^{6,7}$ - and $\Delta^{7,8}$ -unsaturated carboxylates leads to five membered and six membered rings in a 5- or 6-*exo*-trig cyclization [139]. Such an intramolecular cyclization was first reported by Weedon [138a]. In a systematic study on the *Z/E*-isomerization of unsaturated carboxylates with different distances of the double bond from the carboxylate group cyclopentanes and to a smaller extent cyclohexanes were formed by cyclization of the intermediate 5-hexenyl and 6-heptenyl radicals [140]. This reaction has been utilized for the efficient construction of heterocycles (Eq. 11, **40** (41%) [236], **41** (53%) [237], and carbocycles **42** (74%), **43** (75%) [238]. The reaction has been applied to the synthesis of a prostaglandine precursor (Eq. 12) [239]. The stereospecificity of this reaction can be rationalized by the *cis*-annulation of five-membered rings and the predominant coupling of the cyclized radical from the sterically unshielded site. Compared to chemical radical cyclizations [240] these electrochemical ring closures have the advantages that they join two carbon bonds in one step, whilst in the chemical reactions in most of the cases only one carbon-carbon and one carbon-hydrogen bond are formed. Secondly electrolysis avoids the toxic tributyltin hydrides, that are mostly used as initiators in the chemical radical cyclizations.

7 Non-Kolbe Electrolysis to Carbenium Ions as Intermediates

The electrolysis of carboxylic acids in aqueous solution can lead to alcohols and esters as major reaction products [5, 241]. When electrolyses are performed in methanol or acetic acid methyl ethers or acetates can be found as side or major products. These observations led Walling and others [242] to suggest that in these cases the inter-

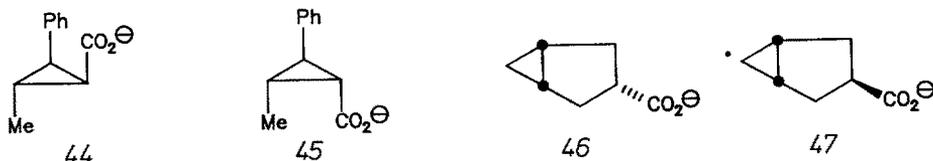


mediate Kolbe radicals are further oxidized to carbenium ions that undergo solvolysis and elimination. The oxidation of carboxylates to carbenium ions has been applied in mechanistic investigations and used in synthesis, this work is summarized in refs. [9, 18, 19, 25].

In order to be more precise the oxidation of carboxylates to radicals shown in Eq. 2, has to be extended by some additional steps outlined in Eq. 13. The free or adsorbed radical is further oxidized to a free or adsorbed carbenium ion. This can solvolyze to ethers, alcohols or esters, can lose a proton to form an olefin, can combine with the unreacted acid to an ester, or can undergo rearrangement or fragmentation prior to these reactions. This part of the anodic decarboxylation, leading to carbenium ions, is often called the Hofer-Moest reaction, when water is used as solvent, or more generally non-Kolbe electrolysis. The two electron oxidation can be recognized by a major portion of olefinic products, the formation of alcohols, esters, ethers, amides and especially by means of products that originate from rearrangement or fragmentation.

Low current densities suppress Kolbe-dimerization and promote the formation of alcohols or ethers [9, 31]. Non-Kolbe electrolysis is further favored by graphite as the electrode material [243, 244, 245, 246b]. However, if nonporous carbon anodes (baked carbon, vitreous carbon, hard carbon) are used Kolbe dimers are formed in moderate to good yields [48]. This suggests that the different real surface areas of the carbon anodes lead to different current densities and thus different radical concentrations at the electrode. High concentrations at dense graphite favor the bimolecular dimerization, whilst low ones at soft graphite support the second electron transfer. With porous graphite even primary alkanoates can be oxidized to primary carbenium ions [52].

A mixture of water/pyridine appears to be the solvent of choice to aid carbenium ion formation [246]. In the Hofer-Moest reaction the formation of alcohols is optimized by adding alkali bicarbonates, sulfates [39] or perchlorates. In methanol solution the presence of a small amount of sodium perchlorate shifts the decarboxylation totally to the carbenium ion pathway [31]. The structure of the carboxylate can also support non-Kolbe electrolysis. By comparing the products of the electrolysis of different carboxylates with the ionization potentials of the corresponding radicals one can draw the conclusion that alkyl radicals with gas phase ionization potentials smaller than 8 eV should be oxidized to carbenium ions [8c] in the course of Kolbe electrolysis. This gives some indication in which cases preferential carbenium ion formation or radical dimerization is to be expected. Thus α -alkyl, cycloalkyl [247, 248], α -chloro [249] or bromo, α -amino, alkoxy, hydroxy, acyloxy, α,α -diphenyl more or less promote the oxidation of the radical to the carbenium ion. Besides electronic effects the oxidation seems also to be controlled by steric factors. In the oxidation of nuclear substituted phenylacetic acids even strongly electron withdrawing



groups, such as CF_3 , do not inhibit the oxidation of the radical. This has been interpreted by a lower extent of adsorption, from which the dimerization is assumed, due to steric shielding [31]. In summary, the experimental factors that favor the carbenium ion pathway are: low current density, a porous graphite anode, addition of foreign anions (e.g. perchlorate), a high pH and structural factors in the carboxylic acid as electron donating groups in the α -position and bulky substituents that retard adsorption of the radicals.

It is generally assumed that the carbenium ion is formed by oxidation of the intermediate radical (Eq. 13). There are, however, small differences in the product ratios of configurational isomers in the non-Kolbe electrolysis of **44/45** and **46/47** that could be interpreted as a result of a synchronous electrocyclic ring opening of an acyloxy cation (RCO_2^+) [249]. The differences are, however, small and do not point to RCO_2^+ as being a significant intermediate. The carbenium ions formed are assumed to be "hot". The product distribution is similar to that obtained from carbenium ions generated chemically by deamination and deoxygenation [243, 250, 251]. Compared to the chemically formed carbocations, the pH in the electrolysis can be chosen rather freely. This way rapid rearrangements can be partially intercepted by electrolysis at high pH [252], e.g. of the anodically generated pinacolyl cation [253]. The degree and rate of rearrangement seems to be independent of the electrode material, whether it is platinum or carbon [254] appears to have no effect.

Non-Kolbe electrolysis may lead to a large product spectrum, especially when there are equilibrating cations of about equal energy involved. However, in cases where the further reaction path leads to a particularly stabilized carbocation and either elimination or solvolysis can be favored, then non-Kolbe electrolysis can become an efficient synthetic method. This is demonstrated in the following chapters.

8 Non-Kolbe Electrolysis of Carboxylic Acids to Ethers, Esters, and Alcohols

Carboxylic acids with an electron donating substituent in the α -position decarboxylate in a two-electron oxidation to carbocations (see chap. 7). These can react with the solvent (alcohol, acetic acid, water) or the unreacted carboxylate to ethers, esters, or alcohols (Eq. 14). In some cases the carbon skeleton rearranges, which is a clear indication of the cationic pathway.

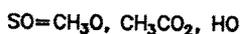
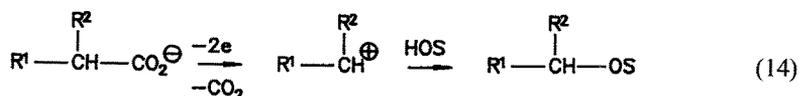
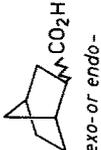
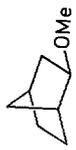
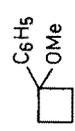
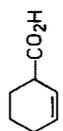
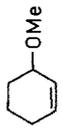


Table 9. Preparation of ethers, esters and alcohols by non-Kolbe electrolysis of carboxylates

No.	Carboxylate	Conditions	Product	Yield (%)	Ref.
1	Adamantane-1-carboxylic acid	MeOH or EtOH, Pt	1-methoxy-, or 1-ethoxy-adamantane	50	248, 255 a, b
2	Homoadamantane-1-carboxylic acid	MeOH or EtOH, Pt	1-methoxy-, or 1-ethoxy homo-adamantane	—	255 c
3	 <i>exo- or endo-</i>	MeOH, Pt		35-40	242 c
4		MeOH, Pt		33	256
5		MeOH		100	96
6		EtOH	$\text{Ph}_2\text{C}=\text{C} \begin{matrix} \text{CO}_2\text{Et} \\ \text{CH}_2\text{OEt} \end{matrix}$	69	257
7	α -Methoxyphenylacetic acid	MeOH	$\text{Ph}_2\text{C}=\text{C} \begin{matrix} \text{OEt} \\ \text{CO}_2\text{Et} \\ \text{CH}_2\text{F} \end{matrix}$	12	
8	α -Methoxydiphenylacetic acid	MeOH	benzaldehyde dimethylacetal	62	258
9	α -Ethoxy-4-nitrophenylacetic acid	MeOH	benzophenone dimethylacetal	74	258
10	Triphenylacetic acid	MeOH	4-nitrobenzaldehyde methyl ethylacetal	50	259
11	Diphenylacetic acid	MeOH, Et ₃ N	triphenylmethyl methyl ether	60	260
12	R ¹ R ² R ³ CCOC ₂ H ₅ R ¹ = R ² = R ³ = CH ₃ R ¹ = R ² = R ³ = C ₅ H ₁₁	MeOH, Pt	methyl benzhydriyl ether R ¹ R ² R ³ CCO ₂ CH ₃	80 50-60	261 262

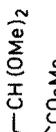
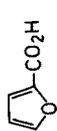
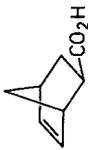
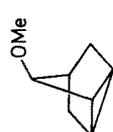
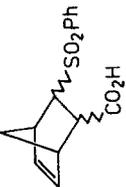
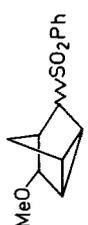
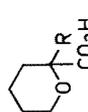
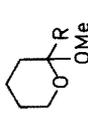
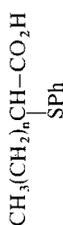
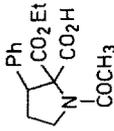
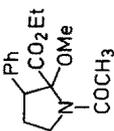
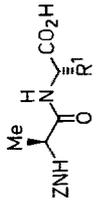
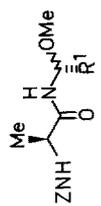
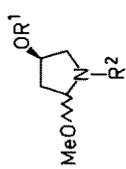
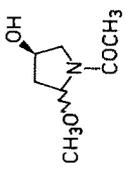
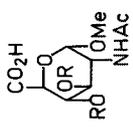
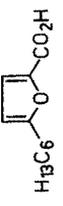
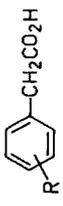
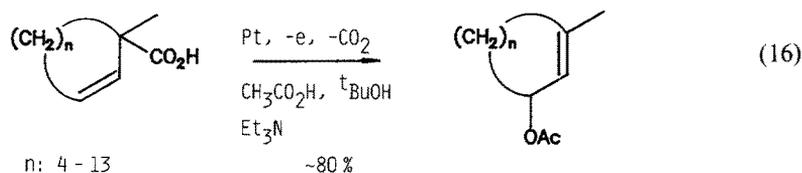
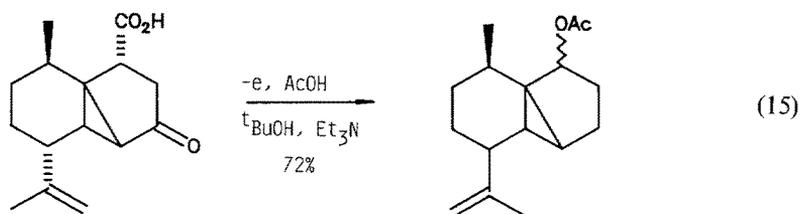
13			MeOH, NH ₄ Br, Et ₃ N, C		78	263
14			MeOH, Et ₃ N, Et ₄ NClO ₄ , Pt		84	264
15	Phenylacetic acid		Pyr.-MeOH, C	benzyl methyl ether	93	119
16	Ph ₂ C(SPh)CO ₂ H		MeOH	benzophenone dimethylacetal	64	265
17	PhSO ₂ CH ₂ CO ₂ H		MeOH	PhSO ₂ CH ₂ OMe	57	266
18			MeOH		56	242c
19			MeOH		49	266
20		R = Allyl, CH ₂ -CH=CHMe, CH ₂ -CMe=CH ₂	MeOH, K ₂ CO ₃ , Pt	<i>exo/endo</i> : 2/1 	67-90	267
21		CH ₃ (CH ₂) _n CH-CO ₂ H SPh	MeOH, LiClO ₄ , Pt	CH ₃ (CH ₂) _n CH(OMe) ₂	72-98	268
22		n = 2,7 R ¹ CONHCHR ² CO ₂ H R ¹ : Ph, Me, PhCH ₂ R ² : H, Me	R ³ OH R ³ : Me, Et, iPr, CH ₃ CO	R ¹ CONHCHR ² OR ³	38-91	269

Table 9. continued

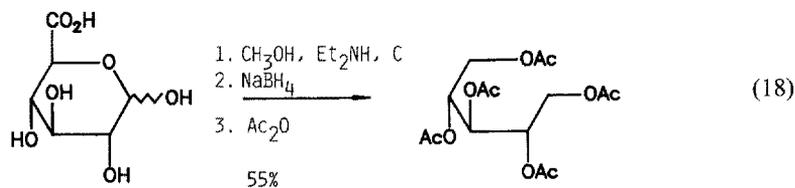
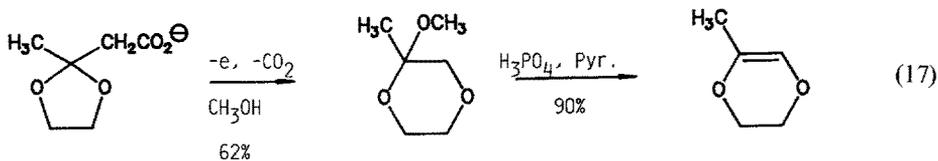
No.	Carboxylate	Conditions	Product	Yield (%)	Ref.
23	$\begin{array}{c} \text{CO}_2\text{Et} \\ \\ \text{R}^1\text{C}-\text{CO}_2\text{H} \\ \\ \text{NHCOMe} \end{array}$ <p>R¹: H, Me, Et iProp, PhCH₂</p>	R ² OH	$\begin{array}{c} \text{CO}_2\text{Et} \\ \\ \text{R}^1\text{C}-\text{OR}^2 \\ \\ \text{NHCOME} \end{array}$	79-96	270
24		MeOH		98	271
25	<i>p</i> -NO ₂ -C ₆ H ₄ -CO-D,L-Val-OH	MeOH	<i>p</i> -NO ₂ -C ₆ H ₄ -CONH-CH(OMe)CHMe ₂	35	272
26		MeOH			273
27	Z: PhCH ₂ O ₂ C; R ¹ : H, iProp	MeOH			274a
	R ¹ : SiMe ₂ ^t But, R ² : CO ₂ Me	MeOH, Pt		97	274b

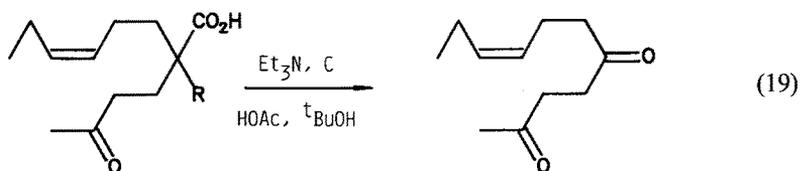
29		AcOH, Pt	89	275
30		AcOH/NaOAc	57	276
31	$\text{R}^1 - \underset{\text{CO}_2\text{H}}{\overset{\text{NHCOR}^2}{\text{C}}} - \text{CO}_2\text{Et}$	AcOH/NaOAc	40-91	277
32	$\text{CH}_3(\text{CH}_2)_n - \underset{\text{Cl}}{\text{CH}} - \text{CHCO}_2\text{H}$	R ² : Me, O-Benzyl MeOH	41-60	249
33	$\text{ROCH}_2\text{CO}_2\text{H}$	MeCN	47-66	278
34		DMSO	41-78	279
35	$\text{R}: 4\text{-MeO}, 4\text{-Cl}, 3\text{-MeO}, \text{H}$ $\text{HO}_2\text{C}(\text{CHOH})_2\text{CO}_2\text{H}$	H ₂ O, W ⁻ -anode	—	280



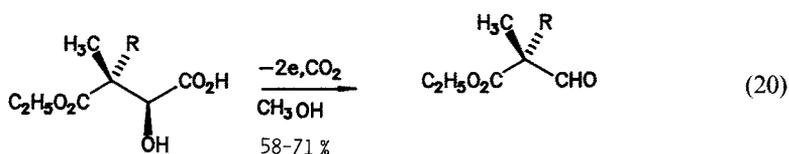
In this way bridgehead carboxylates have been converted into the corresponding ethers (Table 9, Nos. 1–2). Both *exo*- and *endo*-2-norbornylcarboxylic acid yield the *exo*-2-methyl ether indicating that a bridged norbornyl cation is the intermediate (Table 9, No. 3). Steric reasons can prevent the rearrangement as in the conversion of the tricyclic carboxylic acid to the corresponding acetate (Eq. 15) [281]. In other cases the intermediate cyclopropylcarbanyl cation undergoes rearrangement (see also chap. 11). Carboxylic acids formed by a Stobbe condensation can react to an allyl cation that solvolyses in the 1- and 3-position (Table 9, No. 6). In some cases the allyl cation undergoes a regioselective acetolysis (Eq. 16) [282]. In the norbornenyl system the intermediate cation can add intramolecularly to the double bond leading to nortricyclene derivatives (Table 9, Nos. 18, 19).

α -Phenyl substituted carboxylic acids react selectively, because the intermediate phenylmethyl cations cannot undergo elimination or rearrangement (Table 9, Nos. 4, 7–11, 15). α -Ketoesters can be converted to esters possibly via intermediate acylium cations (Table 9, No. 12). The α -alkoxy group is very effective in directing the decarboxylation towards the cation, whose solvolysis leads to acetals (Table 9, Nos. 13, 14, 20, 28, 29, 32). Cyclic ketals of β -keto-carboxylic acids react to 2-methoxy-1,4-dioxenes (Eq. 17) [283]. Uronic acid has been converted to a pentaacetate (Eq. 18) [275].



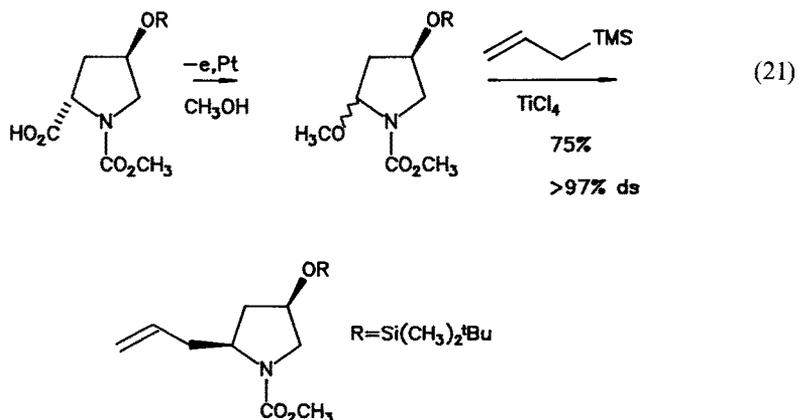


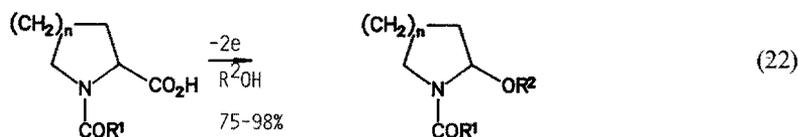
R: S-Benzthiazol: 61%
: CO₂H : 55%



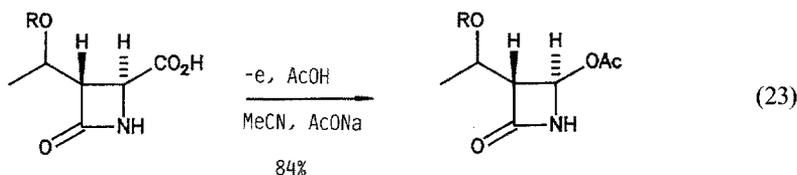
R = C₂H₅, CH₂CH=CH₂, CH₂C₆H₅

2-Furane carboxylic acids are first oxidized to the 1,4-dimethoxy compound and then decarboxylated (Table 9, Nos. 13, 14, 30). The current density and thus the potential at the cathode can determine whether (Table 9, No. 13) or not (Table 9, No. 14) a subsequent reductive hydrogenation at the cathode occurs. The thio- and even the sulfonyl group can promote the further oxidation to the cation (Table 9, Nos. 16, 17, 21) leading to acetals in these cases. When this reaction is combined with an α -alkylation the α -thio carboxylic acid can be used as a d₁-synthon (Eq. 19) [284a-c]. The malonate unit can be employed in the same way (Eq. 19) [284d]. (*S*)-Malic-acid derivatives are transformed into enantiomerically pure alkylmalonaldehyde esters (Eq. 20) [285]. Many examples are reported for the decarboxylation of α -amino acids to the corresponding amino acetals (Table 9, Nos. 22-27, 31).

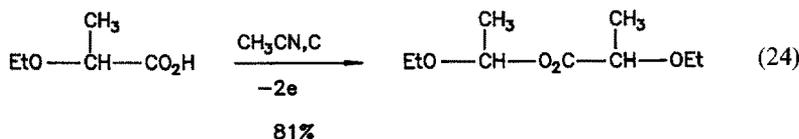




n : 1,2; R^1 : H, CH₃, Ph, OEt; R^2 : CH₃, C₂H₅, H, ¹C₃H₇



R = TBDMS



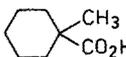
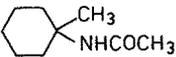
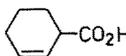
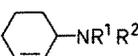
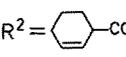
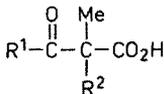
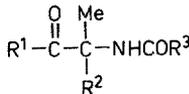
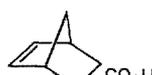
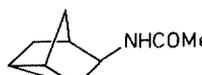
4-Hydroxy-L-prolin is converted into a 2-methoxypyrrolidine. This can be used as a valuable chiral building block to prepare optically active 2-substituted pyrrolidines (2-allyl, 2-cyano, 2-phosphono) with different nucleophiles and employing TiCl₄ as Lewis acid (Eq. 21) [286]. Using these latent *N*-acylimmonium cations (Eq. 22) [287] (Table 9, No. 31), 2-(pyrimidin-1-yl)-2-amino acids [288], and 5-fluorouracil derivatives [289] have been prepared. For the synthesis of β-lactams a 4-acetoxiazetidinone, prepared by non-Kolbe electrolysis of the corresponding 4-carboxy derivative (Eq. 23) [290], proved to be a valuable intermediate. *O*-Benzoylated α-hydroxyacetic acids are decarboxylated in methanol to mixed acylals [291]. By reaction of the intermediate cation, with the carboxylic acid used as precursor, esters are obtained in acetonitrile (Eq. 24) [292] and surprisingly also in methanol as solvent (Table 9, No. 32). Hydroxy compounds are formed by decarboxylation in water or in dimethyl sulfoxide (Table 9, Nos. 34, 35).

The various carbenium ions: *tert*-alkyl, bridgehead-, norbornyl-, allyl-, benzyl- or cyclopropylcarbinyl-cations, which are assumed to be intermediates in these decarboxylations are compiled in ref. [293].

9 Non-Kolbe Electrolysis of Carboxylic Acids to Acetamides

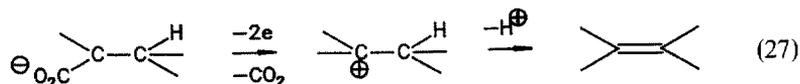
Non-Kolbe electrolysis of carboxylic acids in acetonitrile/water leads to acetamides as main products [294] (Table 10). The mechanism has been investigated by using ¹⁴C-labeled carboxylic acids. The results are rationalized by assuming a reaction layer rich of carboxylate resulting in the formation of a diacylamide that is hydrolyzed

Table 10. Acetamides by non-Kolbe electrolysis of carboxylates in acetonitrile

No.	Carboxylic acid	Product	Yield (%)	Ref.
1	Me ₃ CCO ₂ H	Me ₃ CNHCOCH ₃	40, 80	294a, 295
2	Me ₂ CCO ₂ Me Me ₂ CCO ₂ H	Me ₂ C-CO ₂ Me Me ₂ C-NHCOMe	25	294a
3			68	295
4	C ₂ H ₅ C(CH ₃) ₂ CO ₂ H	C ₂ H ₅ C(CH ₃) ₂ NHCOCH ₃	63	295
5	(CH ₃) ₂ CHCO ₂ H	(CH ₃) ₂ CH-N-COCH ₃ COCH(CH ₃) ₂	50	295, 296
6				54
		R ¹ = H, R ² = 	20	
		R ¹ = CH ₃ CO, R ² = 	45	
		R ¹ = CH ₃ CO, R ² = H	20	
7			18-50	104b
	R ¹ = Me, <i>i</i> -Prop R ² = Me, Et R ³ = Me, Et, <i>i</i> -Prop			
8			35	297

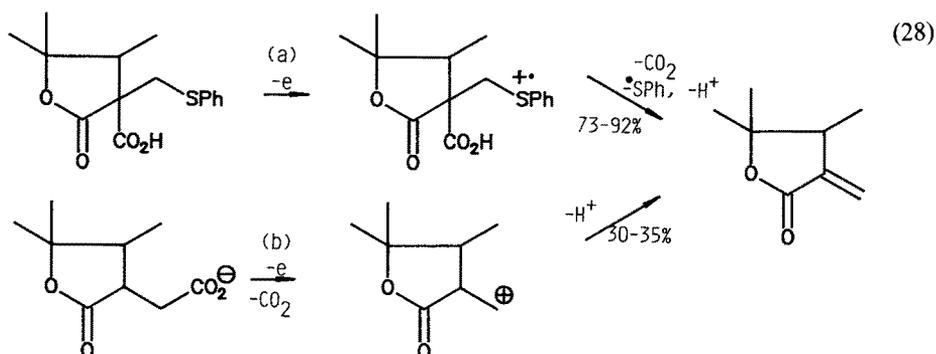
10 Conversion of Carboxylic Acids into Olefins by Non-Kolbe Electrolysis

Carboxylic acids can be converted into olefins, when there is a leaving group such as H (Eq. 27), SiMe₃, SPh or CO₂H in the β-position. The olefin is formed, when the carbocation, that is generated by decarboxylation, undergoes a subsequent E1-elimination. Some examples are summarized in Table 11 (Nos. 1-10).

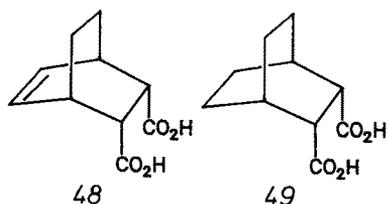
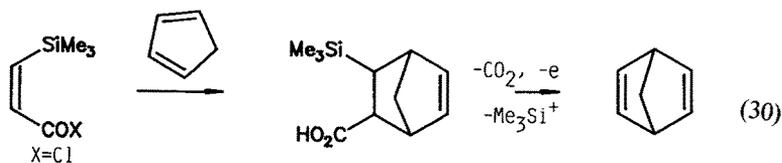
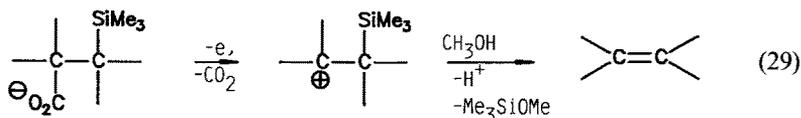


Reaction No. 5 (Table 11) is part of a synthetically useful method for the alkylation of aromatic compounds. At first the aromatic carboxylic acid is reductively alkylated by way of a Birch reduction in the presence of alkyl halides, this is then followed by an eliminative decarboxylation. In reaction No. 9 decarboxylation occurs probably by oxidation at the nitrogen to the radical cation that undergoes decarboxylation (see

pseudo-Kolbe electrolysis, chap. 14). Such a mechanism seems also to be involved in the decarboxylation/desulfenylation (Eq. 28) [318]. There sulfur appears to be oxidized to a radical cation that cleaves to the *exo*-methylene lactone, carbon dioxide and a thiyl radical (reaction a); in the direct electrolysis the yield is much lower (reaction b). In the eliminative decarboxylations of cycloalkanecarboxylic acids (seven- to eleven-membered rings), besides the 1,2-elimination, a 1,3-elimination to cyclopropanes and a transannular 1,5-elimination occur to some extent [247, 319].

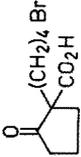
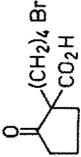
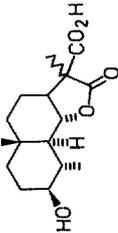
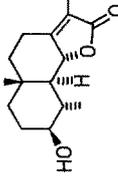
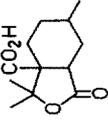
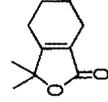
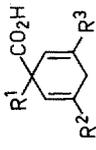
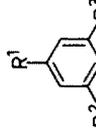
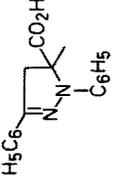
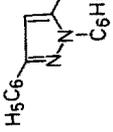


In β -trimethylsilylcarboxylic acids the non-Kolbe electrolysis is favored as the carbocation is stabilized by the β -effect of the silyl group. Attack of methanol at the silyl group subsequently leads in a regioselective elimination to the double bond (Eq. 29) [307, 308]. This reaction has been used for the construction of 1,4-cyclohexadienes. At first Diels-Alder adducts are prepared from dienes and β -trimethylsilylacrylic acid as acetylene-equivalent, this is then followed by decarboxylation-desilylation (Eq. 30) [308]. Some examples are summarized in Table 11, Nos. 12–13.



Bisdecarboxylation of vicinal dicarboxylates is the older method of converting vicinal diacids into olefins. The reaction can be combined with a [4 + 2]- or [2 + 2]-

Table 11. Conversion of Carboxylic acids into Olefins

No.	Carboxylic acid	Reaction Condition	Product	Yield (%)	Ref.
1	$\text{MeCOC}(\text{CH}_2)_2\text{CO}_2\text{H}$ 	H_2O , KOH	$\text{MeCOC}(\text{CH}_2)_2=\text{CH}_2$ 	90	104b, 303
2		H_2O KOH		50	104b, 303
3		Pyr./ H_2O , Et_3N , C		57-63	300
4		Pyr./ H_2O , Et_3N , Pt		91	301
5	 $\text{R}^1 = \text{iso-Prop.}$, $\text{R}^2 = \text{Me}$, MeO , $\text{R}^3 = \text{H}$ $\text{R}^1 = \text{Me}$ (CH_2) $_4$, $\text{R}^2 = \text{R}^3 = \text{OMe}$	MeOH, MeONa		60-70	302
6		CH_3OH , Et_4NBF_4		86	304

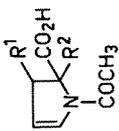
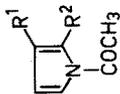
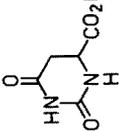
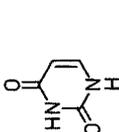
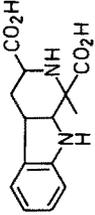
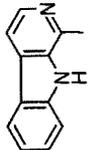
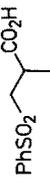
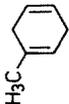
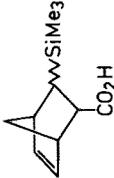
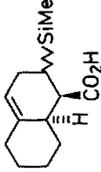
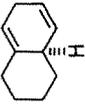
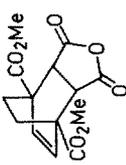
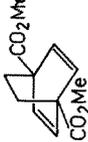
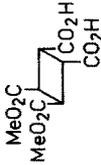
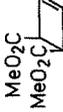
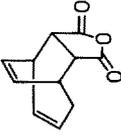
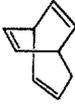
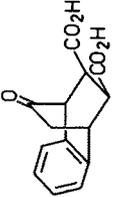
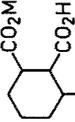
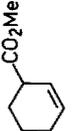
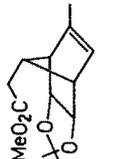
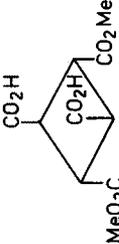
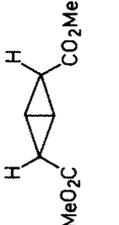
7	 <p>$R^1 = C_6H_5, R^2 = CO_2Et$ $R^1 = C_6H_5, R^2 = CO_2Et$</p>	H_2O, THF, KOH		86-91	271
8		$C, NaOMe, MeOH$		91	305
9		$MeOH, H_2O, KH_2PO_4, C$		75	306
10		$Pyr./MeOH$ (9:1), C	$Ph-SO_2CH_2CH=CH_2$ $Ph-SO_2-CH=CH-CH_3$ (1:1) $RCH=CH_2$	80	266
11	$Me_3SiCH_2CHCO_2H$ R $R: C_{12}H_{25}, Br(CH_2)_6, \text{etc.}$	$MeCN, EtOH, C$	$RCH=CH_2$	65-87	307
12a		$MeCN, EtOH, C$		67	308
12b		$MeCN, EtOH, C$		76	308

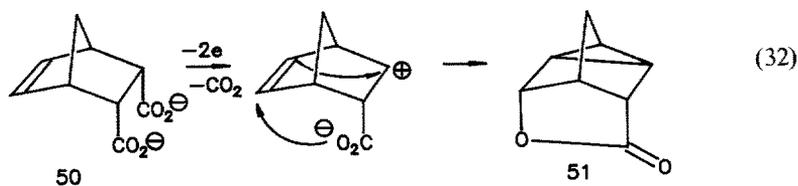
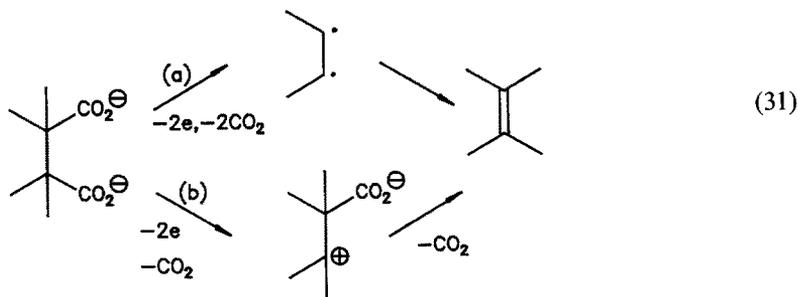
Table 11. continued

No.	Carboxylic acid	Reaction Condition	Product	Yield (%)	Ref.
12c		MeCN, EtOH, C		71	308
13		MeCN, EtOH, C		82	308
14		90% Pyr./H ₂ O, Pt		35	309, 310a
15		90% Pyr./H ₂ O, Pt		40-60	311
16		Pyr., MeCN, Et ₃ N		65	312
17		—		65	313
18		—		—	314

19		90% Pyr./H ₂ O		35	310
20		90% Pyr./H ₂ O		48	309, 310
21		90% Pyr./H ₂ O		63	310a
22		90% Pyr./H ₂ O		15	309
23		90% Pyr./H ₂ O		51	315
24		90% Pyr./H ₂ O		35	96
25		MeOH, MeONa, Pt		50	317
26		90% Pyr. H ₂ O, Pt		15	316

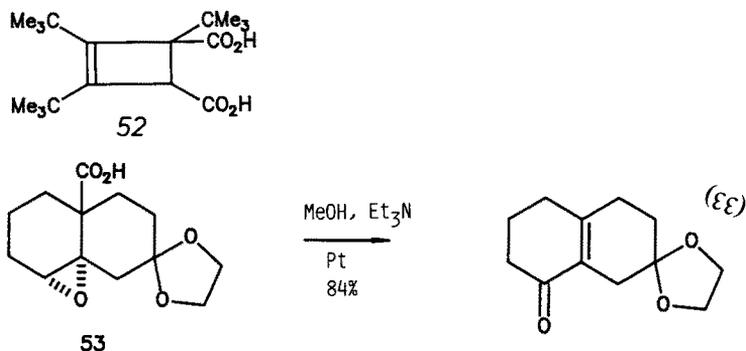
cycloaddition, e.g. with maleic anhydride, whereby unsaturated polycyclic hydrocarbons can be prepared in a few steps (Table 11, Nos. 14–25). 90% Pyridine:triethylamine:water as electrolyte, and platinum as electrode appear to favor this elimination. The optimum choice of conditions has been discussed in ref. [315]. The addition of the radical scavenger 4-*tert*-butyl-catechol to the electrolyte can improve the yield [312]. The anodic bisdecarboxylation is in most cases better than the corresponding oxidation with lead tetraacetate. When reaction No. 14 (Table 11) is conducted with lead tetraacetate only 3% of the product is yielded, sometimes, however, both methods are equivalent [320a]. For the dicarboxylic acids **48** and **49** the influence of the solvent, electrode material, current density, the kind of base and additives have been studied systematically [320b]. Out of the solvents acetonitrile, dimethylformamide, sulfolane, pyridine, 2,6-lutidine or pyridine/water (1:9) the latter leads to the highest yields and lowest passivation. From the anode materials platinum, gold, lead dioxide, graphite or glassy carbon the highest yields are obtained with platinum. At graphite, double bonds are apparently additionally oxidized. Higher current densities also support the reaction. The structure of the base (triethylamine or 1,4-diazabicyclo[2.2.2]octane) influences strongly the degree of passivation but not the yield. Addition of copper(II)acetate lowers the yield, that of lithium perchlorate inhibits the reaction.

As the mechanism, a radical and a cationic pathway are conceivable (Eq. 31). The stereochemical results with *rac*- or *meso*-1,2-diphenyl succinic acid, both yield only *trans*-stilbene [321], and the formation of a tricyclic lactone **51** in the decarboxylation of norbornene dicarboxylic acid **50** (Eq. 32) [309] support a cation (path b, Eq. 31) rather than a "biradical" as intermediate (path a).



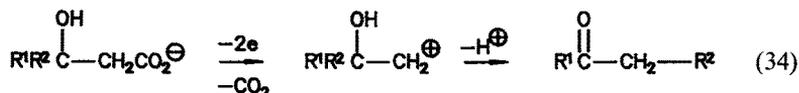
However, the inhibition of the reaction by lithium perchlorate, that strongly favors the cationic pathway (see chap. 2, 7), contradicts this assumption. With regard to yield and the degree of passivation the decarboxylation/desilylation appears to be a better choice than the bisdecarboxylation for the construction of unsaturated polycyclic compounds (see for example Table 11, No. 12b and No. 22).

In the bisdecarboxylation of the cyclobutenedicarboxylic acid **52**, products are obtained whose formation possibly involves a cyclobutadiene intermediate [322]. A case of a 1,3-bisdecarboxylation has been reported in the preparation of a bicyclobutane (Table 11, No. 26). An elimination, that involves the cleavage of a carbon-oxygen bond after the decarboxylation, has been observed with the carboxylic acid **53** (Eq. 33) [282].



11 Rearrangement of Intermediate Carbocations in Non-Kolbe Electrolysis

The carbocations generated by non-Kolbe electrolysis can rearrange by alkyl, phenyl or oxygen migration. The migratory aptitudes of different alkyl groups have been studied in the rearrangement of α -hydroxy carboxylic acids (Eq. 34) [323].

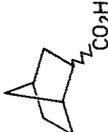
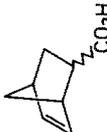
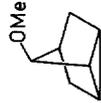
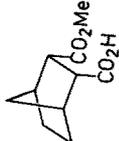
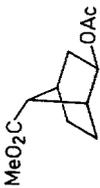
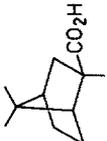
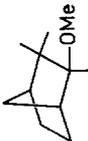
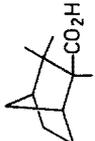
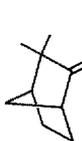
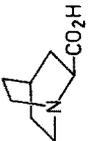


Migratory aptitude: vinyl > iso-propyl > cyclopropyl > benzyl

Rearrangements in the course of a decarboxylation can be taken as strong indicator for the involvement of carbocations. Anodic oxidation of *exo*- or *endo*-norbornane-2-carboxylic acid produced in both cases only the *exo*-norbornyl methyl ether (Table 12, No. 1) [242c]. *Exo*- or *endo*-5-norbornene-2-carboxylic acid react by double bond participation and subsequent rearrangement to 3-methoxynortricyclene (Table 12, No. 2). The kind of products was the same as obtained in solvolysis [329]. The product in reaction No. 3 (Table 12), has been used as intermediate for a methyl (\pm)-jasmonate synthesis. The three isomeric carboxylic acids in reaction No. 4 (Table 12) decarboxylate by rearrangement to the same product mixture. An analogous observation is made for the anodic oxidation of cyclopropylacetic acid, cyclobutylcarboxylic acid and allylacetic acid [252]. The anodic oxidation of cyclopropylcarboxylic acid can lead to Kolbe dimers (see chap. 4) and/or cationic products by ring opening to an allyl cation that undergoes methanolysis or acetolysis depending on the electrolyte [330].

In the electrolysis of quinuclidine-2-carboxylic acid decarboxylation occurs without rearrangement (Table 12, No. 5). Stereospecifically substituted cyclopentanes, that

Table 12. Rearrangements by non-Kolbe electrolysis

No.	Carboxylic acid	Reaction conditions	Product	Yield (%)	Ref.
1	 <i>exo or endo</i>	MeOH, Et ₃ N		35–40	242c
2	 <i>exo or endo</i>	MeOH, Et ₃ N		56	242c
3		AcOH, t-BuOH, Et ₃ N		56	324
4		MeOH, MeONa		74–82	325
				15–25	
5		MeOH, MeONa		43	326

6	<p>Chemical structure of a bicyclic epoxide with substituents R^1, R^2, CO_2Me, and CO_2H.</p>	MeOH, MeONa	87	327
7	<p>Chemical structure of a bicyclic epoxide with substituents CO_2H and a carbonyl group.</p>	MeOH, MeONa	49–58	328

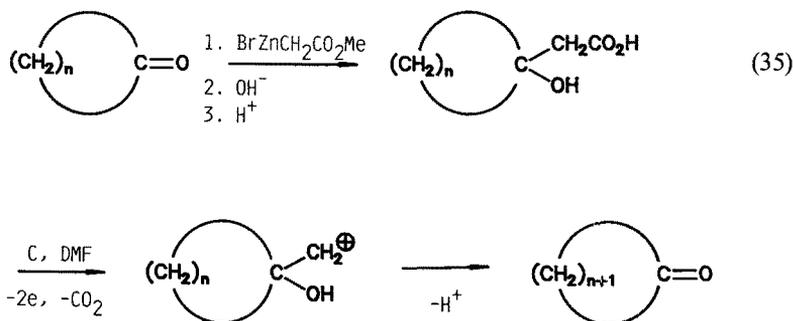
$R^1 = R^2 = Me, H$

Table 13. Ring Extension of alicyclic β -hydroxycarboxylic acids by non-Kolbe electrolysis

No.	Carboxylic acid	Products	Reaction conditions	Yield (%)	Ref.
1			Pt, CH ₃ CN n = 4: n = 5: C, Pyr./H ₂ O n = 9: n = 11:	54-63 54-63 82 82	242c 242c 335 335
2			C, DMF	56	336
3			C, DMF	58	336
4			MeOH, KOH MeOH, KOH	30 5	323

may serve as intermediates for the synthesis of cyclopentanoids, can be prepared by decarboxylation of oxa-bicycloheptanecarboxylic acids (Table 12, Nos. 6, 7). Migration of oxygen has been observed in the decarboxylation of glycidic acids [331, 332] and acetals of β -oxocarboxylic acids [333]. Rearrangement of the phenyl group was encountered in the decarboxylation of 3,3-diphenylpropionic acid, which afforded in acetic acid 1,2-diphenylethylacetate as the major product [334].

Non-Kolbe electrolysis of alicyclic β -hydroxy carboxylic acids offers interesting applications for the one-carbon ring extension of cyclic ketones (Eq. 35) [242c]. The starting compounds are easily available by Reformatsky reaction with cyclic ketones. Some examples are summarized in Table 13. Dimethylformamide as solvent and graphite as anode material appear to be optimal for this reaction.



With unsymmetrical cyclic ketones, however, mixtures due to similar migratory aptitudes of the different groups are obtained (Table 13, Nos. 2, 3). The rearrangement has also been used as key step in a *d,l*-muscone synthesis (Table 13, No. 4).

12 Fragmentation of Carboxylic Acids by Non-Kolbe Electrolysis

Non-Kolbe electrolysis of carboxylic acids can be directed towards a selective fragmentation, when the initially formed carbocation is better stabilized in the γ -position by a hydroxy or trimethylsilyl group. In this way the reaction can be used for a three-carbon (Eq. 36) [335] (Table 14, No. 1) or four-carbon ring extension (Eq. 37) [27] (Table 14, Nos. 2–4). Furthermore it can be employed for the stereo-

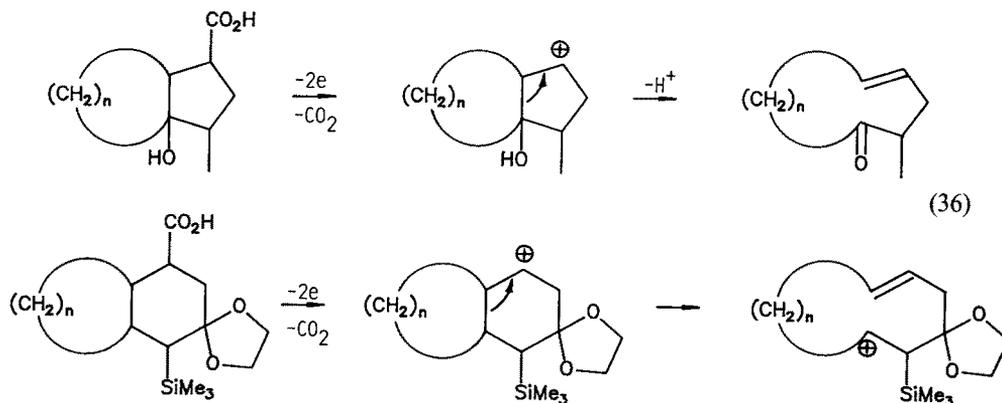
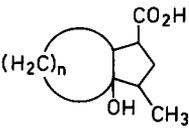
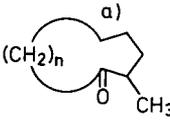
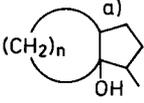
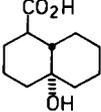
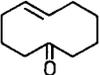
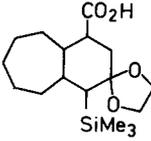
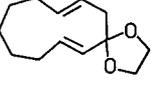
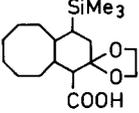
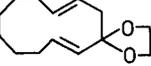
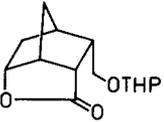
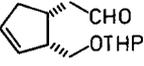
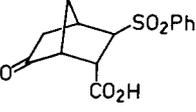
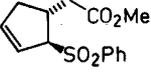
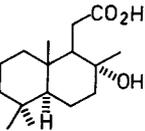
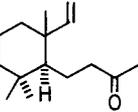
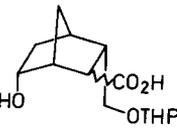
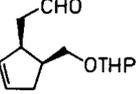
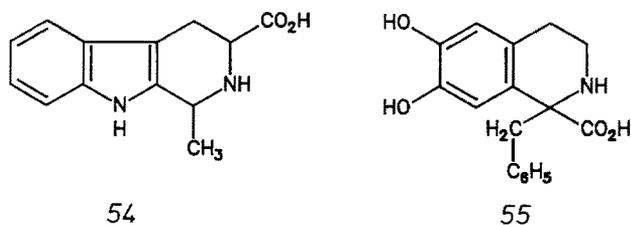
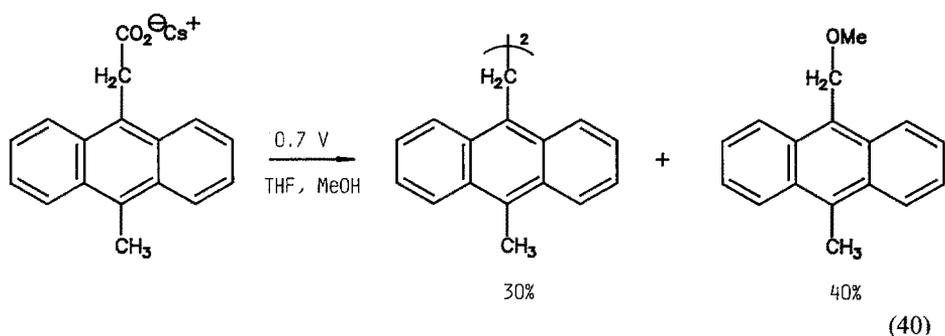


Table 14. Fragmentation of carboxylic acids by non-Kolbe electrolysis

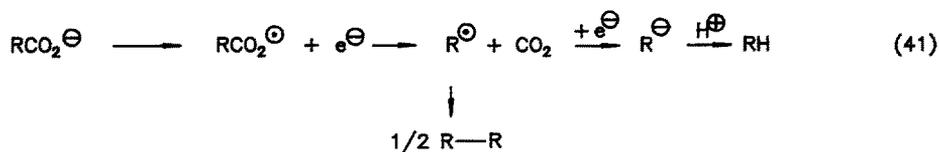
No.	Carboxylic acid	Reaction conditions	Product	Yield (%)	Ref.
1		C-anode, MeCN/EtOH, 100% neutralization		n = 3 6 n = 4 47 n = 10 8	335 -----
				n = 3 39 n = 4 15 n = 10 52	
2		MeOH		44 35	337 335
3		CH3CN/EtOH		85	27
4		CH3CN/EtOH		70	27
5		C-anode, MeCN/EtOH		38	338
6		MeOH, C-anode		63	338
7		MeOH, Pt		34-38	339
8		MeOH, NeONa		53	340
				17	

^a After hydrogenation of the product



The decarboxylation of the caesium salt of 9-methylantracene-10-acetic acid occurs at an even lower potential (0.7 V) and affords the dimer as well as the methyl ether (Eq. 40) [342]. The low oxidation potentials for the decarboxylation of **54** (0.13 to 0.77 V) [306a] and **55** (−0.17 V) [306b] indicate too, that the initial electron transfer occurs from the amino or aryl group rather than from the carboxylate.

14 The Photo-Kolbe Reaction



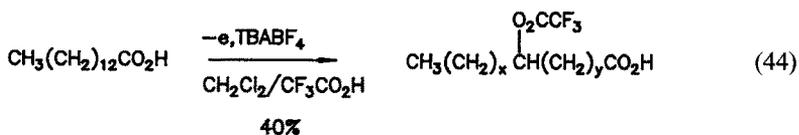
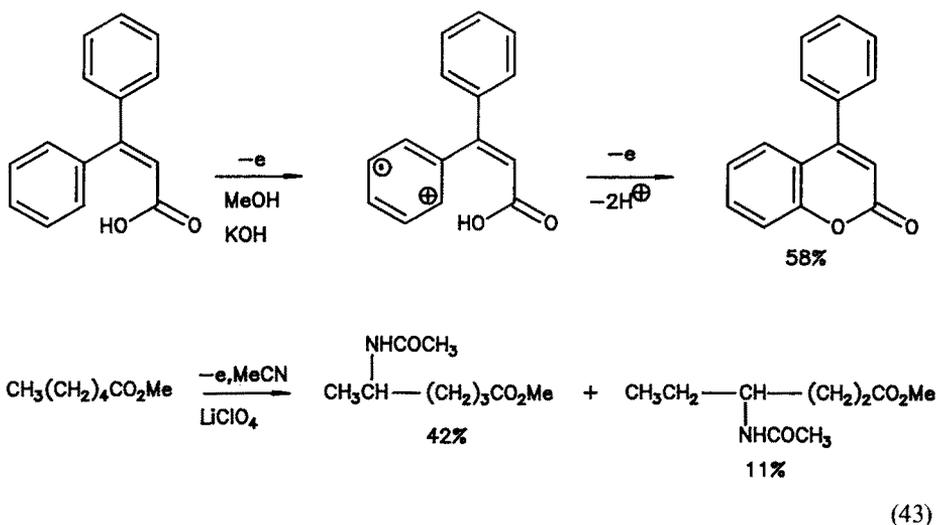
The photo-Kolbe reaction is the decarboxylation of carboxylic acids at low voltage under irradiation at semiconductor anodes (TiO_2), that are partially doped with metals, e.g. platinum [343, 344]. On semiconductor powders the dominant product is a hydrocarbon by substitution of the carboxylate group for hydrogen (Eq. 41), whereas on an n- TiO_2 single crystal in the oxidation of acetic acid the formation of ethane besides methane could be observed [345, 346]. Dependent on the kind of semiconductor, the adsorbed metal, and the pH of the solution the extent of alkyl coupling versus reduction to the hydrocarbon can be controlled to some extent [346]. The intermediacy of alkyl radicals has been demonstrated by ESR-spectroscopy [347], that of the alkyl anion by deuterium incorporation [344]. With vicinal diacids the mono- or bisdecarboxylation can be controlled by the light flux [348]. Adipic acid yielded butane [349] with levulinic acid the products of decarboxylation, methyl ethyl-

ketone, and of C-C bond cleavage, propionic acid, acetic acid, acetone, acetaldehyde were found. These can subsequently undergo decarboxylation to ethane and methane. The product distribution is a complex function of the phase of n-TiO₂ and the level of metalization of the semiconductor powder [350]. Preparative applications of the method have not been reported yet. The reaction seems attractive for several reasons. It needs only a low discharge potential, sun light is sufficient for irradiation and the carboxyl group can be substituted for hydrogen. The latter cannot be achieved by Kolbe electrolysis and needs more steps, if the conversion is done by chemical methods. However, up to now the yields in photo-Kolbe electrolysis are very low.

15 Anodic Oxidation of Carboxylic Acids Without Decarboxylation

In carboxylic acids with an aromatic group or a double bond the π -systems can be oxidized to radical cations that react with the carboxyl group to lactones (Eqs. 7, 42) [142, 351].

In solvents that strongly resist anodic oxidation as MeCN, CH₂Cl₂/CF₃CO₂H, or FSO₃H C-H bonds in the alkyl chain can be oxidized. In acetonitrile a preferential acetamidation in the (ω -2)- and (ω -1)-position occurs (Eq. 43) [352].



y	6	7	8	9	10	11
rel. yield (%)	7	19	28	20	16	7

In methylenechloride/trifluoroacetic acid or fluorsulfonic acid trifluoroacetylation (Eq. 44) [353] or fluorsulfonation [354] of the alkyl chain remote from the protonated carboxyl group occurs.

16 Conclusions

Carboxylic acids can be converted by anodic oxidation into radicals and/or carbocations. The procedure is simple, an undivided beaker-type cell to perform the reaction, current control, and usually methanol as solvent is sufficient. A scale up is fairly easy and the yields are generally good. The pathway towards either radicals or carbocations can be efficiently controlled by the reaction conditions (electrode material, solvent, additives) and the structure of the carboxylic acids. A broad variety of starting compounds is easily and inexpensively available from natural and petrochemical sources, or by highly developed procedures for the synthesis of carboxylic acids.

By the radical pathway 1,*n*-diesters, -diketones, -dienes or -dihalides, chiral intermediates for synthesis, pheromones and unusual hydrocarbons or fatty acids are accessible in one to few steps. The addition of the intermediate radicals to double bonds affords additive dimers, whereby four units can be coupled in one step. By way of intramolecular addition unsaturated carboxylic acids can be converted into five membered hetero- or carbocyclic compounds. These radical reactions are attractive for synthesis because they can tolerate polar functional groups without protection.

Possibly the use of fatty acids as renewable resources and alternative to petrochemical feed stocks can profit from the application of Kolbe electrolysis.

The cationic pathway allows the conversion of carboxylic acids into ethers, acetals or amides. From α -aminoacids versatile chiral building blocks are accessible. The eliminative decarboxylation of vicinal diacids or β -silyl carboxylic acids, combined with cycloaddition reactions, allows the efficient construction of cyclobutenes or cyclohexadienes. The induction of cationic rearrangements or fragmentations is a potent way to specifically substituted cyclopentanoids and ring extensions by one- or four carbons. In view of these favorable qualities of Kolbe electrolysis, numerous useful applications of this old reaction can be expected in the future.

17 Acknowledgement

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