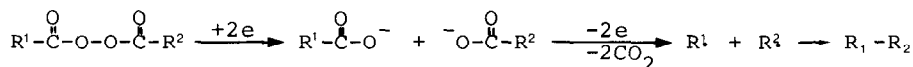


SELECTIVE MIXED COUPLING OF CARBOXYLIC ACIDS VIA UNSYMMETRICAL DIACYL  
 PEROXIDES BY ELECTROLYSIS, THERMOLYSIS AND PHOTOLYSIS

Michael Feldhues, and Hans J. Schäfer\*  
 Organisch-Chemisches Institut der Universität  
 Orléans-Ring 23, D-4400 Münster, Germany

Unsymmetrical diacyl peroxides are prepared in 85-92 % yields. Their square pulse electrolysis affords unsymmetrical dimers in poor yield and selectivity. Whilst thermolysis or photolysis in solution produces high portions of disproportionation products, the photolysis of the neat peroxides at -78° C yields selectively 50-75 % of the mixed dimers.

C-C-coupling to symmetrical products can be achieved by a simple and versatile method: the Kolbe-electrolysis<sup>1)</sup>. Coelectrolysis of different carboxylic acids yields unsymmetrical coupling products, whereby from easily available carboxylic acids, e.g. pheromones<sup>1g)</sup> or unusual fatty acids<sup>1b)</sup> can be prepared. A disadvantage of the mixed Kolbe electrolysis however, is the formation of symmetrical dimers as side products due to the statistical coupling of the intermediate radicals. One possibly could reduce that by generating the different radicals close together, e.g. by electrolysis of unsymmetrical diacyl peroxides with pulsed current.



In the cathodic pulse the peroxide is reductively cleaved into two carboxylates<sup>2)</sup>, which before they can diffuse too far, are decarboxylated in the anodic pulse to radicals, that couple to the mixed dimer. The Kolbe electrolysis is possible with pulsed current<sup>3)</sup>. However, as we found in the square pulse electrolysis of deca-noic acid, the dimer yield decreases with increasing frequency: 60 % (0.05 cps), 47 (0.2), 33 (0.4), 27 (5), 23 (10), 13 (20), 4 (25), 1 (50). This could be due to the competition of Non-Faradaic capacity currents or slow electron transfer<sup>3b)</sup>.

The unsymmetrical diacyl peroxides (Table 1) were prepared by the usual method<sup>4)</sup> from per-dodecanoic acid<sup>5)</sup> and the acid chlorides 1-5 at -10° C in diethyl ether with pyridine.

Table 1: Unsymmetrical Diacyl peroxides: yields and melting points

Acid chloride R-COCl		Diacyl peroxide $R-\overset{\text{O}}{\parallel}{C}-O-O-\overset{\text{O}}{\parallel}{C}-C_{11}H_{23}$ <sup>a)</sup>	yield (%)	mp. (°C)	
CH <sub>3</sub> -	( <u>1</u> )	CH <sub>3</sub> -	( <u>6</u> )	85	37-38 <sup>b)</sup>
CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>2</sub> -	( <u>2</u> )	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>2</sub> -	( <u>7</u> )	90	15-16 <sup>c)</sup>
CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>4</sub> -	( <u>3</u> )	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>4</sub> -	( <u>8</u> )	88	24-25 <sup>d)</sup>
CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>6</sub> -	( <u>4</u> )	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>6</sub> -	( <u>9</u> )	91	33-34 <sup>d)</sup>
CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>8</sub> -	( <u>5</u> )	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>8</sub>	( <u>10</u> ) <sup>e)</sup>	92	40-41 <sup>d)</sup>

a) Elemental and active oxygen analysis in agreement with calculated values; IR (CCl<sub>4</sub>): 1806, 1778 (C=O), 1050 (C-O-O-C), 890 cm<sup>-1</sup> (O-O).-b) From pentane.-c) Crude product,  $n_D^{20} = 1.4413$ .-d) From methanol/ether (2:1).-e) Cathodic reduction potential by differential pulse polarography:  $E_{1/2} = -0.065V$  (vs. SCE).

The diacyl peroxide 9 was electrolysed with anodic and cathodic square pulses in methanol (Table 2) with 5 % octanoic acid and 5 % sodium octanoate; other supporting electrolytes could not be used, because they interfere with the Kolbe electrolysis<sup>6)</sup>.

Table 2: Product distribution in the electrolysis of dodecanoyl octanoyl peroxide (9) with anodic and cathodic square pulses.

Expt.	Frequency <sup>a)</sup> (cps)	yield (%) <sup>b)</sup>		
		Tetradecane	Octadecane	Docosane
1	5.0	5	8	4
2	1.0	8	12	6
3	0.2	10	17	8
4	0.5 <sup>c)</sup>	2	4	0.5
5	0.2 <sup>c)</sup>	2	4	1
6	0.2 <sup>d)</sup>	13	20	11

a) 4mmol 9 in 20 ml methanol at Pt-electrodes with 200 mA/cm<sup>2</sup>.-b) Gaschromatographical yield.-c) Interrupted after consumption of 9.-d) Mixed Kolbe-electrolysis of octanoic and dodecanoic acid (1:1).

When the electrolysis is terminated, as soon as 9 is consumed, the mixed coupling product is indeed favored (Expt. 4,5; the higher portion of tetradecane is caused by the supporting electrolyte). However, if one electrolyses until the carboxylate is totally converted, the product distribution is statistical (Expt. 1,2,3). This is probably, because the peroxide is faster reduced than the carboxylates are oxidized, they can diffuse into the solution and there be coupled in the usual, non statistical way.

Because of the unsatisfactory yield and selectivity in the electrolysis we looked at the thermal and photochemical decomposition of the peroxides. Thermolysis of the diacyl peroxide in solution produces often poor dimer yields<sup>7)</sup>; little is reported on neat thermal decompositions<sup>8)</sup>. Heating 9 without solvent for one hour at 90° C yields 29 % octadecane, 1 % symmetrical dimers, 32 % disproportionation products and 12 % esters. 10 reacts similar, but the portion of disproportionation product is even higher: 50 % at 110° C. Photolysis of 9 in methanol at 20° C, in benzene at 5° C or in pentane at -10° C did not improve the results of the thermolysis; 26-31 % octadecane and 34-43 % disproportionation products were formed, the esters decreased to 1 %, but the symmetrical dimers increased to 7-11 %.

Finally neat 9 was photolysed at different temperatures (Table 3), and here at -78° C the disproportionation product was distinctly reduced<sup>9)</sup>.

Table 3: Photolysis of neat dodecanoyl octanoyl peroxide<sup>a)</sup>

Products	yields (%) <sup>b)</sup>		
	25° C	-20° C	-78° C
1-Heptene, Heptane	15	9	3
1-Heptanol	6	6	3
1-Undecene, Undecane	18	12	3
1-Undecanol	6	6	3
Tetradecane	2	1	0.5
Octadecane	40	53	75
Decyl octanoate	1	1	1
Heptyl dodecanoate			
Docosane	2	1	0.5

a) 30-50 mg diacyl peroxide were irradiated 18-24 hours as crystalline film in a quartz tube with a low pressure mercury arc.-b) Gaschromatographical yields using a standard.

Table 4 summarizes the results for the low temperature photolysis of the peroxides 6-10.

Table 4: Photolysis<sup>a)</sup> of neat diacyl peroxides 6-10 at -78° C

Products <sup>b)</sup>	Diacyl peroxide (yield, %) <sup>c)</sup>				
	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
Unsymmetrical dimer	50	65	72	75	75
Symmetrical dimers	0.5	0.5	1	1	1
Disproportionation products	14	5	2	6	8

a) Reaction condition as in a) Table 3.-b) Additionally 1-6% ester and 3-7% alcohols were formed.-c) Gaschromatographical yields using a standard.

By photolysis of unsymmetrical aliphatic diacyl peroxides different alkyl radicals can be selectively coupled. The yields in unsymmetrical dimer (based on the carboxylic acid to prepare the peroxide) exceed those of the mixed Kolbe electrolysis. Additionally the product purification is facilitated as nearly no symmetrical dimers are produced.

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