Tetrahedron Vol. 41, No. 19, pp. 4213 to 4235, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00
Pergamon Press Ltd.

SELECTIVE MIXED COUPLING OF CARBOXYLIC ACIDS (II). - PHOTOLYSIS OF UNSYMMETRICAL DIACYLPEROXIDES WITH ALKENYL-, HALO-, KETO-, CARBOXYL-GROUPS AND A CHIRAL α-CARBON. COMPARISON WITH THE MIXED KOLBE ELECTROLYSIS.

Michael Feldhues and HANS J. SCHÄFER*
Department of Organic Chemistry, University of Münster
Orleansring 23, 4400 Münster, FRG

(*Received in Germany* 9 *May* 1985)

Abstract. - Alkenoyl and functionalized alkanoyl dodecanoyl peroxides are prepared in 70 to 97 % yield and photolyzed at -78° C. Thereby 4- to 10-alkenoyl and 4-alkynoyl peroxides afford good yields (56 - 68 %) of unsymmetrical coupling products. Similarly α- to δ-haloalkanoyl, cholanoyl or 3- and 4-carboxyalkanoyl peroxides can be coupled (40 - 70 %). The α-chiral diacyl peroxide $\underline{\underline{1s}}$ undergoes the photochemical coupling reaction with 80 % retention of its configuration. The photolysis of diacyl peroxides at -78° C proves to be a favorable supplement of the Kolbe-electrolysis in cases, where the electrolysis fails or produces low yields.

Acyclic alkanes can be easily constructed by photochemical decarboxylation of unsymmetrical diacyl peroxides in the solid state$^{1)}$. This C-C bond-forming reaction supplements the mixed Kolbe-electrolysis$^{2)}$, which, although being in general an efficient synthetic method, fails in some cases. For instance, α-halocarboxylic acids afford poor dimer yields$^{3)}$, with 4-alkenoic acids double bond isomerization$^{4)}$ and with 6-alkenoic acids intramolecular double bond-addition$^{4,5)}$ occurs, with 3-alkenoic acids the coupling is not regioselective$^{6)}$, and in carboxylic acids with a chiral α-carbon the optical activity is totally lost$^{7)}$.We wanted to check wether in these cases the photolysis of diacyl peroxides offered advantages in comparison with the mixed Kolbe-electrolysis. For that purpose we photolysed alkanoyl peroxides with double bonds and functional groups at different distances from the carboxyl group and furthermore a diacyl peroxide with a chiral α-carbon.

RESULTS

Preparation of alkenoyl and functionalized alkanoyl dodecanoyl peroxides 1. The peroxides **1** were prepared either from the acyl chlorides and peroxydodecanoic acid (**2**)[1], or by condensation of **2** and the appropriate carboxylic acid with dicyclohexylcarbodiimide[8].

Table 1: Preparation of Alkenoyl and functionalised alkanoyl(R-C=O) dodecanoyl peroxides **1**

R-C=O in **1**	Method of preparation[a]	Yield (%)	Mp. (°C) or n_D^{20}
Alkenoyl groups			
a: 10-Undecenoyl	A	89	29-30
b: 6-Heptenoyl	A	92	1.4515
c: Z-4-Heptenoyl[b]	B	82	1.4525
d: E-3-Hexenoyl[c,d]	A	93	-
e: 4-Pentenoyl	A	94	1.4490
f: 4-Pentynoyl	A	93	42-43
g: E-2-Butenoyl	A	94	39-40
h: Propynoyl[e]	B	80	27-28
i: Benzoyl	B	84	24-25
Functionalised Alkanoyl groups			
j: 5-Bromopentanoyl	B	89	34-35
k: 2-Bromohexanoyl	A	96	1.4629
l: 2-Chlorpropionyl[f]	A	97	1.4487
m: 4-Oxopentanoyl	B	92	37-38
n: 4-Oxopentanoyl ethylene acetal	g)	70	22-23
o: 3α,7α,12α-Tri-acetoxy-5β-cholanoyl	B	82	
p: 3-Carboxypropionyl	A	92	
q: 4-Carboxybutyryl	A	92	
r: 2-Ethoxycarbonyl-2-ethylbutyryl[h]	B	84	
s: 2-Ethoxycarbonyl-2-methylbutyryl	B	86	

a) A: Acid chloride - method, B: DCC-method. - b) Contains 9 % E-isomer. - c) Contains 6 % Z-isomer.- d) Cannot be isolated at room temperature. -
e) Decomposes at the melting point. - f) Partial decomposition, when purified on silica gel. - g) From **1m** with ethylene glycol - h) At rt. thermally labile.-

Photolyses. The neat peroxides 1 were photolysed with a low pressure mercury arc at -78° C and the products were isolated either by filtration over silica gel or by bulb-to-bulb distillation (Tables 2, 3).

Table 2: Photolysis of neat alkenoyl dodecanoyl peroxides 1 at -78° C

Peroxide	Coupling product	Yield(%)	Yield(%)[a] of Undecane (3)	Ratio 3:coupling product
1a	1-Heneicosene (4)	64(68)[b]	3	0.04
1b	1-Heptadecene (5)[c]	48(61)	5	0.08
1c[d]	Z-3-Heptadecene (6)[e]	45(55)	15	0.3
1d[f,g]	E-3-Hexadecene (7)[h,i]	42(45)	14	0.3
1e	1-Pentadecene (8)	56(61)	6	0.1
1f	1-Pentadecine (9)	51(56)	6	0.1
1g	E-2-Tetradecene(10)[j,k]	10[l](25)	12	0.5
1h	Tridecine (11)	0 (0)	5	-
1i	Phenylundecane (12)[m]	15(16)	5	0.3

a) Yield determined by GLC. - b) Numbers in parenthesis, yield by GLC. - c) Additionally 1 % (GLC) cyclopentyldodecane (13). - d) Contains 9 % E-isomer. - e) Contains 13 % E-isomer 6a. - f) Unpurified crude product. - g) Contains 6 % Z-isomer. - h) Contains 7 % Z-isomer 7a. - i) Additionally 4 % (GLC) 3-ethyl-1-tetradecene (14). - j) Contains 30 % Z-isomer (10a). - k) Additionally 1 % (GLC) 1-tetradecene (15). - l) Stopped after 100 hrs. photolysis. - m) Additionally 11 % undecyl benzoate (16).

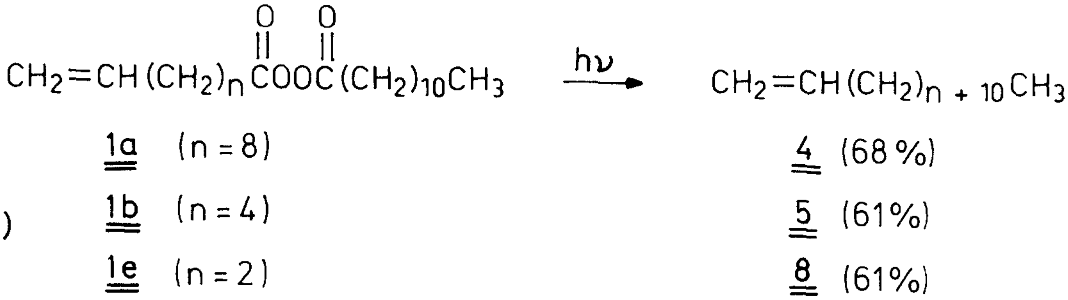
Good yields were obtained with 1a, b, e, f, which afford 4, 5, 8, 9 as products (Scheme 1). The yields are reasonable with 1c, d, which lead to 6, 7, however they were poor with 1g and i; 1h produced polymeric material. 1i forms, besides 16 % phenylundecane (12), 14 % undecyl benzoate (16), which probably arises by coupling of the undecyl radical with the slower decarboxylating benzoyloxy radical[9].

Less than 1 % of symmetrical dimers from 1a-i demonstrate the preferential intramolecular coupling of the intermediate radicals. In the photolysis of 1a-g the portion of undecane (3) increases with decreasing distance of the double bond from the carbonyl groups. This could be due to a increasingly favoured allylic hydrogen abstraction by the undecyl radical.

Table 3: Photolysis of functionalised alkanoyl dodecanoyl peroxides 1

Peroxide	Coupling product	Yield(%)	Yield(%)[a] of Undecane (3)	Ratio 3: Coupling product
1j	1-Bromopentadecane (17)	67(76)[b]	2	0.03
1k	5-Bromohexadecane (18)[c]	40(55)[d]	5[e]	0.2[f]
1l	2-Chlorotridecane (19)	52(61)	18	0.3
1m	2-Pentadecanone (20)[g]	- (50)[h]	5	0.07
1n	2-Pentadecanone ethylene acetal(21)	57[i](67)[i]	5	0.07
1o	24-Decyl-3α,7α,12α-triacetoxy-5β-cholane (22)	74	-	-
1p	Tetradecanoic acid (23)	56(68)[j]	1	0.01
1q	Pentadecanoic acid (24)	59(69)[j]	1	0.01
1r	Ethyl 2,2-diethyl-tridecanoate (25)	30(36)	31	1
1s	(+)-Ethyl 2-ethyl-2-methyl-tridecanoate (26)	18(21)	54	2

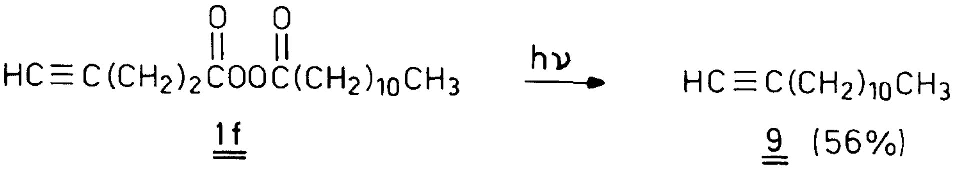
a) Yield determined by GLC. - b) Numbers in parenthesis: GLC-yields. - c) Undergoes photochemical follow-up reaction to isomeric hexadecenes 27 and hexadecane (28). - d) After 12 hrs. 55 % 18, 6 % 27 and 1 % 28. - e) Additionally 5 % 1-bromundecane (29). - f) (3 + 29)/(18 + 27 + 28). - g) Cleaves photochemically to 1-dodecene (30). - h) After 12 hrs. 50 % 20 and 21 % 30. - i) After deprotection. - j) After methylation with diazomethane.

(1)

$$CH_2{=}CH(CH_2)_n\overset{O}{\overset{\|}{C}}O O\overset{O}{\overset{\|}{C}}(CH_2)_{10}CH_3 \xrightarrow{h\nu} CH_2{=}CH(CH_2)_{n+10}CH_3$$

1a (n = 8) → 4 (68 %)

1b (n = 4) → 5 (61 %)

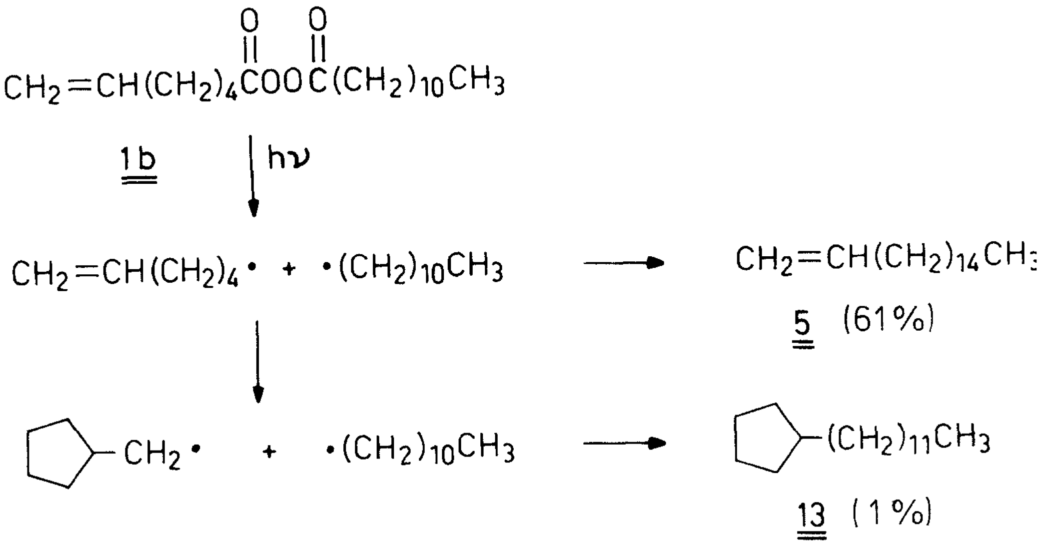
1e (n = 2) → 8 (61 %)


$$HC{\equiv}C(CH_2)_2\overset{O}{\overset{\|}{C}}O O\overset{O}{\overset{\|}{C}}(CH_2)_{10}CH_3 \xrightarrow{h\nu} HC{\equiv}C(CH_2)_{10}CH_3$$

1f → 9 (56 %)

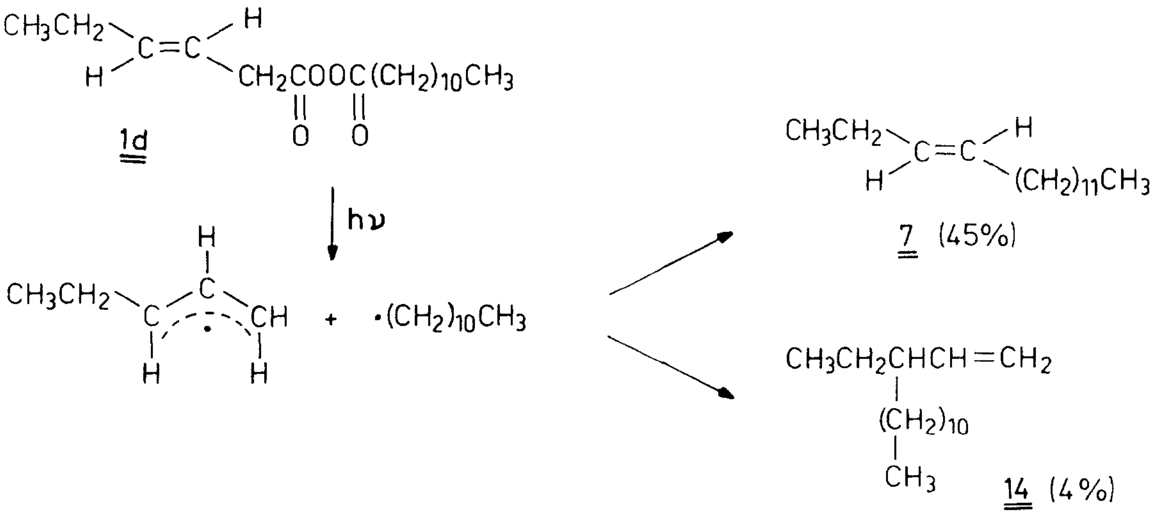
5-Alkenyl radicals can undergo a 5-exo-trig[10] cyclization[11]. The photolysis of 1b generates a 5-hexenyl radical, which couples to 61 % 1-heptadecene (5) and only 1 % cyclopentyldodecane (13) (Scheme 2).

(2)



In the solid state the cyclization is nearly totally suppressed, which indicates the very restricted mobility of the 5-hexenyl radical. This is in accord with the cyclization of the 5-hexenyl radical in solution, where in solvents of low viscosity more than 50% of the radicals cyclize before their combination, whilst in solvents of high viscosity no cyclization occurs[12]).
The photolysis of 1d leads to 45 % E-3-hexadecene (7) and 4 % 3-ethyl-1-tetradecene (14) (Scheme 3).

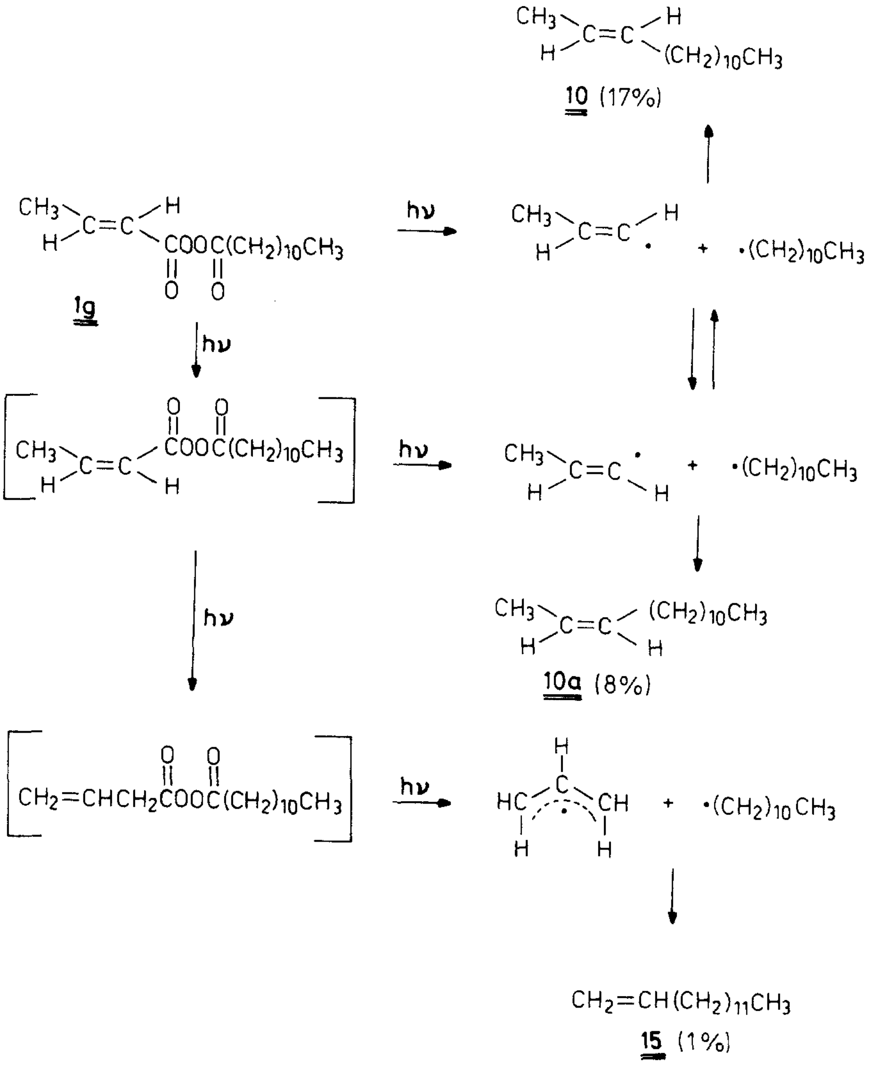
(3)



The intermediate allyl radical, that is formed by decarboxylation of 1d, can

couple in the 1- and 3-position. The low portion of 14 indicates that C-3 of the allyl radical is much less reactive than C-1, which again indicates the restricted mobility of the radical in the solid state. Allyl radicals, that are generated by Kolbe-electrolysis from β,γ-unsaturated carboxylic acids, lead to a three to five times higher portion of C-3 coupling products[6].
The photolysis of 1g produces 17 % E-2-tetradecene (10), 8 % of the Z-isomer 10a and 1 % 1-tetradecene (15) (Scheme 4). The high amount of Z-isomer could be due to the low activation energy for the configurational isomerization of the vinyl radical (8 kJ/mole)[13], but also an E/Z-isomerization before the decomposition of the peroxide is conceivable. Such an isomerization has been discussed for the photolysis of α,β-unsaturated esters and carboxylic acids, where it subsequently leads to a double bond shift into the β,γ-position[14]. Such a double bond transposition is indicated by the formation of 1-tetradecene (15) as side product.

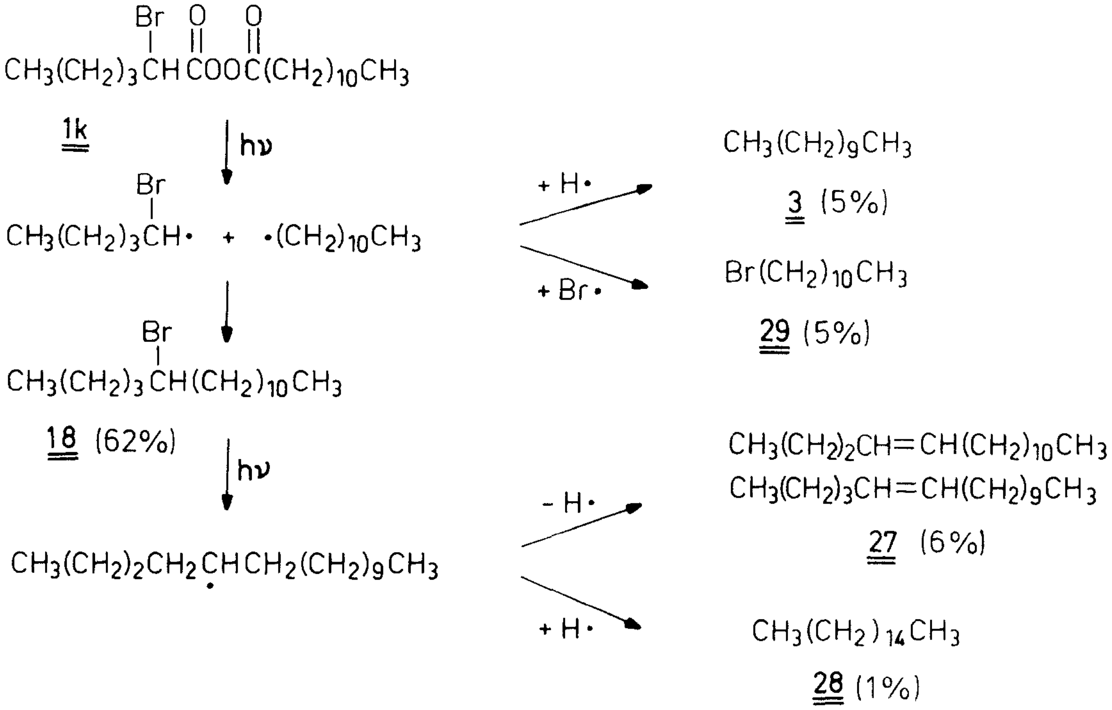
(4)



The products 3-16 are identified by their IR-, NMR-, MS-spectra and elemental analyses. The isomers 6a, 7a, 10a show mass spectra, that are identical to those of 6, 7, 10. They were characterized by configurational isomerization of 6, 7 and 10 with sodium nitrite in dilute HCl[15)] and their comparison by capillary GLC. The position of the double bonds in 6, 7, 10 and 14 was determined by ozonolysis, conversion of the acids into the methyl esters and their mass spectral identification.

A bromo substituent in the δ-position of the peroxide does not influence the coupling yield as can be seen from 1j. Even α-chloro and α-bromo substituents are tolerated, as 1k and 1 indicate. 5-Bromohexadecane (18), the product of 1k, however, undergoes a slow decomposition to hexadecenes 27 and hexadecane (28), when longer irradiated. As secondary bromoalkanes absorb at λ = 254 nm, 18 can be cleaved to the 5-hexadecyl radical, which stabilizes itself by hydrogen transfer to 27 and 28 (Scheme 5)[16)]. Furthermore the photolysis of 1k produces besides undecane (3) 5 % 1-bromoundecane (29) possibly by bromo-transfer from the 1-bromopentyl radical to the undecyl radical. As the homolytic cleavage of the C-Cl bond is more difficult than this of the C-Br bond, the corresponding chloro-transfer is not observed in the photolysis of 1l. However, here the higher portion of undecane indicates here, that the intermediate 1-chloroethyl radical is a good hydrogen donor.

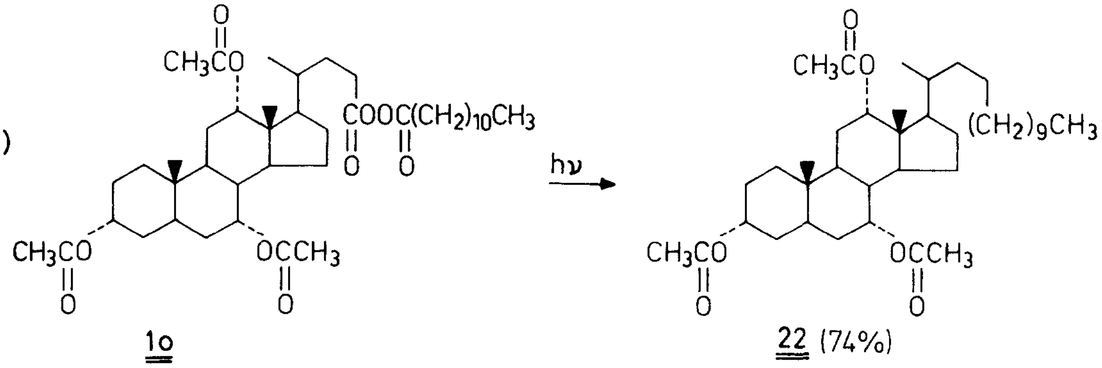
(5)



In the photolysis of ketoalkanoyl peroxides the photoactive keto group leads to a competing side reaction. The irradiation of 1m affords after 12 hrs. 50 % 2-pentadecanone (20) together with 21 % 1-dodecene (30). 30 is most probably formed in a Norrish-type-II reaction from photoexcited 20[17)]. Ketalization of the keto group in 1n excludes the formation of the cleavage products.

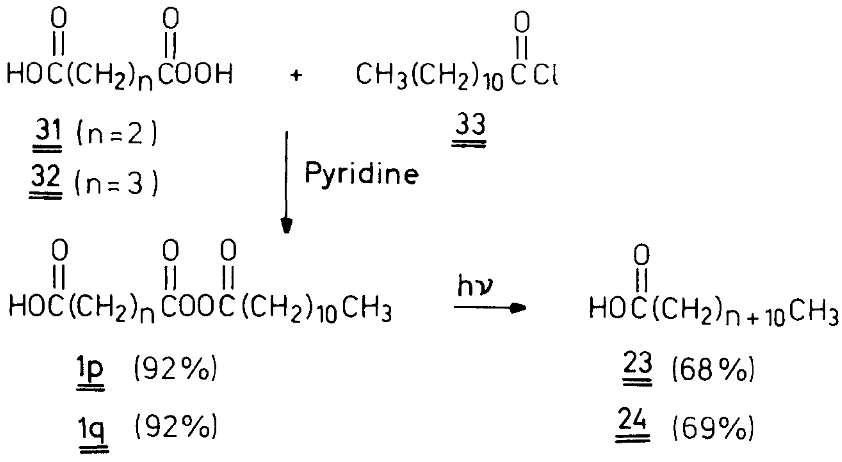
The conversion of 1o to 74 % 22 (Scheme 6) demonstrates that the radical C-C bond-formation can also be applied to the modification of natural products.

(6)



The 3- and 4-carboxyalkanoyl peroxides 1p and 1q afford tetradecanoic (23)and pentadecanoic acid (24). Starting from dodecanoyl chloride (33) and monopersuccinic (31) or monoperglutaric acid (32) overall yields of 63 % are obtained (Scheme 7), which makes this sequence attractive for the two- or three-carbon chain elongation of carboxylic acids.

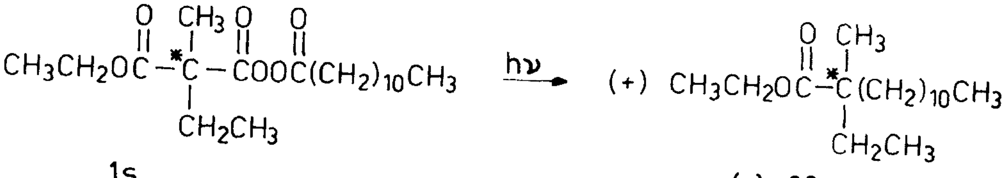
(7)



The peroxides 1r and 1s have a quarternary α-carbon, bearing two alkyl and one ethoxycarbonyl substituent. Steric crowding in the intermediate tertiary radical and an increased number of β-hydrogens lead to low yields of coupling products 25 and 26 and favour the disproportionation to undecane. Products originating from an ionic pathway were not isolated.

α-Chiral peroxide 1s: The relatively stable 1s is a suitable α-chiral diacyl peroxide, that allows to check, how much the radical retains its configuration in the C-C bond-forming reaction. 1s was prepared in 90 % yield by the DCC-method from optically pure (+)-ethyl ethylmethylmalonate[18]. Photolysis of 1s yielded 17 % (+)-26 with 80 % retention of configuration (Scheme 8). The enantiomeric purity of (+)-26 was determined by ^{1}H-NMR with Eu(hfc)$_3$[19].

(8)



1s

(+)-26

(17%, 60% ee)

The high retention found in this photolysis is surprising, as a bond to the chiral carbon is broken, which should lead to its racemization. However, for the racemization the radical additionally has to rotate by 180°, which apparently is strongly hindered in the solid state[20]. Thus the configuration of the chiral carbon is largely retained. The thermal decomposition of an optically active diacyl peroxide with a chiral α-carbon leads to a nearly racemic coupling product[21]. In the Kolbe-electrolysis of carboxylic acids with a chiral α-carbon no optical activity is found in the products[7].

Side products: All diacyl peroxides 1 have the dodecanoyl group in common, which leads to characteristic side products that are found in each photolysis (Table 4).

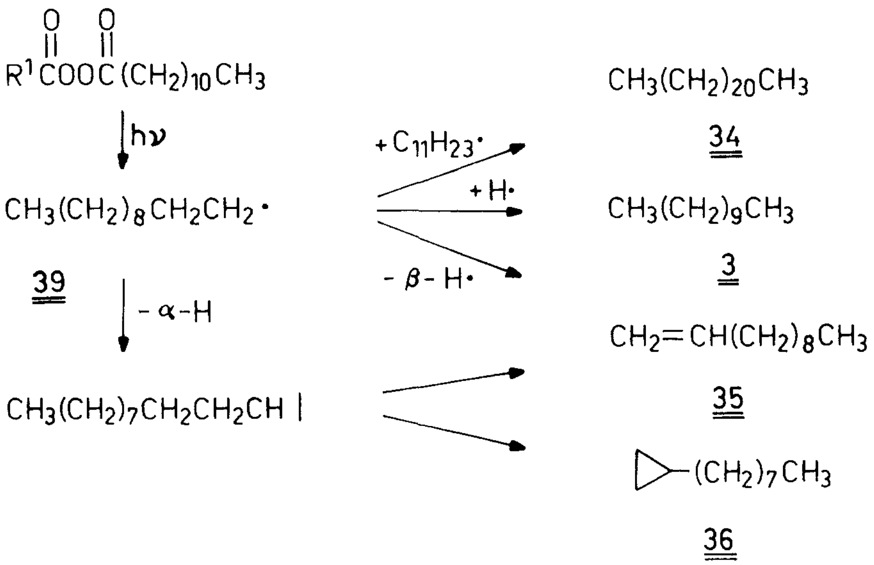
Table 4: Side products in the photolyses from the dodecanoyl group

Product	Yield (%)[a]	Product	Yield (%)
n-Undecane (3)	b)	Cyclopropyloctane (36)	1 - 4
n-Docosane (34)	<1	1-Undecanol (37)	3 - 8
1-Undecene (35)	1 - 9	Dodecanoic acid (38)[c]	1 - 6

a) Yield determined by GLC. - b) See tables 2, 3. - c) As methyl ester.

Undecane (3) is formed by hydrogen abstraction of an undecyl radical (39), docosane (34) by dimerization of 39. 1-Undecene (35) and cyclopropyloctane (36) could arise by disproportionation of 39. Hydrogen abstraction in the β-position 39 leads to 35; abstraction in the sterically better accessible α-position of 39 to a carbene, which could undergo a CH-insertion to 36 (Scheme 9). A similar result is reported for the crystal photolysis of undecanoyl peroxide at 77K[20], which in addition to eicosane yields 20 % n-heptylcyclopropane. 1-Undecanol(37) and dodecanoic acid(38) are possibly formed by an ionic decomposition of the diacyl peroxide.

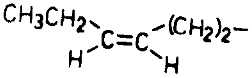
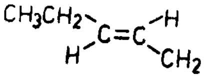
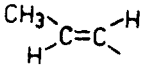
(9)



Comparison of the diacyl peroxide decompositions with the corresponding mixed Kolbe-electrolyses. The yields of the corresponding mixed Kolbe-electrolyses are compared in Table 5 with those of the photolyses of 1.

The mixed Kolbe-electrolyses of unsaturated carboxylates with dodecanoic acid (40) afford similar yields of coupling product as did the saturated carboxylates[1], however the portion of side products is higher.Furthermore marked differences of the product distribution in the Kolbe-electrolysis and in the photolysis demonstrate again the restricted mobility of the radicals in the solid state as compared to this in solution. From the anodically generated 5-hexenyl radicals 22 % cyclize to cyclopentylcarbinyl radicals[5b, 22], whilst only 2% of those generated in the solid state undergo cyclization. Only 4% the Z-3-hexenyl radicals formed in the solid state interconvert to the E-isomer, but 9 % of the anodically formed[4]. The ratio of C1:C3-coupling is 72 : 28 for the E-2-pentenyl radical generated by Kolbe-electrolysis, whilst this for the photogenerated radical is 92 : 8.

Table 5. Yields in the photolysis of **1** and in the corresponding Mixed Kolbe-electrolysis

R^1 in $R^1CO_2H/C_{11}H_{23}CO_2H$ and R^1CO_2-$O_2CC_{11}H_{23}$	Yields (%)[a] Mixed coupling product			Docosane (**34**)		Undecane (**3**)	
		K	P	K	P	K	P
CH_2=$CH(CH_2)_8$-	**4**	28	68	16	<1	8	3
CH_2=$CH(CH_2)_4$-	**5**[b]	25	61	20	<1	10	5
	**6**[c]	19	55	24	<1	7	15
	**7**[d]	15	45	22	<1	8	14
CH_2=$CH(CH_2)_2$-	**8**	25	61	12	<1	9	6
$HC{\equiv}C(CH_2)_2$-	**9**	11	56	25	<1	9	6
	**10**[e]	0	25	-	<1	-	12
$HC{\equiv}C$-	**11**	0	0	-	<1	-	5
Phenyl-	**12**[f]	0	16	-	<1	-	5
$Br(CH_2)_4$-	**17**	15	76	9	<1	4[g]	2
$CH_3(CH_2)_3$-$CHBr$-	**18**	0	55	-	<1	-	5
CH_3CHCl-	**19**	0	61	-	<1	-	18
$CH_3CO(CH_2)_2$-	**21**	19	67[h]	18	<1[h]	8	5[h]
$HO_2C(CH_2)_2$-	**23**[j]	22[i]	68	24[i]	<1	7[i]	1
$HO_2C(CH_2)_3$-	**24**[j]	25[i]	69	21[i]	<1	8[i]	1
$CH_3CH_2O_2CC(CH_2CH_3)_2$-	**25**	21	36	20	<1	16	31
$CH_3CH_2O_2CCCH_3(CH_2CH_3)$-	**26**	17	21	27	<1	18	54

a) Yield determined by GLC; K = Kolbe electrolysis, P = photolysis of **1**.- b) Additionally 7 % (K) or 1 % (P) cyclopentyldodecane (**13**).- c) Increase of E-isomer from 9 % in **1c** to 18 % (K) or 13 % (P) in **6**.- d) Contains 7 % Z-isomer of **7**, additionally 6 % (K) or 4 % (P) 3-ethyl-1-tetradecene (**14**).- e) Contains 30 % (P) Z-isomer of **10** and 1 % (P) 1-tetradecene (**15**).- f) Additionally 14 % (P) undecyl benzoate (**16**).- g) Additionally 6 % 1-bromoundecane (**29**).- h) Ethylene acetal **1n** as educt.- i) Methyl dicarboxylate as educt. - j) Methylester.

The mixed Kolbe-electrolysis of 4-pentynoic acid leads to 11% coupling product **9**, this is less satisfactory than the photolysis in the solid state, which affords 56 % **9**. Halocarboxylates give poor yields in the Kolbe-electrolysis3), e.g. 5-bromopentanoic acid couples with dodecanoic acid to form 15 % 1-bromopentadecane (**17**), with 2-bromohexanoate or 2-chloropropionate no coupling products can be isolated. However, the photolysis of the halo substituted peroxides **1j**-**l** produces good yields of the haloalkanes **17**-**19**.
In the photolysis of ketoacyl peroxides the keto group has to be protected to exclude the Norrish-Type-II cleavage, here the electrolysis has the advantage, that no protection is necessary. On the other hand carboxy substituted peroxides can be used for the synthesis of the alkanoic acids **23** and **24**, whilst for the corresponding preparation by way of the Kolbe-electrolysis the halfesters of the diacids have to be prepared, because the electrolysis of dicarboxylic acids leads to polymeric products[25].

Summarizing one can say, that the photolysis of substituted diacyl peroxides in the solid state is a favorable supplement of the Kolbe-electrolysis, as it leads to successful coupling reactions, where the electrolysis fails or produces low yields.

EXPERIMENTAL

GENERAL.- The structures of products already described in the literature were confirmed by comparing their IR, NMR and mass spectra with the data reported. ^{1}H-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. For the Kolbe-electrolyses an undivided cell of 100 ml content with two platinum electrodes (1 cm^2/sheet) and the HERI instrument TN 250-1250 for constant DC current were used. -

GENERAL PROCEDURES.- Preparation of the acyl dodecanoyl peroxides (**1**):
Method A: Perdodecanoic acid and alkanoyl chloride1).
Method B: Perdodecanoic acid, alkanoic acid and dicyclohexylcarbodiimide (DCC): Equimolar amounts of DCC, peracid and alkanoic acid, each dissolved in 40 ml ether and cooled to -20° C, are mixed and held 12 hrs. at -20° C. Precipitated dicyclohexyl urea is filtered off, 5 ml of the etheral solution are concentrated at 0°C at the rotary evaporator and warmed to room temperature. If the corresponding peroxide is unstable at 20° C, from the remaining etheral solution the ether is evaporated at 0° C, the residual peroxide purified by chroma-

tography on silica gel at 5° C and directly photolysed. The more stable peroxides are purified by chromatography at room temperature. Analytical and preparative photolyses see lit.$^{1)}$.

PREPARATION OF THE ALKENOYL DODECANOYL PEROXIDES

Dodecanoyl 10-undecenoyl peroxide (**1a**): 2.03 g (10 mmol) 10-Undecenoylchloride, 2.16 g (10 mmol) **2** and 0.79 g (10 mmol) pyridine afford 3.40 g (8.9 mmol, 89 %) **1a**. Mp. 29-30° C. - IR (film) 1810, 1780 (C=O), 1640, 995, 910 (C=C), 1060 (C-O-O-C) cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ 169.2 (s, C-1,1'), 138.9 (d, C-10), 114.1 (t, C-11), 33.7 (t, C-9), 31.9 (t, C-10'), 29.9 (C-2,2'), 29.5 (C-6,7', 8'), 29.3 (C-5,6', 9'), 29.0 (C-7,8,5'), 28.8 (C-4,4'), 24.8 (t, C-3,3'), 22.7 (t, C-11'), 14.0 (C-12') ppm. Calcd. active oxygen: 4.18 %; Found: 4.22 %. Anal. calcd. for $C_{23}H_{42}O_4$ (382.6): C, 72.21; H, 11.06. Found: C, 72.32; H, 11.35.

Dodecanoyl 6-heptenoyl peroxide (**1b**): 2.93 g (20 mmol) 6-Heptenoylchloride, 4.33 g (20 mmol) **2** and 1.58 g (20 mmol) pyridine yield 6.00 g (18.4 mmol, 92 %) **1b**. n_D^{20} = 1.4515. IR (film): 1810, 1780 (C=O), 1640, 990, 905 (C=C), 1055 (COOC) cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 169.1 (s, C-1'), 169.0 (s, C-1), 137.9 (d, C-6), 114.9 (t, C-7), 33.1 (t, C-5), 31.8 (t, C-10'), 29.9 (C-2'), 29.8 (C-2), 29.5 (C-7', 8), 29.2 (C-6', 9'), 29.0 (C-5'), 28.8 (C-4'), 27.9 (C-4), 24.7 (C-3'), 24.2 (C-3), 22.6 (t, C-11'), 14.0 (q, C-12') ppm. Calcd. active oxygen: 4.90 %; Found: 4.80 %. Anal. calcd. for $C_{19}H_{34}O_4$ (326.5): C, 69.90; H, 10.50. Found: C, 69.79; H, 10.62.

Dodecanoyl Z-4-heptenoyl peroxide (**1c**): 0.64 g (5.0 mmol) Z-4-Heptenoic acid (9 % E-isomer), 1.08 g (5.0 mmol) **2** and 1.03 g (5.0 mmol)DCC afford after column chromatography (silica gel, petrolether - ether, 10:1) 1.34 g (4.1 mmol, 82 %) **1c**. n_D^{20}: 1.4525. IR (film): 1810, 1780 (C=O), 1650, 720 (C=C), 1070 (COOC) cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 169.0 (s, C-1'), 168.5 (s, C-1), 133.9 (d, C-5), 125.5 (d, C-4), 31.8 (t, C-10'), 30.1 (C-2), 29.8 (C-2'), 29.4 (C-7', 8'), 29.2 (C-6', 9'), 29.0 (C-5'), 28.8 (C-4'), 24.7 (t, C-3'), 22.5 (C-11'), 22.4 (C-3), 20.4 (t, C-6), 14.0 (q, C-7, 12'), ppm. - Calcd. for active oxygen: 4.90 %; Found: 4.83 %. Anal. calcd. for $C_{19}H_{34}O_4$ (326.5): C, 69.90; H, 10.50. Found: C, 70.06; H, 10.61.

Dodecanoyl E-3-hexenoyl peroxide (**1d**): 2.65 g (20 mmol) E-3-Hexenoylchloride (6 % Z-isomer), 4.33 g (20 mmol) **2** and 1.58 g (20 mmol) pyridine lead to 5.81 g (18.6 mmol, 93 %) **1d**; unstable at room temperature.

Dodecanoyl 4-pentenoyl peroxide (**1e**): 1.19 g (10 mmol) 4-Pentenoylchloride, 2.16 g (10 mmol) **2** and 0.79 g (10 mmol) pyridine yield 2.80 g (9.4 mmol, 94 %) **1e**. n_D^{20}: 1.4490. IR (film): 1810, 1780 (C=O), 1640, 995, 915 (C=C), 1065 (COOC) cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 169.0 (s, C-1'), 168.3 (s, C-1), 135.4 (d, C-4), 116.3 (t, C-5), 31.8 (t, C-10'), 29.8 (C-2'), 29.4 (C-7', 8'), 29.2 (C-2,6',9'), 29.0 (C-5'), 28.8 (C-4'), 28.5 (C-3), 24.7 (t, C-3), 22.5 (t, C-11'), 13.9 (q, C-14') ppm. Calcd. for active oxygen: 5.36 %. Found: 5.43 %. Anal. calcd. for $C_{17}H_{30}O_4$ (298.3): C, 68.42; H, 10.13. Found: C, 68.59; H, 10.32.

Dodecanoyl 4-pentynoyl peroxide (**1f**): 2.33 g (20 mmol) 4-Pentynoylchloride, 4.33 g (20 mmol) **2** and 1.58 g pyridine lead to 5.47 g (18.5 mmol, 93 %) 1f. Mp. 42 - 43° C. IR (film): 2110 (C≡C), 1810, 1780 (C=O), 1090 (COOC) cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 169.0 (s, C-1'), 167.4 (s, C-1), 81.0 (s, C-4), 69.9 (d, C-5), 31.8 (t, C-10'), 29.8 (C-2'), 29.5 (C-7', 8'), 29.2 (C-2, 6', 9'), 29.0 (C-5'), 28.8 (C-4'), 24.7 (t, C-3'), 22.6 (t, C-11'), 14.2 (t, C-3), 14.0 (q, C-12') ppm. Calcd. for active oxygen: 5.41 %; Found: 5.44 %. Anal. calcd. for $C_{17}H_{28}O_4$ (296.4): C, 68.89; H, 9.53. Found: C, 68.80; H, 9.45.

E-2-Butenoyl dodecanoyl peroxide (**1g**): 2.09 g (20 mmol) E-2-Butenoylchloride, 4.33 g (20 mmol) **2** and 1.58 g pyridine yield 5.36 g (18.9 mmol, 94 %) **1g**. Mp. 39 - 40° C. IR (film): 1800, 1760 (C=O), 1645, 955 (C=C), 1080 (COOC) cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 169.1 (s, C-1'), 162.4 (s, C-1), 148.7 (d, C-2), 116.1 (d, C-3), 31.8 (t, C-10'), 29.9 (C-2'), 29.4 (C-7', 8'), 29.2 (C-6', 9'), 29.0 (C-5'), 28.8 (C-4'), 24.7 (t, C-3'), 22.5 (t, C-11'), 18.4 (q, C-4), 14.0 (q, C-12') ppm. Calcd. for active oxygen: 5.62 %; Found: 5.57 %. Anal. calcd. for $C_{16}H_{28}O_4$ (284.4): C, 67.57; H, 9.92. Found: C, 67.29; H, 10.06.

Dodecanyol propynoyl peroxide (**1h**): 0.70 g (10 mmol) Propynoic acid, 2.16 g **2** and 2.06 g DCC afford after column chromatography (petrolether : ether, 10 : 1, 5° C) 2.14 g (8.0 mmol, 80 %) 1h. Mp. 27 - 28° C. IR (film): 2120 (C≡C), 1805, 1765 (C=O), 1055 (COOC) cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 168.4 (s, C-1'), 148.9 (low intensity, C-1), 81.2 (d, C-3), 69.5 (s, C-2), 31.9 (t, C-10'), 29.8 (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'), 22.7 (t, C-11'), 14.1 (q, C-12') ppm. Calcd. for active oxygen: 5.96 %, Found: 5.98 %. Anal. calcd. for $C_{15}H_{24}O_4$ (268.4): C, 67.14; H, 9.01. Found: C, 67.01; H, 9.29.

Benzoyl dodecanoyl peroxide (**1i**): 1.22 g (10 mmol) benzoic acid, 2.16 g (10 mmol) **2** and 2.06 g DCC yield after column chromatography (petrolether : ether, 10 : 1) 2.69 g (8.4 mmol, 84 %) 1i. Mp. 24 - 25° C. IR (film): 1800, 1765 (C=O), 1595 (C=C), 1035 (COOC) cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 169.2 (s, C-1'), 158.2 (low intensity, C-1), 134.1 (d, C-5), 129.6 (d, C-3), 128.7 (d, C-4), 125.7 (s, C-2), 31.8 (t, C-10'), 30.0 (C-2'), 29.5 (C-7', 8'), 29.3 (C-6', 9'), 29.0 (C-5'), 28.9 (C-4'), 24.8 (t, C-3'), 22.6 (t, C-11'), 14.0 (q, C-12') ppm. Calcd. for active oxygen: 4.99 %; Found: 4.94 %. Anal. calcd. for $C_{19}H_{28}O_4$ (320.4): C, 71.22; H, 8.81. Found: C, 71.38; H, 9.04.

FUNCTIONALIZED ALKANOYL DODECANOYL PEROXIDES

5-Bromopentanoyl dodecanoyl peroxide (**1j**): 1.81 g (10 mmol) 5-Bromopentanoic acid, 2.16 g (10 mmol) **2** and 2.06 g (10 mmol) DCC afford after column chromatography (petrolether : ether, 5 : 1) 3.37 g (8.9 mmol, 89 %) **1j**. Mp. 34 - 35° C. IR (film): 1810, 1780 (C=O), 1070 (C-OO-C) cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 169.1 (s, C-1'), 168.6 (s, C-1), 32.4 (C-4), 31.8 (C-10'), 31.4 (C-5), 29.9 (C-2'), 29.5 (C-7', 8'), 23.3 (C-3), 22.6 (C-11'), 14.0 (q, C-12') ppm. Calcd. for active oxygen: 4.22 %; Found:4.25 %. Anal. calcd. for $C_{17}H_{31}BrO_4$ (379.3): C, 53.83; H, 8.24. Found: C, 53.95; H, 8.22.

2-Bromohexanoyl dodecanoyl peroxide (**1k**): 2.14 g (10 mmol) 2-Bromohexanoyl chloride[24], 2.16 g (10 mmol) **2** and 0.79 g (10 mmol) pyridine yield 3.79 g (9.6 mmol, 96 %) **1k**. n_D^{20} : 1.4629. IR (film): 1815, 1785 (C=O), 1055 (COOC) cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 168.7 (s, C-1'), 166.0 (s, C-1), 40.2 (d, C-2), 34.8 (t, C-3), 31.8 (t, C-10'), 29.8 (C-2'), 29.5 (C-7', 8'), 29.2 (C-6', 9'), 29.0 (C-5'), 28.8 (C-4'), 28.1 (C-4), 24.7 (t, C-3'), 22.6 (C-11'), 21.8 (C-5), 14.0 (C-12'), 13.6 (C-6) ppm. Calcd. for active oxygen: 4.07 %; Found: 4.01 %. Anal. calcd. for $C_{18}H_{33}BrO_4$ (393.4): C, 54.96; H, 8.46. Found:C, 55.03; H, 8.70.

2-Chloropropionoyl dodecanoyl peroxide (**1l**): 1.27 g (10 mmol) 2-Chloropropionoyl chloride, 2.16 g (10 mmol) **2** and 0.79 g (10 mmol) pyridine lead to 2.98 g (9.7 mmol, 97 %) **1l**. n_D^{20}: 1.4487. IR (film): 1815, 1785 (C=O), 1050 (COOC) cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 168.7 (s, C-1'), 166.2 (s, C-1), 48.7 (d, C-2), 31.9 (t, C-10'), 29.8 (C-2'), 29.5 (C-7', 8'), 29.3 (C-11'), 21.6 (C-3), 14.0 (q, C-12') ppm. Calcd. for active oxygen: 5.21 %; Found: 5.11 %. Anal. calcd. for $C_{15}H_{27}ClO_4$ (306.8): C, 58.72; H, 8.87. Found: C, 58.76; H, 9.07.

Dodecanoyl 4-oxopentanoyl peroxide (**1m**): 1.16 g (10 mmol) 4-Oxopentanoic acid, 2.16 g **2** and 2.06 g DCC afford after column chromatography (petrolether : ether, 1 : 1) 2.88 g (9.22 mmol, 92 %) **1m**. Mp. 37 - 38° C. IR (film): 1790, 1715 (C=O), 1055 (COOC) cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 205.0 (s, C-4), 169.0 (s, C-1'), 168.6 (s, C-1), 37.6 (t, C-3), 31.8 (t, C-10'), 29.8 (C-2'), 29.5 (C-7', 8'), 29.2 (C-6', 9'), 29.0 (C-5'), 28.8 (C-4'), 24.7 (C-3'), 24.0 (C-2, 5), 22.6 (t, C-11'), 14.0 (q, C-12') ppm. Calcd. for active oxygen: 5.09 %; Found: 5.10 %. Anal. calcd. for $C_{17}H_{30}O_5$ (314.4): C, 64.94; H, 9.62. Found: C, 64.98; H, 9.90.

Dodecanoyl 4-oxopentanoyl ethylene acetal peroxide (**1n**): From a solution of 1.57 g (5 mmol) **1m**, 0.47 g (7.5 mmol) ethyleneglycol and 0.1 g p-toluenesulfonic acid in 30 ml dry CH_2Cl_2 the water is removed by azeotropic distillation and distilled off CH_2Cl_2 is continously replaced by dry CH_2Cl_2. After 4 hrs. the chilled solution is washed with a $KHCO_3$-solution and water, dried and the CH_2Cl_2 evaporated. After column chromatography (petrolether : ether, 2 : 1) 1.25 g (3.5 mmol, 70 %) **1n** are obtained. Mp. 22 - 23°C. n_D^{23} : 1.4528. IR (film): 1810, 1780 (C=O), 1055 (COOC) cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ = 169.2 (s, C-1, 1'), 108.6 (s, C-5), 64.8 (t, C-6, 7), 33.7 (t, C-3), 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'), 24.7 (C-5, 3'), 23.8 (C-2), 22.6 (C-2), 22.6 (t, C-11'), 14.0 (q, C-12') ppm. Calcd. for active oxygen: 4.46 %. Found: 4.43 %. Anal. calcd. for $C_{19}H_{34}O_6$ (358.5): C, 63.66; H, 9.56. Found: C, 63.66; H, 9.71.

Dodecanoyl 3α,7α,12α-triacetoxy-5β-cholanoyl peroxide (**1o**): 1.07 g (2 mmol) 3α,7α,12α-Triacetoxy-5β-cholanoic acid (Mp. 95-97° C), 0.43 g **2** and 0.41 g DCC afford after column chromatography (ether : petrolether, 1 : 1) 1.2 g (1.64 mmol, 82 %) **1o**. n_D^{20} = 1.4845. - IR (film): 1810, 1780, 1735 (C=O), 1060 (COOC) cm^{-1}. - ^{13}C-NMR ($CDCl_3$) δ = 170.3 (C = O in acetate), 169.4 (C-1), 169.2 (s, C-1'), 75.3, 74.0, 70.6 (C-3,7,12 in steroid), 47.2, 45.0, 43.3, 40.9, 37.7, 34.6, 34.4, 34.2, 33.8, 31.8 (C-10'), 31.2, 30.7, 29.9 (C-2'), 29.4 (C-7',8'), 29.2 (C-6',9'), 29.0 (C-5'), 28.8 (C-4'), 27.1, 26.8, 25.5, 24.6 (C-3'), 22.5 (C-11'), 21.4, 21.3, 17.3, 14.0 (C-12'), 12.1 ppm. - Calcd. for active oxygen: 2.18 %; Found: 2.17 %. - Anal. calcd. for $C_{42}H_{68}O_{10}$ (733.0): C, 68.82; H, 9.35.

Found: C, 68.52; H, 9.64.

3-Carbonyloxypropionyl dodecanoyl peroxide (**1p**): 2.19 g (10 mmol) dodecanoyl chloride, 1.76 g (10 mmol) monopersuccinic acid (76 %) and 0.79 g (10 mmol) pyridine afford 2.10 g (9.2 mmol, 92 %) **1p** (method A). - Mp. 90 - 91° C, from ligroin, (lit.$^{25)}$ 94° C). - IR (KBr): 1805, 1775, 1705 (C=O), 1065 (COOC) cm^{-1}. - ^{13}C-NMR (CDCl$_3$): δ = 177.3 (s, C-4), 169.1 (s, C-1'), 168.0 (s, C-1), 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'), 28.5 (C-2), 24.9 (C-3), 24.7 (C-3'), 22.6 (t, C-11'), 14.0 (q, C-12')ppm.- Calcd.for active oxygen: 5.06 %; Found: 5.02 %.

4-Carbonyloxybutyryl dodecanoyl peroxide (**1q**): 2.19 g (10 mmol) Dodecanoyl chloride, 2.31 g (10 mmol) monoperglutaric acid and 0.79 g (10 mmol) pyridine afford 3.05 g (9.2 mmol, 92 %) **1 q**. Mp. 72 - 73° C (from ligroin). - IR (KBr): 1805, 1775, 1705 (C=O), 1065 (COOC) cm^{-1}. - ^{13}C-NMR (CDCl$_3$): δ = 178.8 (s, C-5), 169.1 (s, C-1'), 168.4 (s, C-1), 32.4 (C-4), 31.8 (C-10'), 29.8 (C-2'), 29.5 (C-7',8'), 29.2 (C-6',9'), 28.9 (C-2,4',5'), 24.7 (t, C-3'), 22.6 (t, C-11'), 19.6 (t, C-3), 14.0 (q, C-12') ppm. Calcd. for active oxygen: 4.84 %; Found: 4.90 %. - Anal. calcd. for $C_{17}H_{30}O_6$ (330.4): C, 61.79; H, 9.15. Found: C, 61.53; H, 9.07. -

Dodecanoyl 2-ethoxycarbonyl-2-ethylbutyryl peroxide (**1r**): 1.88 g Ethyl diethylmalonate, n_D^{20}= 1.4357, Mp. 16 - 17° C), 2.16 g **2** and 2.06 g DCC yield after column chromatography (petrolether : ether, 8 : 1 at 5° C) 3.23 g (8.4 mmol, 84 %) 1r. - n_D^{20} : 1.4478. - IR (film): 1810, 1780, 1735 (C=O), 1060 (COOC) cm^{-1}. - ^{13}C-NMR (CDCl$_3$): δ = 169.8 (s, $\underline{C}O_2C_2H_5$), 168.6 (s, C-1'), 167.5 (s, C-1), 61.5 (t, $O\underline{C}H_2CH_3$), 57.5 (s, C-2), 31.8 (t, C-10'), 29.7 (C-2'), 29.4 (C,7',8'), 29.2 (C-6',9'), 29.0 (C-5'), 28.8 (C-4'), 25.1 (C-3), 24.7 (C-3'), 22.5 (t, C-11'), 13.9 (q, $OCH_2\underline{C}H_3$ and C-12'), 8.0 (q, C-4) ppm. - Calcd. for active oxygen: 4.14 %. Found:4.08 %. - Anal. calcd. for $C_{21}H_{38}O_6$ (386.5): C, 65.25; H, 9.91. Found: C, 67.44; H, 10.72. - The peroxide decomposes quickly at r.t., which leads to the incorrect analysis.

Dodecanoyl (±)-2-ethoxycarbonyl-2-methylbutyryl peroxide (**1s**): 1.74 g (10 mmol) (±)-Ethyl ethylmethylmalonate (from diethyl methylmalonate by alkylation with ethyliodide$^{18)}$, n_D^{20}: 1.4188, 82 % yield, and subsequent partial hydrolysis, n_D^{20}: 1.4306, 74 %), 2.16 g **2** and 2.06 g DCC afford after column chromatography (petrolether : ether, 8 : 1 at 5° C) 3.20 g (8.6 mmol, 86 %) 1s. - n_D^{20}: 1.4457. - IR (film): 1810, 1780, 1735 (C=O), 1065 (COOC) cm^{-1}. - ^{13}C-NMR (CDCl$_3$): δ = 170.6 (s, $CO_2C_2H_5$), 168.7 (s, C-1'), 168.1 (s, C-1), 61.7 (t, OCH_2CH_3), 53.2 (s, C-2), 31.8 (t, C-10'), 29.8 (C-2'), 29.5 (C-7',8'), 29.3 (C-6',9'), 29.0 (C-4',5'), 24.7 (t, C-3'), 22.6 (t, C-11'), 19.4 (t, C-3), 14.0 (OCH_2CH_3 and C-12'), 13.8 (C-5), 8.4 (q, C-4) ppm. - Calcd. for active oxygen: 4.30 %; Found: 4.29 %. - Anal. calcd. for $C_{20}H_{36}O_6$ (372.5): C, 64.49; H, 9.74. Found: C, 66.29; H, 10.46. Deviations due to decomposition at r.t.

Dodecanoyl 2-ethoxycarbonyl-2-methylbutyryl peroxide (**1s**): 1.05 g (6 mmol) (+)-Ethyl ethylmethylmalonate (obtained from (±)-ethyl ethylmethylmalonate by resolution with quinine in 34 % yield as pure enantiomer$^{18)}$, $[\alpha]_D^{22}$ = +3.51°, c = 15 in CHCl$_3$, lit.$^{18)}$ $[\alpha]_D^{18}$= +3.38°, c = 15 in CHCl$_3$), 1.30 g **2** and 1.24 g DCC afford after column chromatography 2.02 g (5.4 mmol, 90 %) **1s**.

The optical rotation of **1s** could not be determined due to its instability.

PHOTOLYSES

Dodecanoyl 10-undecenoyl peroxide (**1a**): Analytical (GLC, column 1, 50 - 280° C, 10° C/min): 68 % 1-Heneicosene (**4**), 3 % n-undecane. Preparative: 1.91 g (5.0 mmol) **1a** afford after 50 hrs. photolysis 0.94 g (32 mmol, 64 %) **4**. 1-Heneicosene (**4**): Mp. 32 - 33° C (lit.[26] 33° C). IR (film): 3070, 1640, 990, 910 cm^{-1} (C=C). - ^1H-NMR ($CDCl_3$): δ = 5.81 (m, 1H), 4.96 (m, 2H), 2.04 (m, 2H), 1.36 (m, 2H), 1.216 (m, 32H), 0.88 (t, 3H) ppm. - MS: *m/e* = 294 (2%, M), 266 (1%, $M^+ - C_2H_4$), 182 (2%), 181 (2%), 167 (3%), 154 (3%), 153 (4%), 140 (5%), 139 (10%), 125 (17%), 111 (35%), 97 (62%).

Dodecanoyl 6-heptenoyl peroxide (**1b**): Analytical: (GLC, column 1, 50 - 280° C, 10° C/min): 61 % **5**, 1 % **13**, 5 % n-undecane. Preparative: 3.27 g (10 mmol) **1b** yield after 70 hrs. irradiation 1.14 g (4.8 mmol, 48 %) **5**. 1-Heptadecene (**5**): n_D^{20} : 1.4434 (lit.[27] 1.4436). - IR (film): 3070, 1640, 990, 910 cm^{-1} (C=C). - ^1H-NMR ($CDCl_3$): δ = 5.81 (m, 1H), 4.96 (m,2H), 2.04 (m, 2H), 1.36 (m, 2H), 1.26 (m, 24H), 0.88 (t, 3H) ppm. - MS: *m/e* = 238 (4%, M^+), 210 (2%, $M^+ - C_2H_4$), 154 (4%), 153 (3%), 140 (5%), 139 (7%), 125 (18%), 111 (41%), 57 (100%). Cyclopentyldodecane (**13**): MS: *m/e* = 238 (8%, M^+), 210 (3%, $M^+ - C_2H_4$), 195 (1%), 181 (2%), 167 (3%), 154 (3%), 153 (4%), 139 (9%), 125 (19%), 111 (38%). 69 (100%, $C_5H_9^+$).

Dodecanoyl Z-4-heptenoyl peroxide (**1c**): Analytical (GLC, column 1, 50 - 280° C; column 4, 130 - 230° C, 3° C/min: 48 % **6**, 9 % E-**6**, 15 % n-undecane.
Preparative: 0.82 g (2.5 mmol) **1c** afford after 30 hrs. irradiation 0.27 g (1.13 mmol, 45 %) **6** and E-isomer. *Z-3-Heptadecene* (**6**, mixture of 86 % Z and 12 % E), n_D^{20}: 1.4447. - IR (film): 3010, 1655, 720 cm^{-1} (C=C). - ^1H-NMR ($CDCl_3$): δ = 5.34 (m, 2H, J = 10 Hz), 2.04 (m, 4H),1.26 (m, 22H), 0.95 (t, 3H), 0.88 (t, 3H) ppm. - MS: *m/e* = 238 (22%, M^+), 210 (3%, $M^+ - C_2H_4$), 196 (1%), 172 (2%), 168 (3%), 154 (5%), 153 (4%), 140 (7%), 139 (7%), 125 (20%), 111 (41%), 97 (70%), 55 (100%). - **6** and its E-isomer have identical MS-spectra. - Anal. calcd. for $C_{17}H_{34}$ (326.5): C, 85.63; H, 14.37. Found: C, 85.45; H, 14.65. - The strucure of the E-isomer of **6** was confirmed by double bond isomerization: 50 mg **6**, 2 ml 2n HCl and 100 mg sodium nitrite lead to 18 % **6** and 82 % E-isomer of **6**. - Ozonolysis of **6** (50 mg **6** ozonized in ether/methanol, oxidative workup: 2n H_2SO_4, chromic trioxide, methylation with diazomethane) yields methyl tetradecanoate: MS[28]: *m/e* = 242 (4%, M^+), 213 (4%, $M^+ - C_2H_5$), 211 (4%, $M^+ - OCH_3$), 199 (7%), 185 (3%), 171 (1%), 157 (4%), 143 (11%), 129 (5%), 115 (2%), 111 (3%), 101 (6%), 74 (100%, $C_3H_6O_2^+$, McLafferty).

Dodecanoyl E-3-hexenoyl peroxide (**1d**): Analytical (GLC, column 1, 50 - 280° C; column 4, 120 - 230° C, 3°C (min): 42 % **7**, 3 % Z-isomer of **7**, 4 % **14**, 14 % n-undecane. Preparative: 3.12 g (10 mmol) **1d** produce after 100 hrs. irradiation 0.94 g (42 %) **7**, Z-**7**, **14**. E-3-Hexadecene (**7**, mixture of 84 % **7**, 6 % **7a**, 8 % **14**): n_D^{20}: 1.4227 (lit.[29]: 1.4220). - IR (film): 3020, 965 cm^{-1} (C=C). - ^1H-NMR ($CDCl_3$): δ = 5.40 (m, 2H, J = 16 Hz), 1.98 (m, 4H), 1.26 (m, 20H), 0.94 (t, 3H), 0.88 (t, 3H) ppm. - MS: *m/e* = 224 (30%, M^+), 196 (4%, $M^+ - C_2H_4$), 182 (2%), 169 (2%), 168 (2%), 168 (3%), 154 (6%), 140 (8%), 139 (7%), 126 (11%), 125 (17%), 112 (18%), 111 (37%), 69 (100%). **7** and Z-**7** exhibit the same MS-spectra. - Anal. calcd. for $C_{16}H_{32}$ (224.4): C, 85.63; H, 14.37. Found: C, 85.85; H, 14.66. - Isomerization of the double bond in **7** (as in **6**) affords 85 % **7** and 15 % Z-**7**. - Ozonolysis of **7** (as in **6**) yields methyl tridecanoate: MS[28]: *m/e* = 228 (15%, M^+), 199 (4%, $M^+ - C_2H_5$), 197 (9%, $M^+ - OCH_3$), 185 (10%), 143 (12%), 129 (8%), 115 (2%), 101 (7%), 74 (100%, $C_3H_6O_2{}^+$, McLafferty). 3-Ethyl-1-tetradecene (**14**): MS : *m/e* = 224 (5%, M^+), 197 (4%), 196 (5%, $M^+ - C_2H_4$), 154 (5%), 139 (5%), 125 (9%), 111 (14%), 84 (100%, $C_6H_{12}{}^+$), Ozonolysis of **14** (as in **6**) leads to methyl 2-ethyltridecanoate: MS: *m/e* = 256 (10%, M^+), 228 (7%, $M^+ - C_2H_4$), 227 (4%, $M^+ - C_2H_5$), 225 (3%, $M^+ - OCH_3$), 199 (6%), 185 (5%), 171 (4%), 157 (8%), 143 (3%), 129 (3%), 115 (32%, $C_6H_{11}O_2{}^+$, McLafferty + 13), 102 (100%, $C_5H_{10}O_2{}^+$, McLafferty).

Dodecanoyl 4-pentenoyl peroxide (**1e**): Analytical (GLC, column 1, 50 - 280° C, 10° C (min): 61 % **8**, 6 % undecane. - Preparative: 1.49 g (5 mmol) **1e** yields after 50 hrs. irradiation 0.59 g (2.8 mmol, 56 %) **8**. 1-Pentadecene (**8**): n_D^{20}: 1.4388[30]. - IR (film): 3070, 1640, 990, 910 cm^{-1} (C=C). - ^1H-NMR ($CDCl_3$): δ =5.81 (m, 1H), 4.96 (m, 2H), 2.04 (m, 2H), 1.36 (m, 2H), 1.26 (m, 20H), 0.88 (t, 3H) ppm. - MS: *m/e* = 210 (2%, M^+), 182 (1%, $M^+ - C_2H_4$), 154 (2%), 140 (3%), 139 (3%), 126 (6%), 125 (10%), 111 (22%), 43 (100%).

Dodecanoyl 4-pentynoyl peroxide (**1f**): Analytical GLC, column 1, 50 - 280° C, 10° C (min): 56 % **9**, 6 % undecane. Preparative: 2.96 g (10 mmol) **1f** are irradiated for 70 hrs. to afford 1.07 g (5.1 mmol, 51 %) **9**. 1-pentadecyne (**9**): n_D^{20} 1.4423 (lit.[31] n_D^{20} = 1.4422). - IR (film): 3310, 2120 (C≡C) cm^{-1}. ^1H-NMR ($CDCl_3$): δ = 2.18 (dt, 2H), 1.94 (t, 1H), 1.53 (m, 2H), 1.39 (m, 2H), 1.26 (m, 18H), 0.88 (t, 3H) ppm. - MS: *m/e* = 208 (0.1%, M^+), 123 (3%), 109 (13%), 81 (100%, $C_6H_9{}^+$).

E-2-Butenoyl dodecanoyl peroxide (**1g**): Analytical (GLC, column 1, 50 - 280°C, 10°C (min): 17 % **10**, 8 % Z-**10**, 1 % **15**, 12 % n-undecane. Preparative: The photolysis of 2.84 g (10 mmol) **1g** (interrupted after 100 hrs. though conversion of **1g** was incomplete) afforded 0.2 g (1.0 mmol, 10 %) **10**, Z-**10** and **15**. E-2-Tetradecene (**10**) and Z-2-Tetradecene (Z-**10**): (GLC, column 3: 63 % **1**, 29 % Z-**10a**, 4 % **15**). - IR (film): 3020, 1655, 965, 720 cm^{-1} (C=C). - ^1H-NMR ($CDCl_3$): δ = 5.40 (m, 2H), 2.04 (m, 0.65H, cis-CH_2CH=CH), 1.98 (m 1.35 H, trans-C_2CH=CH), 1.64 (m, 2H, trans-CH=$CHCH_3$), 1.60 (m, 1H, cis-CH=$CHCH_3$), 1.26 (m, 18H), 0.88 (t, 3H) ppm. - MS: *m/e* = 196 (41%, M^+), 168 (6%, $M^+ - C_2H_4$), 154 (3%), 153 (3%), 140 (5%), 139 (5%), 126 (9%), 125 (10%), 112 (15%), 111 (29%), 55 (100%, $C_4H_7{}^+$). Identical MS for **10** and Z-**10**. - Anal. calcd. for $C_{14}H_{28}$ (196.4): C, 85.63; H, 14.37. Found: C, 85.44; H, 14.42. - Isomerization (as in **6**) changed the **10** : Z-**10** ratio to 78 : 22. - Ozonolysis of **10**, Z-**10** (as in **6**) afforded methyl dodecanoate: MS[28] : *m/e* = 214 (8%, M^+), 185 (6%), 183 (8%, $M^+ - OCH_3$), 171 (13%), 157 (5%), 143 (16%), 129 (8%), 115 (7%), 101 (9%), 74 (100%, $C_3H_6O_2{}^+$, McLafferty). 1-Tetradecene (**15**): MS: *m/e* = 196 (5%, M^+),168 (2%, $M^+ - C_2H_4$), 140 (2%), 139 (3%), 126 (5%), 125 (7%), 111 (10%), 55 (100%, $C_4H_7{}^+$).

Dodecanoyl propynoyl peroxide (**1h**): Analytical (GLC, column 1, 50 - 280° C, 10°C (min): 0 % **11**, 5 % n-undecane and polymer of unknown structure (IR: 2120 (C≡C), 1715 (C=O) cm^{-1}).

Benzoyl dodecanoyl peroxide (**1i**): Analytical (GLC, column 1, 50 - 280° C, 10° C/min): 16 % **12**, 14 % undecyl benzoate (**16**), 5 % n-undecane. Preparative: 1.60 g (5 mmol) **1i** were irradiated for 100 hrs. and the photolysis then interrupted, though the conversion was not complete. Column chromatography (petrolether : ether, 20 : 1) afforded 0.17 g (0.73 mmol, 15 %) **12** and 0.15 g (0.54 mmol, 11 %) **16**. Phenyl undecane (**12**): n_D^{20} = 1.4800 (lit.$^{32)}$ n_D^{20} = 1.4783). - IR (film): 3055, 3020, 1600, 1495, 740, 695 (Phenyl) cm^{-1}. - ^{1}H-NMR ($CDCl_3$): δ = 7.26 (m, 2H), 7.16 (m, 3H), 2.60 (t, 2H), 1.61 (m, 2H), 1.26 (m, 16H), 0.88 (t, 3H) ppm. - MS: m/e = 232 (25%, M^+), 147 (2%), 133 (7%), 119 (3%), 105 (11%), 104 (7%), 92 (100%, $C_7H_8{}^+$). Undecyl benzoate (**16**): n_D^{20} = 1.4841. - IR (film): 3050, 3010, 1600, 710 (phenyl), 1715 (C=O) cm^{-1}. - ^{1}H-NMR ($CDCl_3$): δ = 8.05 (m, 2H), 7.55 (m, 1H), 7.44 (m, 2H), 4.32 (t, 2H), 1.77 (tt, 2H), 1.44 (m, 2H), 1.26 (m, 14H), 0.88 (t, 3H) ppm. - MS: m/e = 276 (2%, M^+), 154 (16%, M^+ - $C_7H_6O_2$), 123 (100%, $C_7H_7O_2{}^+$), 105 (63%, $C_6H_5CO^+$). - Anal. calcd. for $C_{18}H_{28}O_2$ (276.4): C, 78.21; H, 10.21. Found: C, 78.25; H, 10.50.

5-Bromopentanoyl dodecanoyl peroxide (**1j**): Analytical (GLC, column 1, 50 - 280° C, 10° C/min): 76 % 1-Bromopentadecane (**17**), 2 % n-undecane. Preparative: 1.90 g (5 mmol) **1j** afford after 50 hrs. irradiation 0.98 g (3.4 mmol, 67 %) **17**. 1-Bromopentadecane (**17**): n_D^{20} = 1.4611 (lit.$^{33)}$ 1.4612). - ^{1}H-NMR ($CDCl_3$): δ = 3.40 (t, 2H), 1.85 (tt, 2H), 1.42 (m, 2H), 1.26 (m, 22H), 0.88 (t, 3H) ppm. - MS: m/e =292 (0.2%, M^+), 290 (0.2%, M^+), 179 (1%), 177 (1%), 165 (3%), 163 (3%), 151 (15%), 149 (16%), 137 (75%), 135 (78%), 113 (6%), 111 (8%), 57 (100%).

2-Bromohexanoyl dodecanoyl peroxide (**1k**): Analytical (GLC, column 1, 50 - 280 ° C; column 3, 50 - 250° C, 5° C/min): 55 % **18**, 6 % **27**, 1 % **28**, 5 % n-undecane, 5 % **29**. Preparative: 1.97 g (5 mmol) **1k** lead after 50 hrs. photolysis to 0.61 g (2 mmol, 40 %) **18** and 0.05 g (0.2 mmol, 4 %) **29**. - 5-Bromohexadecane (**18**): n_D^{20} = 1.4620 (lit.$^{34)}$ 1.4614). - ^{1}H-NMR ($CDCl_3$): δ = 4.03 (tt, 1H), 1.80 (m, 4H), 1.60-1.36 (2m, 4H), 1.26 (m, 18H), 0.92 (t, 3H), 0.88 (t, 3H) ppm. - MS: m/e = 225 (10%, M^+ - Br), 169 (3%), 155 (4%), 141 (6%), 127 (7%), 113 (11%), 111 (8%), 57 (100%). - 1-Bromoundecane (**29**): n_D^{20} = 1.4575 (lit.$^{35)}$ 1.4571). - ^{1}H-NMR ($CDCl_3$): δ = 3.40 (t, 2H), 1.85 (tt, 2H), 1.42 (m, 2H), 1.26 (m, 14H), 0.88 (t, 3H) ppm. - MS: m/e = 236 (0.1%, M^+), 234 (0.1%, M_+), 151 (12%), 149 (12%), 137 (85%), 135 (93%), 57 (100%). - Isomeric Hexadecenes (**27**): MS: m/e = 224 (10%, M^+), 196 (2%), 153 (2%), 140 (3%), 139 (3%), 125 (10%), 111 (22%), 55 (100%). - n-Hexadecane (**28**): MS: m/e = 226 (2%, M^+), 183 (1%), 169 (2%), 155 (1%), 141 (3%), 140 (2%), 127 (2%), 126 (3%), 113 (5%), 57 (100%).

2-Chloropropionyl dodecanoyl peroxide (**1l**): Analytical (GLC, column 1, 50 - 280° C, 10° C (min): 61 % **19**, 18 % n-undecane. Preparative: 1.53 g (5 mmol) **1l** afford after 50 hrs. 0.57 g (2.6 mmol, 52 %) **19**. - 2-Chlorotridecane (**19**): n_D^{20}= 1.4429 (lit.$^{36)}$ 1.4430). - ^{1}H-NMR ($CDCl_3$): δ = 4.03 (tq, 1H), 1.70 (m, 2H), 1.50 (d, 3H), 1.47 (m, 2H), 1.26 (m, 16H), 0.88 (t, 3H) ppm. - MS: m/e = 183 (2%, M^+ - Cl), 182 (14%, M^+ - HCl), 154 (7%), 140 (5%), 139 (5%), 126 (7%), 125 (12%), 112 (13%), 111 (22%), 107 (3%), 105 (10%), 43 (100%).

Dodecanoyl 4-oxopentanoyl peroxide (**1m**): Analytical (GLC, column 1, 50 - 280° C; column 3, 50 - 250° C) 50 % **20**, 21 % **30**, 5 % n-undecane. 1-Dodecene (**30**): MS: *m/e* = 168 (8%, M$^+$), 140 (3%), 125 (5%), 111 (12%), 43 (100%).

Dodecanoyl 4-oxopentanoyl ethylene acetal peroxide (**1n**): Analytical (GLC, column 1, 50 - 280° C, 10° C/min); after cleavage of the acetal with HCl (MeOH): 67 % **20**, 5 % n-undecane. Preparative: 0.90 g (2.5 mmol) **1n** afford after 30 hrs. irradiation, deprotection (MeOH/HCl) and column chromatography (petroleumether : ether, 3 : 1) 0.32 g (1.41 mmol, 57 %) **20**. - 2-Pentadecanone (**20**): Mp. 38 - 39° C (lit.[37] 39 - 39.5° C). - IR (film): 1710 cm^{-1} (C=O). - ^{1}H-NMR ($CDCl_3$): δ = 2.42 (t, 2H), 2.13 (s 3H), 1.57 (m, 2H), 1.26 (m, 20H), 0.88 (t, 3H) ppm. - MS: *m/e* = 226 (5%, M$^+$), 211 (2%, M$^+$ - CH_3), 197 (1%), 183 (1%), 168 (4%), 166 (3%), 58 (100%, $C_3H_6O^+$, McLafferty).

Dodecanoyl 3α,7α,12α-triacetoxy-5β-cholanoyl dodecanoyl peroxide (**1o**): Preparative: 0.73 g (1 mmol) **1o** leads after 30 hrs. irradiation and column chromatography to 0.48 g (0.74 mmol, 74 %) **22**. *24-Decyl-3α,7α,12α-triacetoxy-5β-cholane* (**22**): Mp. 84 - 85° C. - IR (KBr): 1735 cm^{-1} (C=O). - ^{1}H-NMR ($CDCl_3$): δ = 5.10 (m, 1H, 12β-CHO), 4.92 (m, 1H, 7β-CHO), 4.58 (m, 1H, 3β-CHO), 2.14 (s, 3H, CH_3CO_2), 2.09 (s, 3H, CH_3C_2), 2.05 (s, 3H, C_3CO_2), 1.26 (m, 24H, CH_2), 2.06 - 0.95 (several m, 20H), 0.92 (s, 3H, H_3C - C19), 0.88 (t, 3H, CH_2CH_3), 0.80 (d, 3H, H_3C - C21), 0.74 (s 3H, H_3C - C18) ppm. - MS: *m/e* = 524 (17%, M$^+$ - 2 CH_3CO_2H), 464 (22%, M$^+$ - 3 CH_3CO_2H), 449 (11%), 410 (7%), 358 (7%), 313 (47%), 253 (100%, M$^+$ - 3 CH_3CO_2H, -$C_{15}H_{31}$), 226 (22%), 211 (17%). - Anal. calcd. for $C_{40}H_6O_6$ (645.0): C, 74.49; H, 10.63. Found: C, 74.47; H, 10.71.

3-Carboxypropionyl dodecanoyl peroxide (**1p**): Analytical (GLC after esterification with diazomethane, column 1, 50 - 280° C): 68 % **23**, 1 % n-undecane. Preparative: 1.58 g (5 mmol) **1p** yield after 50 hrs. 0.64 g (2.8 mmol, 56 %) **23**. Tetradecanoic acid (**23**): Mp. 52 - 53° C (lit.[38] 54° C). - IR (film): 1695 (C=O) cm^{-1}. - ^{1}H-NMR ($CDCl_3$): δ = 2.34 (t, 2H), 1.64 (m, 2H), 1.26 (m, 20H), 0.88 (t, 3H) ppm.

4-Carboxybutyryl dodecanoyl peroxide (**1q**): Analytical (GLC after esterification with diazomethane, column 1, 50 - 280° C, 10° C/min): 69 % **24**, 1 % n-undecane. Preparative: 1.65 g (5 mmol) **1q** are converted after 50 hrs. photolysis into 0.72 g (2.97 mmol, 59 %) **24**. Pentadecanoic acid (**24**): Mp. 51 - 52° C (lit.[39] 53 - 54°C). - IR (film): 1695 cm^{-1} (C=O). - ^{1}H-NMR ($CDCl_3$): δ = 2.34 (t, 2H), 1.64 (m, 2H), 1.26 (m, 22H), 0.88 (t, 3H) ppm. - MS (methylester): *m/e* = 256 (4%, M$^+$), 227 (3%), 225 (6%), 213 (11%), 199 (5%), 185 (3%), 171 (4%), 157 (6%), 143 (17%), 129 (8%), 115 (3%), 111 (3%), 101 (8%), 74 (100%, $C_3H_6O_2^+$, McLafferty); corresponds to MS in lit.[28].

Dodecanoyl 2-ethoxycarbonyl-2-ethylbutyryl peroxide (**1r**): Analytical (GLC, column 1, 50 - 280° C, 10° C (min): 36 % **25** 31 % n-undecane.- Preparative: 1.95 g (5 mmol) **1r** are irradiated for 50 hrs. to afford after column chromatography (petroleumether: ether, 10 : 1) 0.45 g (1.51 mmol, 30 %) **25**.

Ethyl 2,2-diethyl tridecanoate (25): n_D^{20} = 1.4432. - IR (film): 1725 cm^{-1} (C=O). - ^{1}H-NMR ($CDCl_3$): δ = 4.14 (q, 2H), 1.58 (q, 4H), 1.54 (t, 2H), 1.26 (m, 18H), 1.25 (t, 3H), 0.88 (t, 3H), 0.77 (t, 6H) ppm. - MS: m/e = 298 (2%, M^+), 270 (11%), 225 (27%), 144 (100%, $C_8H_{16}O_2^+$, McLafferty), 129 (14%), 113 (8%). Anal. calcd. for $C_{19}H_{38}O_2$ (298.5): C, 76.45; H, 12.88. Found: C, 76.64; H, 12.97.

Dodecanoyl (rac)-2-ethoxycarbonyl-2-methylbutyryl peroxide ((±)-1s): Analytical (GLC, column 1, 50 - 280° C): 21 % 26, 54 % n-undecane. Preparative: 1.86 g (±)-1s afford after 50 hrs. irradidation and column chromatography (petroleumether: ether, 15 : 1) 0.25 g (0.88 mmol, 1 %) 26.- (rac)-Ethyl 2-ethyl-2-methyltridecanoate (±)-26).- n_D^{20} 1.4390. - IR (film): 1725 cm^{-1} (C=O). - ^{1}H-NMR ($CDCl_3$): δ = 4.14 (q, 2H), 1.64 (m, 2H), 1.44 (m, 2H), 1.26 (m, 18H), 1.25 (t, 3H), 1.11 (s, 3H), 0.88 (t, 3H), 0.82 (t, 3H) ppm. - MS: m/e = 284 (2%, M^+), 256 (5%), 211 (20%), 199 (2%), 185 (2%), 143 (5 %), 130 (100 %, $C_7H_{14}O_2^+$, McLafferty), 115 (10%). Anal. calcd. for $C_{18}H_{36}O_2$ (284.5): C, 76.00; H, 12.76. Found: C, 75.95; H, 12,63.

Dodecanoyl 2-ethoxycarbonyl-2-methylbutyryl peroxide (1s): Preparative: 1.49 g (4 mmol) 1s afford after 50 hrs. photolysis and column separation (petroleumether: ether, 15 : 1) 0.19 g (0.67 mmol, 17 %) (+)-26.- (+)-Ethyl 2-ethyl-2-methyltridecanoate ((+)-26) n_D^{20} = 1.4394. - $[\alpha]_D^{22}$ = +2.55° (c = 15 in $CHCl_3$). - The optical purity of (+)-26 was determined from the corresponding alcohol 26a by ^{1}H-NMR with $Eu(hfc)_3$.
0.14 g (+)-26 were reduced with 0.10 g (2.6 mmol) $LiAlH_4$ in 25 ml ether. The usual work-up yields 0.11 g (0.45 mmol, 90 %) (+)-2-ethyl-2-methyltridecanol (26a): n_D^{20} = 1.4531. - ^{1}H-NMR ($CDCl_3$): δ = = 3.35 (s, 2H), 1.39 (s, 1H), 1.26 (m, 18H), 1.20 (m, 4H), 0.88 (t, 3H), 0.81 (s, 3H) ppm. - MS:m/e = 211 (8%, M^+ - CH_2OH), 181 (2%), 169 (1%), 155 (4%), 141 (6%), 127 (7%), 113 (10%), 57 (100%). Anal. calcd. for $C_{16}H_{34}O$ (242.5): C, 79.26; H, 14.14. Found: C, 79.45; H, 14.43. - ^{1}H-NMR with 50 % $Eu(hfc)_3$: 80 % (+)-26a, 20 % (-)-26a.

SIDE PRODUCTS ORIGINATING FROM THE DODECANOYL GROUP. n-Undecane (3): MS (70eV):m/e = 156 (M^+, 5%), 127 (3), 113 (3), 99 (10).- n-Docosane (34): MS (70eV):m/e = 310 (2%, M^+), 281 (2), 267 (1), 253 (1), 239 (1), 225 (1), 211 (1), 197 (2), 183 (3), 169 (4), 155 (5), 141 (7), 127 (11), 113 (16), 99 (26). 1-Undecene (35): MS (70eV):m/e = 154 (5%, M^+), 126 (2), 125 (3), 111 (9).- Cyclopropyloctane (36) was prepared from 1-decene by Simmons-Smith reaction[40)]; n_D^{20} : 1.4294 (lit.[40)]: $n^{25}{}_D$: 1.4280). - MS (70eV):m/e = 154 (M^+, 3%), 126 (8), 125 (4), 112 (6), 111 (11).- 1-Undecanol (37): MS (70eV):m/e = 154 (1%, M^+ - H_2O), 126 (9), 111 (10).

KOLBE-ELECTROLYSES as described in the preceding paper[1)].

Support of this work by a generous scholarship to M. Feldhues from the Fonds der Chemischen Industrie is gratefully acknowledged.

REFERENCES

1) M. Feldhues and H.J. Schäfer, Selective coupling of carboxylic acids (I), Tetrahedron, preceding paper.
2) a) B.C.L. Weedon, Adv.Org.Chem. **1**, 1 (1960); b) H.J. Schäfer, Chem.Phys. Lipids **24**, 321 (1979); c) H.J. Schäfer, Angew. Chem. **93**, 978 (1981), Angew. Chem. Int. Ed. Engl. **20**, 911 (1981).
3) Lit. 2a), p. 6.
4) M. Huhtasaari, H.J. Schäfer and H. Luftmann, Acta Chem. Scand. B **37**, 537 (1983).
5) a) R.F. Garwood, Naser-ud-Din, C.J. Scott, B.C.L. Weedon, J. Chem. Soc. Perkin I (1973) 2714; b) M. Huhtasaari, H.J. Schäfer and L. Becking, Angew. Chem. **96**, 995 (1984); Angew. Chem. Int. Ed. Engl. **23**, 981 (1984).
6) J. Knolle, Dissertation, Univ.Münster 1976.
7) L. Eberson and G. Ryde-Petterson, Acta Chem. Scand. **27**, 1159 (1973); L. Eberson, K. Nyberg, R. Servin and I. Wennebreck, Acta Chem. Scand. B **30**, 186 (1976); L. Eberson, K. Nyberg and R. Servin, Acta Chem. Scand. B **30** 906 (1976).
8) F.D. Greene and J. Kazan, J. Org. Chem. **28**, 2168 (1963).
9) J.D. Coyle, Chem. Rev. **78**, 97 (1978) there p. 108.
10) J.E. Baldwin, J.C.S. Chem. Commun. **1976**, 734.
11) A.L.J. Beckwith, Tetrahedron **37**, 3073 (1981); A.L.J. Beckwith and G. Moad, J.C.S. Chem. Commun. **1974**, 472.
12) R.A. Sheldon and J.K. Kochi, J. Am. Chem. Soc. **92**, 4395 (1970).
13) R.W. Fessenden and R.H. Schuler, J. Chem. Phys. **39**, 2147 (1963).
14) R.R. Rando and W.v.E. Doering, J. Org. Chem. **33**, 1671 (1968).
15) R.B. Cundall and T.F. Palmer, Actes du Deuxieme Congres International de Catalyse, p. 573, Ed. Tech., Paris 1961.
16) J.G. Calvert and J.N. Pitts, Photochemistry, p. 522, J. Wiley, New York 1966.
17) Lit. 16), p. 382.
18) J. Kenyon and W.A. Ross, J. Chem. Soc. **1951**, 3407.
19) G.R. Sullivan in Topics of Stereochemistry, Vol. 10, p. 287, J. Wiley, New York 1978.
20) J.M. McBride, Acc. Chem. Res. **16**, 304 (1983).
21) F.D. Greene, J. Am. Chem. Soc. **77**, 4869 (1955); J.P. Engstrom and F.D. Greene, J. Org. Chem. **37**, 968 (1972).
22) M. Huhtasaari, Dissertation, Univ. Münster, 1984.
23) L. Funt and J. Tanner, in Technique of Electroorganic Synthesis, Part II, N.L. Weinberg, Ed., p. 559, there p. 597, Wiley 1975.
24) D.N. Harpp, C.Q. Bao, Ch. Coyle, J.G. Gleason, S. Horovitch, Org. Syntheses **55**, 27 (1976).
25) G. Schroeder and R. Lombard, Bull. Soc. Chim. France, **1964**, 542.
26) Beilstein, Vol. I, 3. Suppl., p. 883.
27) Beilstein, Vol. I, 4. Suppl., p. 929.

28) S.P. Markey, W.G. Urban and S. Levine, Mass Spectra of Compounds of Biological Interest, Vol. 2, Part 1, p. 226, 256, 284, 314, Spectra Nat. Tech. Inf.-Service, Springfield 1974.

29) F. Asinger und H. Eckholdt, Chem. Ber. 76, 585 (1943), 1 : 1 - mixture of 3- and 4-hexadecenes.

30) Lit. 27, p. 926.

31) Lit. 27, p. 1072.

32) R.L. Huang, H.H. Lee and Lai-Yoong Wong, J. Chem. Soc. 1965, 6730.

33) Lit. 26, p. 531.

34) Lit. 26, p. 542.

35) Beilstein, Vol. I, 2. Suppl., p. 132.

36) W. Schlenk jr., Liebigs Ann. Chem. 1973, 1156.

37) Beilstein, Vol. I, 3. Suppl., p. 2921.

38) Beilstein, Vol. II, 2. Suppl., p. 324.

39) Lit. 38, p. 329.

40) R.J. Crawford and R. Raap, Can. J. Chem. 43, 356 (1965).