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SELECTIVE MIXED COUPLING OF CARBOXYLIC ACIDS (I). ELECTROLYSIS, THERMOLYSIS AND PHOTOLYSIS OF UNSYMMETRICAL DIACYL PEROXIDES WITH ACYCLIC AND CYCLIC ALKYL GROUPS[1)]

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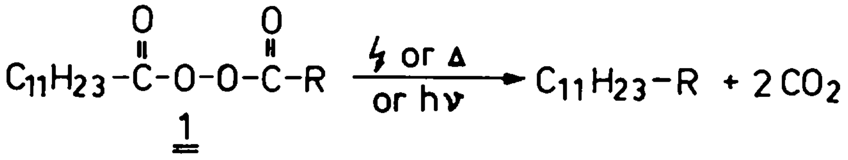
Abstract - 14 Unsymmetrical diacyl peroxides (R^1CO_2-O_2CR^2 with R^1: undecyl; R^2: e.g. methyl, propyl, pentyl, nonyl, 2-methylpropyl, 2-propyl, 2-pentyl, cyclopropyl, cyclobutyl, cyclohexyl) are prepared in 85 to 92 % yield. Square pulse electrolysis of dodecanoyl octanoyl peroxide (**1i**) affords the unsymmetrical coupling product octadecane (**4**) in poor yield and selectivity. Thermolysis or photolysis in solution produces preferentially **4**, but also considerable amounts of disproportionation products. At -78° C the neat peroxides are photolysed selectively to the mixed dimers. With straight chain and β-branched alkyl groups high yields are obtained (63 - 76 %), with cycloalkyl groups medium yields (42 - 56 %), and with α-branched diacyl peroxides moderate yields (20 - 33 %). A comparison of the mixed Kolbe-electrolysis with the low temperature photolysis of the neat peroxide demonstrates the superiority of the latter method in small scale conversion with regard to yield and selectivity.

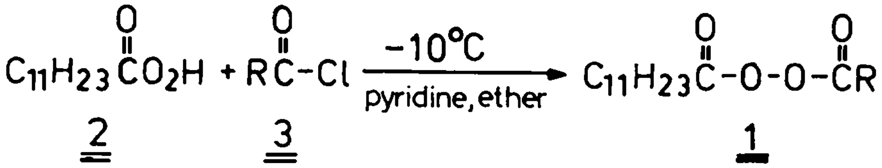
Symmetrical compounds can be prepared simply and in good yield by the versatile Kolbe-electrolysis of carboxylic acids[2)]. Coelectrolysis of different carboxylates yields unsymmetrical products, which allows the efficient synthesis of e.g. pheromones[3)] or rare fatty acids[4)]. A disadvantage of the mixed Kolbe-electrolysis is the simultaneous formation of symmetrical dimers due to the statistical coupling of the intermediate radicals. Here results on the selective mixed coupling of carboxylic acids by pulsed current electrolysis, thermolysis and photolysis of unsymmetrical diacyl peroxides **1** are reported (eq. 1).

(1) 

$$C_{11}H_{23}-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-R \xrightarrow[\text{or } h\nu]{\text{ϟ or } \Delta} C_{11}H_{23}-R + 2\,CO_2$$

1

Preparation of unsymmetrical diacyl peroxides: In order to characterize the influence of different alkyl groups R on yield and selectivity of the coupling reaction, one alkyl substituent was held constant in all peroxides. To avoid hazards due to explosion[5] the relatively stable undecyl group was chosen for that purpose. The acyl dodecanoyl peroxides **1a-n** were obtained in 85 to 96 % yield (Table 1) by reaction of the acyl chlorides **3** and peroxydodecanoic acid (eq. 2)[6], prepared in 65 % yield from dodecanoic acid and 30 % H_2O_2.
In their IR-spectra the diacyl peroxides exhibit two strong bands at 1810 and 1780 cm^{-1} (C=O)[6a,7] and as a characteristic feature of unsymmetrical diacyl peroxides a broad absorption at 1050 cm^{-1} for the O=C-O-O-C=O group[8]. In the ^{13}C-NMR the carbonyl carbon atoms appear as signals around δ = 170 ppm.

(2) 

$$C_{11}H_{23}\overset{\overset{O}{\|}}{C}O_2H + R\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[\text{pyridine, ether}]{-10^{\circ}C} C_{11}H_{23}\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}R$$

2 **3** **1**

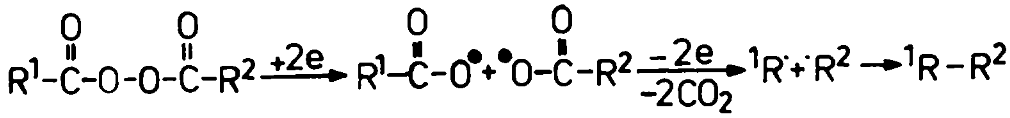
	R		R		R		R
a	CH_3	e	$(CH_3)_3CCH_2$	i	C_7H_{15}	m	$c\text{-}C_5H_9$
b	C_3H_7	f	$(CH_3)_2CH$	j	C_9H_{19}	n	$c\text{-}C_6H_{11}$
c	C_5H_{11}	g	$CH_3CH_2CH(CH_3)$	k	$c\text{-}C_3H_5$		
d	$(CH_3)_2CHCH_2$	h	$CH_3CH_2CH(C_2H_5)$	l	$c\text{-}C_4H_7$		

Electrolysis of unsymmetrical diacyl peroxides with pulsed direct current: A selective mixed coupling is conceivable, if two different radicals are generated close together, e.g. by electrolysis of unsymmetrical diacyl peroxides with pulsed direct current (eq. 3). The cathodic pulse cleaves the peroxide reductively into two different carboxylates[9], which, before they can diffuse too far, are decarboxylated in the anodic pulse to radicals, that couple preferentially to the mixed dimer.

Table 1: Alkanoyl dodecanoyl peroxides (**1**)

R-C=O in **1**	Yield (%) of R(C=O)-O-O-(O=C)R	m.p. (°C) or n_D^{20}
a: Acetyl	85	37-38
b: Butyryl	90	15-16
c: Hexanoyl	88	24-25
d: 3-Methylbutyryl	89	1.4397
e: 3,3-Dimethylbutyryl	91	1.4425
f: 2-Methylpropionyl	94	1.4393
g: 2-Methylbutyryl	90	1.4403
h: 2-Ethylbutyryl	85	
i: Octanoyl	91	33-34
j: Decanoyl	92	40-41
k: Cyclopropanecarbonyl	87	28-29
l: Cyclobutanecarbonyl	96	1.4542
m: Cyclopentanecarbonyl	95	1.4563
n: Cyclohexanecarbonyl	90	1.4601

(3)



$$R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-O-O-}\overset{O}{\overset{\|}{C}}\text{-}R^2 \xrightarrow{+2e} R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^\bullet + {}^\bullet O\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^2 \xrightarrow[-2CO_2]{-2e} {}^1R^\bullet + {}^\bullet R^2 \longrightarrow {}^1R\text{-}R^2$$

1i is reduced at $E_{1/2}$: -0.065 V (vs. SCE). Results from other diacyl peroxides demonstrate, that this is a two-electron reduction, leading to two carboxylates[9]. A successful Kolbe-electrolysis with pulsed direct current has been reported[10]. The choice of the pulse frequency is critical for this electrolysis. It should be high to keep the diffusion of the two carboxylates low, but at the same time moderate to hold down Non-Faradaic capacity currents . These lead with decanoic acid to a continuous drop in dimer yield with increasing pulse frequency, e.g. 60 % current yield octadecane at 0.05 cps, 57 at 0.2, 33/0.4, 27/5, 23/10, 13/20, 4/25, 1/50. Furthermore the Kolbe-electrolysis requires distinct reaction conditions[2]: weakly acidic methanol as solvent, platinum electrodes, none of the anions usually employed in supporting electrolytes, as these can totally suppress the dimerization[11]. After these considerations **1i** was electrolyzed in methanol and in the presence of sodium octanoate and octanoic acid with pulsed direct current (Table 2). The octanoate and octanoic acid concentrations were kept low with regard to this of **1i**, to influence the product distribution as little as possible. When the electrolysis is stopped just after the consumption of **1i**, the mixed coupling product **4** is indeed favoured (Table 2, expts. 4,5; the higher portion of **5** is caused by the supporting electrolyte). However, if the electrolysis is continued until the carboxlate is totally converted, the product distribution becomes statistical (Table 2, expts. 1, 2, 3). The reason could be, that **1i** is reduced faster than the carboxylate is oxidized, this would diffuse into the bulk solution and undergo the mixed Kolbe-electrolysis in the usual, statistical way (Table 2, expt. 6). In principle the non-statistical coupling of carboxylates by square pulse electrolysis of unsymmetrical diacyl peroxides is possible, however, it appears difficult, to find suitable reaction conditions for preparative conversions. We therefore turned our attention towards the thermal and photochemical decomposition of the diacyl peroxides.

Table 2: Dimer distribution in the electrolysis of **1i**[a)] with pulsed direct current.

Expt.	Pulse frequency (cps)	Yield [b)] (%) of mixed dimer Octadecane (**4**)	symmetrical dimers Tetradecane (**5**)	Docosane (**6**)
1	5.0	8	5	4
2	1.0	12	8	6
3	0.2	17	10	8
4	0.5[c)]	4	2	0.5
5	0.2[c)]	4	2	1
6	0.2[d)]	20	13	11

a) 4 mmol **1i** and 0.2 mmol sodium octanoate, 0.2 mmol octanoic acid in 20 ml methanol; $\bar{i}$ = 200 mA/cm^2 at platinum electrodes. - b) Current yield, determined by GLC. - c) Stopped after consumption of **1i**. - d) Coelectrolysis of octanoic and dodecanoic acid (1 : 1, w/w).

Thermolysis of diacyl peroxides: Thermolysis of diacyl peroxides in solution has been studied in detail[7a)]. In some cases diacyl peroxides with primary alkyl groups afford good dimer yields[12a)]; with secondary or tertiary alkyl groups besides radical products polar compounds are formed in an ionic pathway[12b)]. Little has been reported concerning thermal decompositions[13)]. At 90 - 110° C neat **1i** or **1j** decompose smoothly within one hour; at 110 to 120° C decomposition occurs explosive. Heating **1i** without solvent for 1 h at 90° C produces 29 % unsymmetrical dimer, 1 % symmetrical dimers, 32 % disproportionation products and 12 % ester (Table 3). **1j** reacts similar (Table 4), but the portion of disproportionation products is even larger: 50 % at 110° C. The dimer ratio $R\text{-}R : R\text{-}C_{11}H_{23} : C_{22}H_{46}$ = 1:30:1 at controlled thermal decomposition indicates a marked cage effect, that also has been found in the thermolysis of other diacyl peroxides[14,15)]. Apparently the concentration of alkyl radicals is fairly small below the explosion temperature, which favours their preferential cage recombination. Even if **1i**, **j** are decomposed explosively, the dimer ratio 1:5:1 is still nonstatistical. In the controlled thermal decomposition the unsymmetrical dimers are formed selectively, however, their yields do not exceed 27 to 29 % due to a competing disproportionation. It was hoped, to reduce this unwanted side reaction by photolytic decomposition at lower temperatures.

Table 3: Thermal decomposition of dodecanoyl octanoyl peroxide (**1i**)

Decomposition products[a,b]	Yield (%) at decomposition temperature 90° C	110°	explosive dec.[c]
Disproportionation and polar products			
1-Heptene (**7**) and n-Heptane (**8**)[d]	9	12	13
1-Heptanal (**9**)[e]	4	4	-
1-Heptanol (**10**)[e]	5	4	-
1-Undecene (**11**) and 1-Undecane (**12**)[d]	23	23	20
1-Undecanal (**13**)[e]	3	3	-
1-Undecanol (**14**)[e]	4	4	-
Undecyl octanoate (**15**)[e] and Heptyl dodecanoate (**16**)[e]	12	10	6
Coupling products			
Branched Tetradecanes	-	-	1
n-Tetradecane (**5**)	0.5	1	7
Branched Octadecanes[e,f]	-	-	3
n-Octadecane (**4**)	29	27	34
Branched Docosanes[e,f]	-	-	1
n-Docosane (**6**)	0.5	1	7

a) Yield determined by GLC; b) In sections ordered according to raising GLC-retention times; c) Explosion temperature: 115° C; d) Combined yields due to incomplete separation by GLC; e) Yield determined by GLC without calibration; f) Exact structure not determined.-

Photolysis of the diacyl peroxides in solution: Photolysis offers the possibility to decompose diacyl peroxides at low temperatures[16]. Saturated solutions (0.01 to 0.5 M) of **1i** (λ_{max} = 210 nm, ε = 400, λ = 254 nm, ε = 60) were photolysed in different solvents at the lowest possible temperature (Table 5). The products were the same as those in the thermolysis: 26-31 % octadecane[17] and 34-43 % disproportionation products were formed, the esters decreased to 1 %, but the amount of symmetrical dimers increased to 7-11 %, indicating a smaller cage effect. It was hoped however, that photolysis of the solid diacyl peroxides at low temperatures would increase the selectivity of the dimerization due to the restricted mobility of the radicals.

Table 4: Thermal decomposition of decanoyl dodecanoyl peroxide (**1j**)

Decomposition products$^{a,b)}$	Yield (%) at decomposition temperature	
	110°	explosive dec.$^{c)}$
Disproportionation and polar products		
1-Nonene (**17**) and n-Nonane (**18**)$^{d)}$	23	12
1-Nonanol (**19**)$^{e)}$	2	-
1-Undecene (**11**) and n-Undecane (**12**)$^{d)}$	27	15
1-Undecanal (**13**)$^{e)}$	2	-
1-Undecanol (**14**)$^{e)}$	2	-
Nonyl dodecanoate (**21**)$^{e)}$ and Undecyl decanoate (**22**)$^{e)}$	9	5
Coupling products		
Branched Octadecanes$^{e,f)}$	-	1
n-Octadecane (**4**)	1	8
Branched Eicosanes$^{e,f)}$	-	4
n-Eicosane (**20**)	27	38
Branched Docosane$^{e,f)}$	-	1
n-Docosane (**6**)	1	8

a) Yield determined by GLC; b) In sections ordered according to raising GLC-retention times; c) Explosion temperature: 115°C; d) Combined yield due to incomplete separation in GLC; e) Yield determined by GLC without calibration; f) Exact structure not determined.

Table 5. Photolysis of dodecanoyl octanoyl peroxide (**1i**) in different solvents

Products$^{a,b)}$	Yield (%) for different solvents and temperatures Methanol 20°C	 Benzene 5°C	 Pentane -10°C
Disproportionation and polar products			
1-Heptene (**7**) and n-Heptane (**8**)$^{c)}$	19	18	16
1-Heptanal (**9**)$^{d)}$	2	6	7
1-Heptanol (**10**)$^{d)}$	3	2	2
1-Undecene (**11**) and n-Undecane (**12**)$^{c)}$	24	20	18
1-Undecanal (**13**)$^{d)}$	3	3	6
1-Undecanol (**14**)$^{d)}$	3	3	3
Heptyl dodecanoate (**16**) and Undecyl octanoate (**15**)$^{c,d)}$	1	2	1
Coupling products			
n-Tetradecane (**5**)	4	6	7
n-Octadecane (**4**)	31	26	30
n-Docosane (**6**)	3	4	4

a) Yield determined by GLC; b) Ordered in sections according to increasing GLC-retention times; c) Combined yields due to incomplete separation; d) Yield determined by GLC but without calibration.

Photolysis of solid diacyl peroxides: Until now only few photolyses of neat diacyl peroxides have been reported. The photolysis of diacetyl peroxide or dibenzoyl peroxide forms ethane or biphenyl in good yields$^{18)}$. Furthermore free radicals have been generated and observed by photolysis of acetyl benzoyl peroxide and symmetrical aliphatic diacyl peroxides in an argon matrix at 4 K$^{16,19)}$.

Neat **1i** has been photolyzed at different temperatures (Table 6). At -78° C octadecane is obtained in 75 % yield. Relatively small amounts of disproportionation products are formed and the formation of symmetrical dimers is almost completely suppressed. The dimer ratios of 1:20:1 at 25° C and 1:100:1 at -78° C clearly indicate the expected strong increase of the cage effect at lower temperatures. A similar pronounced cage effect has been detected in the photolysis of acetyl benzoyl peroxide at -78° C$^{20)}$. The photolyses of the solid diacyl peroxides with unbranched aliphatic alkyl chains **1a**, **1b**, **1c**, **1i**, **1j** at 78° C are summarized in Table 7. The selectivity for the formation of the unsymmetrical dimer is in all cases high; the dimer ratio is in general 1:100:1, in accord with a general strong cage effect. Competing reactions which give rise to disproportionation products, esters and alcohols are satisfactorily suppressed. In **1a** the more reactive methyl radical leads to a higher portion of hydrogen abstraction products. The results demonstrate that by photolysis of neat unsymmetrical diacyl peroxides at -78° C different alkyl radicals can be selectively coupled on a preparative scale.

Table 6: Photolysis of solid dodecanoyl octanoyl peroxide (**1i**)

Products$^{a,b)}$	Yields at different temperatures 25° C	-20° C	-78° C
Disproportionation and polar products			
1-Heptene (**7**) and n-Heptane (**8**)$^{c)}$	15	9	3
1-Heptanol (**9**)$^{d)}$	6	6	3
1-Undecene (**11**) and n-Undecane (**12**)$^{c)}$	18	12	3
1-Undecanol (**14**)$^{d)}$	6	6	3
Undecyl octanoate (**25**)$^{c,d)}$ and Heptyl dodecanoate (**16**)$^{c,d)}$	1	1	1
Coupling products			
n-Tetradecane (**5**)	2	1	0.5
n-Octadecane (**4**)	40	53	75
n-Docosane (**6**)	2	1	0.5

a) Yield determined by GLC; b) In sections ordered according to increasing GLC-retention times; c) Combined yields due to incomplete separation; d) Yield determined by GLC but without calibration.

Table 7: Photolysis of solid diacyl peroxides **1a-c**, **1i,j** at -78° C.

Products$^{a)}$	Yields (%) from **1a**	**1b**	**1c**	**1i**	**1j**
Unsymmetrical dimer	50	65	72	75	75
Symmetrical dimers$^{b)}$	0.5	0.5	1	1	1
Disproportionation products$^{c)}$	14	5	2	6	8
Ester$^{d)}$	6	1	1	1	1
Alcohols$^{d,e)}$	7	3	6	6	6

a) Yield determined by GLC; b) For **1a**, **1b** only **6**; c) For **1a-c** only **11**, **12**; d) Yield by GLC but without calibration; e) For **1a,b** only **14**.

After these encouraging findings the photolysis of diacyl peroxides with cyclic, α- and β-branched alkyl groups was studied (Table 8).

Table 8: Photolysis of neat diacyl peroxides 1d-h and 1k-n at -78° C

Peroxide	Coupling product	Yield (%)[a)]	Undecane (12)[b)]	Ratio: 12/Coupling product
1d	2-Methyltetradecane (17)	72 (76)	3	0.04
1e	2,2-Dimethyltetradecane (18)	60 (63)	2	0.03
1f	2-Methyltridecane (19)	22 (27)	25	1
1g	3-Methyltetradecane (20)	31 (33)	37	1
1h[c)]	3-Ethyltetradecane (21)	14 (20)	22	1
1k	Cyclopropylundecane (22)[d)]	37 (42)	5	0.1
1l	Cyclobutylundecane (23)	41 (50)	15	0.3
1m	Cyclopentylundecane (24)	38 (48)	17	0.3
1n	Cyclohexylundecane (25)	47 (56)	12	0.2

a) Yields in parenthesis determined by GLC; b) GLC-yield; c) Unpurified, crude product; d) Additionally 5 % (11 % by GLC) undecyl cyclopropanecarboxylate (26).

Good yields of coupling products are obtained with the peroxides 1d and 1e which contain β-branched alkyl substituents, those with alicyclic groups 1k-n are medium and those with α-branched alkyl chains 1f-h low. Whilst the portion of ester as side product is with most of the examined peroxides around 1 %, 1k produces 11 % ester 26, which reflects the slower decarboxylation rate of the intermediate cyclopropanecarboxyl radical[21)]. The dimer ratio 1:100:1 corresponds in all cases to this of the unbranched diacyl peroxides.

The decrease in coupling product in 1f-h, compared to 1d,e, is accompanied by a 10-fold increase of the side product undecane 12, which appears to be formed by disproportionation. The ratio of the disproportionation to combination rate constant (k_{dis}/k_{com}) for the solution and gas phase is reported to be 0.15 for primary radicals and 1.0 for secondary ones[17)]. The statistically corrected ratio of k_{dis}/k_{com} for 1d/1g should then be 1x0.15/5x1 = 0.03, which fits well to the experimental value 0.04 (Table 8).

Comparison with the mixed Kolbe-electrolysis: Following the achievement of selective coupling of different alkyl radicals by photolysis, it appeared necessary, to compare these results with those of the corresponding mixed Kolbe-electrolyses (Table 9).

The primary aliphatic and alicyclic radicals, generated by electrolysis, afford only 14 to 31 % of mixed coupling product; this is a two to three times lower yield than this obtained by photolysis. The major loss in the mixed Kolbe-electrolysis is due to the statistical coupling of the radicals, which is reflected by the high portion of docosane in electrolysis contrary to photolysis.

Although in both methods the products are formed from similar radical pairs, the relative extent of disproportionation is different. In the electrolysis the portion of undecane produced from secondary radicals is only 1.5 to 2 times greater than with primary radicals, whilst in the photolysis a 10 to 15-fold increase is observed. Apparently the singly generated Kolbe-radicals tend to disproportionate less than those formed in pairs. Despite the greater amount of disproportionation the photochemical yields of coupling product distinctly exceed the electrochemical ones.

Table 9: Comparison of the product distribution in the mixed Kolbe-electrolysis (K) and the diacyl peroxide photolysis (P)

R^1 in electrolysis$^{a)}$:	Coupling product	Yield (%)$^{b)}$		Docosane (6) yield (%)$^{b)}$		Undecane (12) yield (%)$^{b)}$	
$R^1CO_2^- + C_{11}H_{23}CO_2^-$ photolysis: $R^1CO_2{-}O_2C{-}C_{11}H_{23}$		K	P	K	P	K	P
2-Methylpropyl-	**17**	31	76	19	<1	8	3
2,2-Dimethylpropyl-	**18**	25	63	19	<1	7	2
Isopropyl-	**19**	16	27	21	<1	11	25
sec. Butyl-	**20**	14	33	20	<1	11	37
sec. Amyl	**21**	14	20	20	<1	12	22
Cyclopropyl-	**22**	14	42$^{c)}$	17	<1	9	5
Cyclobutyl-	**23**	21	50	21	<1	13	15
Cyclopentyl-	**24**	16	48	26	<1	13	17
Cyclohexyl-	**25**	16	56	20	<1	12	12

a) 1 eq. $R^1CO_2^-$ and 1 eq. $C_{11}H_{23}CO_2^-$ at 150 to 200 mA/cm^2 in methanol between platinum electrodes; further details, see experimental; b) Yield determined by GLC; Additionally 11 % undecyl cyclopropylcarboxylate (**26**).

Comparison of the photolysis with the Kolbe-electrolysis and other methods of C-C- bond formation: The advantage of the Kolbe-electrolysis is the easy availability of carboxylic acids and their high conversion in short reaction times. The work up of the electrolysis product, however, is more difficult than that of the photolysis product because of the need to separate the symmetrical side products of electrolysis. Moreover Table 9 demonstrates, that the yield of unsymmetrical dimer in the photolysis is distinctly higher than that from the mixed Kolbe-electrolysis. This is still valid, if one considers the additional steps for the preparation of the diacyl peroxides in 70 to 90% overall yield from the carboxylic acids. The same products can also be prepared by the reaction of lithium dialkyl cuprates with alkyl halides[22]. With primary halides 75 to 80 % of coupling product are yielded, similar results are obtained in the photolysis of the corresponding diacyl peroxides. Cycloalkyl halides, however, react often poorly, whereas by photolysis of the appropriate diacyl peroxides the cycloalkylalkanes can be synthesized in 42 to 56 % yield.

EXPERIMENTAL

The structures of products already described in the literature were confirmed by comparing their IR, NMR and mass spectra with the data reported. ^1H-NMR spectra were obtained with the Bruker WM 300 spectrometer, ^{13}C-NMR spectra with a Bruker WH 90 or WM 300 spectrometer. IR-spectra were recorded on the Perkin-Elmer instruments 177, 257, 421; UV-spectra were taken with the Leitz SP 800a spectrometer; mass spectra were obtained with the GC-MS combinations Varian MAT 111 (packed columns) and Varian CH 7A (capillary columns). Melting points were determined with a Kofler hot stage apparatus and are uncorrected; refraction indices were obtained with a Zeiss refractometer. The purity of starting compounds and products was checked by GLC with the Varian instruments 1400 and 3700 with the glass columns: column 1 (4.3 m x 2 mm) 4 % SE 30 on chromosorb W AWDMCS 100/120, column 2 (1.4 m x 2 mm) 4 % SE 30 on chromosorb W AWDMCS 100/120, column 3 (capillary, 25 m x 0.3 mm) 0.3 % SE 30, column 4 (capillary, 25 m x 0.3 mm) 0.25 % Superox 4. For analytical TLC Merck TLC-plates silicagel 60 F_{254} were used. Photolyses were carried out with Gräntzel low-pressure mercury arcs 1 and 5a. - Reduction potentials were obtained with the Bruker polarograph Type E. Electrolyses were carried out in an undivided cell (50 or 100 ml) at platinum electrodes; pulsed current was obtained from a PAR galvanostat 173 and a Wavetek function generator 133; constant DC was supplied from the Heri instrument TN 250 - 1250. - Organic extracts were dried over $MgSO_4$ and the solvent evaporated at reduced pressure.

General procedures

Preparation of the acyl dodecanoyl peroxides **1**: Equimolar amounts of peracid and dry pyridine were dissolved in 100 ml dry ether and cooled to -20° C. Equimolar amounts of the acyl chloride in 100 ml dry ether are added under stirring and the reaction temperature maintained at -10° C to -20° C. After additional stirring for 30 min at 10° C precipitated pyridinium chloride is removed by filtration. Peroxides not stable at room temperatures are obtained by evaporation of the ether at 0° C and the remaining peroxide used directly for photolysis. In case of the more stable peroxides the etheral solution is washed with a $KHCO_3$-solution, dried and the ether evaporated. The peroxide is purified by either filtration over silicagel (petrolether : ether, 10:1) or recrystallization. Active oxygen in the peroxide is determined by titration with sodium iodide in acetic acid-$CHCl_3$ in the presence of a catalytic amount of $FeCl_3$.

Photolysis of the acyl dodecanoyl peroxides

Analytical scale: Compounds **1** (30 to 50 mg) are deposited from an etheral solution as a film at the inner wall of a dry quartz ampoule (NS 14.5, diameter 15 mm). The ampoule is immersed in a methanol-dry ice bath in oblique position and irradiated whilst under rotation. After 12 h the product is dissolved in 2 ml ether, a weighed amount of n-dodecane is added and the yields determined by GLC using detector response factors obtained from the isolated product.

Preparative scale: Compounds **1** (1 to 3 g) are precipitated as a layer at the bottom of a quartz ampoule (NS 29, diameter 40 mm). The ampoule is immersed in a horizontal position in a methanol-dry ice bath and irradiated. Photolysis is continued until the IR absorption for the diacyl peroxide has disappeared (30 - 100 h). The photolysis time can be shortened by thaw-freezing the sample several times during the photolysis. The crude product is purified by column filtration on silica gel with petroleum ether or bulb-to-bulb distillation.

Preparation of the acyl dodecanoyl peroxides

Perdodecanoic acid: To 20 g (0.1 mol) dodecanoic acid dissolved in 50 ml conc.H_2SO_4 p.a. are added under stirring at 10 to 20° C 22.6 g (0.2 mol) 30 % aqueous hydrogen peroxide. When the mixture solidifies additional 30 ml H_2SO_4 are added. After 1 h stirring at 10° C the mixture is poured on 500 ml ice water, the product filtered, then dissolved in 300 ml ether, washed, dried and the ether evaporated. The crude product (18.8 g) is recrystallized from petrolether (35 - 40° C) to give 14.0 g (65 mmol, 65 %) perdodecanoic acid. Most of the unreacted dodecanoic acid can be recovered from the mother liquors. - Mp:. 51 - 52° C. - IR (KBr, disk) 1745, 1100 cm^{-1}. - ^{13}C-NMR ($CDCl_3$): δ = 174.5 (s, C-1), 31.8 (t, C-10), 30.3 (C-2), 29.5 (C-7, 8), 29.2 (C-6, 9), 29.0 (C-5), 28.8 (C-4), 24.6 (t, C-3), 22.6 (t, C-11), 13.9 (q, C-12) ppm. Active oxygen: Calcd.7.4; Found: 7.41.

Acetyl dodecanoyl peroxide (**1a**): 4.54 g (21 mmol) **2**, 1.57 g (20 mmol) acetyl chloride, 1.66 g (21 mmol) pyridine afford 4.4 g (17 mmol, 85 %) **1a**. Mp. (pentane) 37 - 38° C.- IR (CCl_4): 1812, 1785 (C=O), 1045 (C-O-O-C) cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 169.1 (s, C-1'), 166.0 (s, C-1), 31.8 (t, C-10'), 29.9 (C-2'), 29.5 (C-7',8'),29.3 (C-6', 9'), 28.8 (C-4'), 24.7 (t, C-3'), 22.6 (t, C-11'), 16.4 (q, C-2), 14.0 (q, C-12') ppm. Active oxygen: Calcd. 6.19; Found: 6.21.

Butyryl dodecanoyl peroxide (**1b**): 4.54 g (21 mmol) **2**, 2.13 g (20 mmol) butyrylchloride, 1.66 g (21 mmol) pyridine yield 5.2 g (18.0 mmol, 90 %) **1b**. Mp. 15 - 16° C; n_D^{20} 1.4413.- IR (CCl_4): 1806, 1778 (C=O), 1048 cm^{-1} (C-O-O-C).- ^{13}C-NMR ($CDCl_3$): δ = 169.1 (s, C-1'), 168.9 (s, C-1), 31.8, 29.9, 29.5, 29.2, 29.0, 28.8, 24.7, 22.6, 18.4, 14.0 (q, C-12), 13.3 (q, C-4) ppm. - Anal. calcd. for $C_{16}H_{30}O_4$: C, 67.10; H, 10.56. Found: C, 67.31; H, 10.88.

Dodecanoyl hexanoyl peroxide (**1c**): 4.54 g **2**, 2.69 g hexanoylchloride, 1.66 g pyridine afford 5.5 g (17 mmol, 88 %) **1c**. Mp. (methanol : ether, 2 : 1) 24 - 25° C. - IR (CCl_4) 1806, 1778, 1050 cm^{-1}.- ^{13}C-NMR ($CDCl_3$): δ = 169.1 (s, C-1, C-1'); 31.8; 31.0; 29.9; 29.5; 29.2; 29.0; 28.8; 24.7; 24.4; 22.6; 22.1; 14.0 (q, C-12'); 13.6 (q, C-6). - Anal. calcd. for $C_{18}H_{34}O_4$: C, 68.75; H, 10.90. Found: C, 68.72; H,11.06.

Dodecanoyl 3-methylbutyryl peroxide (**1d**): 4.33 g **2**, 1.58 g pyridine and 2.41 g (20 mmol) 3-methylbutyrylchloride yield 5.36 g (89 %) **1d**. n_D^{20}= 1.4397.- IR (film): 1810, 1780, 1055 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 169.0 (s, C-1'), 168.2 (C-1), 38.8 (t, C-2), 31.8 (t, C-10'), 29.8 (C-2'), 29.4 (C-7', 8'), 29.2 (C-6', 9'), 29.0 (C-5'), 28.8 (C-4'), 25.9 (d, C-3), 24.7 (t, C-3'), 22.5 (t, C-11'), 22.1 (q, C-4), 14.0 (q, C-12') ppm. Active oxygen: calcd. 5.33; Found: 5.36. Anal. calcd. for $C_{17}H_{32}O_4$: C, 67.96; H, 10.74. Found: C, 68.11; H, 11.02.

3,3-Dimethylbutyryl dodecanoyl peroxide (**1e**): From 4.33 g **2** 1.58 g pyridine and 2.69 g (20 mmol) 3,3-dimethylbutyryl chloride 5.70 g (18.2 mmol, 91 %) **1e** are obtained. n_D^{20}= 1.4425.- IR (film) 1810, 1780, 1075 cm^{-1}. - ^{13}C-NMR ($CDCl_3$): δ = 169.1 (s, C-1'), 167.4 (s, C-1), 43.7 (t, C-2), 32.8 (t, C-10'), 31.0 (s, C-3), 29.9 (C-2'), 29.5 (C-6', 7'), 29.4 (C-4), 29.3 (C-6', 9'), 29.0 (C-5'), 28.9 (C-4'), 24.7 (t, C-3'), 22.6 (t, C-11'), 14.0 (q, C-12'). Active oxygen: Calcd.: 5.08; Found: 5.00. Anal. calcd for $C_{18}H_{34}O_4$: C, 68.75; H, 10.90. Found: C, 68.87; H, 11.18.

Dodecanoyl 2-methylpropionyl peroxide (**1f**): 4.33 g **2**, 1.58 g pyridine and 2.13 g 2-methylpropionylchloride afford 5.39 g (18.8 mmol, 94 %) **1f**. n_D^{20}: 1.4393.- IR (film): 1810, 1780, 1050 cm^{-1}.-^{13}C-NMR ($CDCl_3$): δ = 172.5 (s, C-1), 169.2 (s, C-1'), 31.8 (t, C-10'), 31.0 (d, C-2), 29.9 (C-2'), 29.6 (C-7', 8'), 29.3 (C-6', 9'), 29.0 (C-5'), 28.8 (C-4'), 24.7 (t, C-3'), 22.6 (t, C-11'), 18.9 (q, C-3), 14.0 (q, C-12') ppm. Active oxygen: Calcd. 5.59; Found: 5.60.- Anal. calcd. for $C_{16}H_{30}O_4$: C, 67.10; H, 10.56. Found C, 67.76; H, 11.32.

Dodecanoyl 2-methylbutyryl peroxide (**1g**): 4.33 g **2**, 1.58 g pyridine and 2.41 g 2-methylbutyrylchloride yield 5.40 g (18.0 mmol, 90 %) **1g**. n_D^{20}: 1.4403.- IR (film): 1810, 1780, 1055 cm^{-1}.^{13}C-NMR ($CDCl_3$): δ = 172.1 (s, C-1), 169.2 (s, C-1'), 37.9 (d, C-2), 31.8 (t, C-10'), 29.9 (C-2'), 29.6 (C-7', 8'), 29.3 (C-6', 9'), 29.0 (C-5'), 28.8 (C-4'), 26.9 (t, C-3), 24.7 (t, C-3'), 22.6 (t, C-11'), 16.8 (q, C-5), 14.0 (q, C-12'), 11.4 (q, C-4) ppm. - . Active oxygen: Calcd. 5.33; Found: 5.24. Anal. calcd. for $C_{17}H_{32}O_4$: C, 67.96; H, 10.74. Found: C, 70.23; H, 11.61 (deviation due to decomposition of **1g** at r.t.).

Dodecanoyl 2-ethylbutyryl peroxide (**1h**): 4.33 g **2**, 1.58 g pyridine and 2.69 g 2-ethylbutyrylchloride react to 5.31 g (16.9 mmol, 85 %) **1h**. Purification of **1h** was not possible due to its decomposition at r.t.

Dodecanoyl octanoyl peroxide (**1i**): From 4.54 g **2**, 1.66 g pyridine and 3.25 g octanoylchloride 6.2 g (18.1 mmol, 91 %) **1i** were obtained.- Mp. (from methanol : ether, 2 : 1) 33 - 34° C.- IR (CCl_4):1806, 1778, 1050 cm^{-1}.- ^{13}C-NMR ($CDCl_3$): δ = 169.1 (s, C-1, C-1, C=O); 31.8, 31.5, 29.9, 29.6, 29.3, 29.0, 28.8, 28.7, 24.8, 22.6, 22.5, 14.0 (q, C-12', C-8) ppm. Anal. calcd.for $C_{20}H_{38}O_4$: C, 70.13; H, 11.18. Found: C, 70.03; H, 11.42.

Decanoyl dodecanoyl peroxide (**1j**): 4.54 g **2**, 1.66 g pyridine and 3.81 g decanoylchloride form 6.8 g (18.4 mmol,. 92 %) **1j**. Mp. (from methanol : ether, 2 : 1) 40-41° C. IR (CCl_4): 1806, 1778, 1050 cm^{-1}. - ^{13}C-NMR ($CDCl_3$): δ = 169.1 (s, C-1, C-1, C=O), 31.8, 30.0, 29.5, 29.3, 29.0, 28.9, 24.8, 22.6, 14.0 (q, C-12', C-10) ppm. - Anal. calcd. for $C_{22}H_{42}O_4$: C, 71.31; H, 11.42. Found: C, 71.27; H, 11.46.

Cyclopropanecarbonyl dodecanoylperoxide (**1k**): From 4.33 g **2**, 1.58 g pyridine and 2.09 g cyclopropanecarbonylchloride 4.96 g (17.3 mmol, 87 %) **1k** are obtained. Mp. 28 - 29° C. IR (film): 1805, 1765, 1080 cm^{-1}.- ^{13}C-NMR ($CDCl_3$): δ = 170.7 (s, C-1), 169.2 (s, C-1'), 31.8 (t, C-10'), 29.9 (C-2'), 29.5 (C-7', 8'), 29.3 (C-6', 9'), 29.0 (C-5'), 28.8 (C-4'), 24.7 (t, C-3'), 22.6 (t, C-11'), 14.0 (q, C-12'), 9.3 (d, C-2), 9.2 (t, C-3) ppm. - Active oxygen: Calcd. 5.63. Found: 5.65. - Anal.calcd. for $C_{16}H_{28}O_4$: C, 67.57; H, 9.92. Found: C, 67.89; H, 10.20.

Cyclobutanecarbonyl dodecanoyl peroxide (**1l**): 4.33 g **2**, 1.58 g pyridine and 2.37 g cyclobutanecarbonylchloride yield 5.73 g (19.2mmol, 96 %) **1l**. n_D^{20}: 1.4542. - IR (film): 1810, 1780, 1080 cm^{-1}.- ^{13}C-NMR ($CDCl_3$): δ = 170.8

(s, C-1), 169.2 (s, C-1'), 34.0 (d, C-2), 31.8 (t, C-10'), 29.9 (C-2'), 29.5 (C-7', 8'), 29.2 (C-6', 9'), 29.0 (C-5'), 28.8 (C-4'), 25.3 (t, C-3), 24.7 (t, C-3'), 22.6 (t, C-11'), 18.8 (t, C-4), 14.0 (q, C-12') ppm. - Active oxygen: calcd. 5.36. Found: 5.33. Anal.calcd. for $C_{17}H_{30}O_4$: C, 68.42; H, 10.13. Found: C, 68.57; H, 10.29; C, 68.42; H, 10.13. Found: C, 68.57; H, 10.29.

Cyclopentanecarbonyl dodecanoyl peroxide (**1m**): 4.33 g **2**, 1.58 g pyridine and 2.65 g cyclopentanecarbonylchloride form 5.91 g (18.9 mmol, 95 %) **1m**. n_D^{20}: 1.4563.- IR (Film): 1810, 1780, 1055 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 172.3 (s, C-1), 169.2 (s, C-1'), 39.6 (d, C-2), 31.8 (t, C-10'), 30.1 (C-3), 29.9 (C-2'), 29.4 (C-7', 8'), 29.2 (C-6', 9'), 29.0 (C-5'), 28.8 (C-4'), 25.7 (t, C-4), 24.7 (t, C-3'), 22.5 (t, C-11'), 14.0 (q, C-12').- Active oxygen: calcd. 5.12. Found: 5.13. Anal. Calcd. for $C_{18}H_{32}O_4$: C, 69.19; H, 10.32. Found: C, 69.42; H, 10.62.

Cyclohexanecarbonyl dodecanoyl peroxide (**1n**): 4.33 g **2**, 1.58 g pyridine and 2.93 g cyclohexanecarbonylchloride yield 5.87 g (18.0 mmol, 90 %) **1n**. n_D^{20}: 1.4601.- IR (film): 1810, 1780, 1070 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 171.4 (s, C-1), 169.3 (s, C-1'), 40.0 (d, C-2), 31.9 (t, C-10'), 30.0 (C-2'), 29.5 (C-7', 8'), 29.3 (C-6', 9'), 29.0 (C-3,4', 5'), 25.4 (C-5), 25.1 (C-4), 24.8 (C-3'), 22.7 (t, C-11'), 14.0 (q, C-12'). - Active oxygen: calcd. 4.90. Found: 4.94. Anal.calcd. for $C_{19}H_{34}O_4$: C, 69.90; H, 10.50. Found: C, 69.73; H, 10.45.

KOLBE ELECTROLYSIS OF DIACYL PEROXIDES AND CARBOXYLIC ACIDS WITH PULSED DIRECT CURRENT

Decanoic acid: 1.72 g (10 mmol) decanoic acid dissolved in 50 ml methanol, neutralized with 5 ml of 0.1 m sodium hydroxide in methanol are electrolyzed at platinum electrodes (1 cm^2), 20-30° C, different pulse frequencies, a current density of 200 mA/cm^2. After the electrolysis 170 mg (1 mmol) dodecane and 200 ml water are added, then extracted with 3x50 ml ether, the ether extract is washed with aqueous KOH and water and dried ($MgSO_4$). The yield of octadecane (**4**) was determined by GLC (standard: dodecane, column 1). MS as in lit.[23], p. 204.

Coelectrolysis of octanoic acid and dodecanoic acid:
0.72 g (5 mmol) octanoic acid and 1.0 g (5 mmol) dodecanoic acid were electrolyzed as above; yields (table 2, Nr.6). MS of tetradecane (**5**) and docosane (**6**) as in lit.[23], p. 162 and p. 231.

Electrolysis of dodecanoyl octanoyl peroxide (**1i**):
1.37 g (4 mmol) **1i**, 58 mg (0.4 mmol) octanoic acid and 2 ml 0.1 n sodium hydroxide are dissolved in 20 ml methanol and electrolyzed as above: 15-30° C, current density: 200 mA/cm^2. Unreacted **1i** was destroyed by reflux for 0.5 h with potassium hydroxide. Yields were determined by GLC and dodecane as standard as above (table 2).

THERMOLYSIS OF DIACYL PEROXIDES

Standard procedure: Measured amounts of 30-50 mg diacyl peroxide are heated under nitrogen in a dry test tube in an oil bath. At temperatures above 115° C the reaction is spontaneous, at lower temperatures 0.5 - 1 h are needed for the complete decomposition. The products are condensed by cooling the test tube to

-78° C and determined by GLC (standard: dodecane, column 1).

Dodecanoyl octanoyl peroxide (**1i**): Yields (table 3); the MS of the product were identical with those in the lit.: 1-heptene (**7**) lit.$^{23)}$ p. 33, heptane (**8**) lit.$^{23)}$ p. 36, 1-heptanal (**9**) lit.$^{23)}$, p. 53, 1-heptanol (**10**) lit.$^{23)}$, p. 56, 1-undecene (**11**) lit.$^{23)}$, p. 111, 1-undecane (**12**) lit.$^{23)}$, p. 131, 1-undecanol (**14**) lit.$^{23)}$, p. 131. Undecyl octanoate (**15**) and heptyl dodecanoate (**16**): MS (70 eV): m/e = 298 (2%), 201 (19%), 200 (6%), 191 (2%), 183 (10%), 171 (3%),, 157 (4%), 154 (8%), 145 (32%), 127 (13%), 111 (12%), 98 (40%). Hydrolysis of (**15**) and (**16**) yields (**10**) and (**14**).

Decanoyl dodecanoyl peroxide (**1j**): Yields (Table 4). The MS of the products were identical with those in the lit.: 1-nonene (**17**) lit. $^{23)}$, p. 69, nonane (**18**) lit. $^{23)}$ p. 72, 1-nonanol (**19**) lit. $^{23)}$ p. 96, n-eicosane (**20**) lit. $^{23)}$ p. 219. Nonyl dodecanoate (**21**) and undecyl decanoate (**22**): MS (70 eV): m/e = 326 (1%), 201 (33%), 200 (8%), 183 (12%), 173 (46%), 157 (6%), 155 (19%), 154 (20%), 143 (7%), 129 (17%), 126 (38%), 111 (22%), 98 (37%). Hydrolysis of **21** and **22** yields **14** and **19**.

PHOTOLYSES

Dodecanoyl octanoyl peroxide (1i) in solution: 50 - 100 mg **1i** being accurately weighed and dissolved in 5 - 10 ml solvent (methanol, benzene, pentane) are irradiated in a quartz tube with a low pressure mercury arc. After irradiation dodecane is added as standard and the yields determined by GLC.

Photolysis of neat acyl dodecanoyl peroxides at -78° C: Yields see tables 6, 7, 8; product data not mentioned here, see: Electrolysis and thermolysis of diacyl peroxides.

Acetyl dodecanoyl peroxide (**1a**): Undecyl acetate: MS (70 eV): m/e = 154 (4 %), 126 (13), 111 (15), 98 (20), 43 (100). Methyl dodecanoate: MS (70 eV): m/e = 214 (2 %, M^+), 185 (2), 183 (4), 171 (6), 143 (11), 129 (8), 115 (4), 101 (5), 74 (100).

Butyryl dodecanoyl peroxide (**1b**): Propyl dodecanoate and undecyl butyrate: MS (70 eV): m/e = 242 (2 %, M^+), 201 (20), 200 (4), 183 (19), 171 (9), 157 (9), 154 (11), 129 (10), 126 (13), 125 (11), 115 (18), 111 (19), 102 (20).

Dodecanoyl hexanoyl peroxide (**1c**): 1-Pentanol: MS as in lit.^{23} p.24; n-decane: MS as in lit$^{23)}$ p. 93; n-hexadecane: MS as in lit.$^{23)}$ p. 186. Pentyl dodecanoate and undecyl hexanoate: MS (70 eV):m/e = 270 (2 %, M^+), 201 (19), 200 (5), 183 (13), 171 (3), 157 (7), 154 (6), 143 (5), 129 (8), 126 (8), 117 (34), 116 (5), 115 (11), 111 (11).

Dodecanoyl 3-methylbutyryl peroxide (**1d**): Analytical: GLC (column 1, 50-280°, 10°min). Preparative: 3 g (10 mmol) **1d** are irradiated for 70 hrs to yield 1.52 g (7.2 mmol) **17**. 2-Methyltetradecane (**17**): n_D^{20}= 1.4307 (lit.$^{24)}$) 1.4306).- ^{1}H-NMR ($CDCl_3$): δ = 1.53 (m, 1H), 1.26 (m, 20 H), 1.16 (m, 2H), 0.88 (t, 3H), 0.86 (d, 6H).- MS (70eV): m/e = 212 (M^+, 2 %), 197 (5), 169 (12) as in lit.$^{25)}$).

3,3-Dimethylbutyryl dodecanoyl peroxide (1e): Analytical:GLC (column 1, 50-280° C, 10°/min). Preparative: 3.15 g (10 mmol) 1e are irradiated for 70 hrs to afford 1.35 g (6.0 mmol) 18. 2,2-Dimethyltetradecane (18): n_D^{20}= 1.4323.- ^{1}H-NMR (CDCl$_3$): δ = 1.26 (m, 20 H), 0.88 (t, 3H), 0.86 (s, 9H).- MS (70 eV): m/e = 226 (M$^+$, 0.1 %), 211 (6), 168 (9), 155 (1), 127 (1), 113 (2). Anal. calc. for C$_{16}$H$_{34}$ (226.5): C, 84.87; H, 15.13. Found: C, 84.61; H, 15.40.

Dodecanoyl 2-methylpropionyl peroxide (1f): Analytical: GLC (column 1, 50-280° VC, 10°/min). Preparative: 2.86 g (10 mmol) 1f are irradiated for 70 hrs to 0.88 g (4.4 mmol) 19. 2-Methyltridecane (19): n_D^{20}: 1.4278 (lit.^{24} 1.4280). ^{1}H-NMR (CDCl$_3$): δ = 1.53 (m, 1H), 1.26 (m, 18H), 1.17 (m, 2H), 0.88 (t, 3H), 0.86 (d, 6H).- MS (70 eV): m/e: 198 (M$^+$, 1 %), 183 (4), 155 (11), 154 (7), 141 (2) as in lit.$^{25)}$).

Dodecanoyl 2-methylbutyryl peroxide (1g): Analytical: GLC (column 1, 50-280° C, 10° C/min). Preparative: 3.0 g (10 mmol) 1g are irradiated for 70 hrs to 0.66 g (3.1 mmol) 20. 3-Methyltetradecane (20): n_D^{20} = 1.4329 (lit.$^{24)}$ 1.4329). ^{1}H-NMR (CDCl$_3$): δ = 1.26 (m, 23H), 0.88 (t, 3H), 0.85 (d, 3H), 0.83 (t, 3H), MS (70 eV):m/e = 212 (0.5 %, M$^{+)}$, 197 (0.5), 183 (10), 182 (6), 169 (0.5), 155 (2), 154 (2).

Dodecanoyl 2-ethylbutyryl peroxide (1h): Analytical: GLC (column 1, 50-28° C, 10° C/min). Preparative: 3.15 g (10 mmol) 1h are irradiated 100 hrs to 0.32 g (1.4 mmol) 21. 3-Ethyltetradecane (21): n_D^{20}= 1.4365 (lit.$^{26)}$, 1.4366. ^{1}H-NMR (CDCl$_3$): δ = 1.26 (m, 23H), 1.12 (m, 2H), 0.88 (t, 3H), 0.85 (t, 6H).- MS (70 eV):m/e = 226 (0.1 %, M$^+$), 197 (15), 196 (10), 183 (1), 169 (1), 155 (3), 141 (7).

Cyclopropanecarbonyl dodecanoyl peroxide (1k): Analytical: GLC (column 1, 50-280° C, 10° C/min). Preparative: 2.84 g (10 mmol) 1k are irradiated for 100 hrs to afford after chromatography on silica gel (petrolether: ether, 20:1, v/v) 0.72 g (3.7 mmol) 22 and 0.12 g (0.5 mmol) 26. Cyclopropylundecane (22): n_D^{20}= 1.4384. IR (film): 3070, 2995 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ= 1.26 (m, 18H), 1.17 (m, 2H), 0.88 (t, 3H), 0.64 (m, 1H), 0.38 (m, 2H), -0.02 (m, 2H). MS (70 eV): m/e = 196 (0.5 %, M$^+$), 168 (3), 154 (1), 140 (3), 126 (7), 125 (8), 112 (12), 111 (19). Anal. calc. for C$_{14}$H$_{28}$ (196.4): C, 85.63; H, 14.37. Found: C, 85.58; H, 14.56. - Undecyl cyclopropanecarboxylate (26): n_D^{20} = 1.4538. IR (film): 3010, 1725 (C=O) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ = 4.06 (t, 2H), 1.61 (m, 3H), 1.26 (m, 16H), 0.97 (m, 2H), 0.88 (t, 3H), 0.85 (m, 2H). MS (70 eV):m/e = 240 (M$^+$, 0.1 %) 154 (6). 126 (7), 112 (5), 111 (9). Anal. calcd. for C$_{15}$H$_{18}$O$_2$: C 74.95; H, 11.74. Found: C, 75.08; H, 11.79.

Cyclobutanecarbonyl dodecanoyl peroxide (1l): Analytical: GLC (column 1, 50-280° C, 10° C/min). Preparative:2.98 g (10 mmol) 1l were irradiated for 70 hrs. to yield 0.86 g (4.1 mmol) 23. Cyclobutylundecane (23): n_D^{20}= 1.4446. ^{1}H-NMR (CDCl$_3$): δ = 2.24 (m, 1H), 2.02 (m, 2H), 1.81 (m, 2H), 1.57 (m, 2H), 1.36 (m, 2H), 1.26 (m, 18H), 0.88 (t, 3H). MS (70 eV):m/e = 210 (M$^+$, 0.5 %), 182 (4), 154 (3), 140 (4), 139 (4), 126 (8), 125 (13), 111 (38). Anal. calcd. for C$_{15}$H$_{30}$ (210.4): C, 85.63; H, 14.37. Found: C, 85.90; H 14.67.

Cyclopentane carbonyl dodecanoyl peroxide (**1m**): Analytical: GLC (column 1, 50-280° C, 10° C/min). Preparative: 3.12 g (10 mmol) **1m** were photolyzed for 70 hrs to 0.85 g (3.8 mmol) (**24**). Cyclopentylundecane (**24**): n_D^{20} = 1.4501 (lit.$^{27)}$), 1.4503).- ^{1}H-NMR ($CDCl_3$): δ = 1.74 (m, 3H), 1.57 (m, 2H), 1.49 (m, 2H), 1.26 (m, 20H), 1.06 (m, 2H), 0.88 (t, 3H).- MS (70 eV): *m/e* = 224 (M^+, 9 %), 196 (3), 168 (2), 154 (3), 139 (6), 125 (12), 111 (26).

Cyclohexanecarbonyl dodecanoyl peroxide (**1n**): Analytical: GLC (column 1, 50-280° C, 10° C/min). Preparative: 3.27 g (10 mmol) **1n** are irradiated for 70 hrs to yield 1.12 g (4.7 mmol) **25**. Cyclohexylundecane (**25**): n_D^{20}= 1.4548 (lit.^{27} 1.4547). ^{1}H-NMR ($CDCl_3$): δ = 1.71 (m, 2H), 1.67 (m, 3H), 1.26 (m, 21H), 1.18 (m, 3H), 0.88 (t, 3H), 0.84 (m, 2H).- MS (70 eV): *m/e* = 238 (8 %, M^+), 154 (5), 139 (1), 125 (4), 111 (8).

MIXED KOLBE-ELECTROLYSIS

Standard procedure: In a 100 ml undivided, double walled electrolysis cell 5 mmol of the corresponding carboxylic acid and 1.00 g (5 mmol) dodecanoic acid are dissolved in 50 ml methanol, and are neutralized to 5 % with sodium hydroxide. This solution is electrolized between two platinum electrodes (1 cm^2/sheet) with stirring and cooling (-20° C in cooling jacket) at 150-200 mA/cm^2 current density and 100-200 V cell voltage until the electrolyte reached pH 9, generally after 3F/mole. For work up 100 ml water and a weighed amount of dodecane was added, extracted with pentane (2 x 50 ml), the extract dried ($MgSO_4$) and the yields determined by GLC.

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