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Z/E-Isomerization of Unsaturated Carboxylic Acids during the Kolbe Electrolysis*

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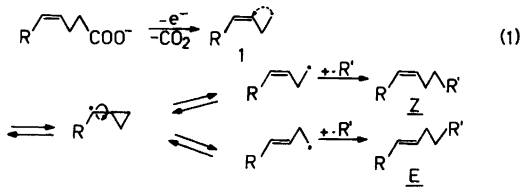
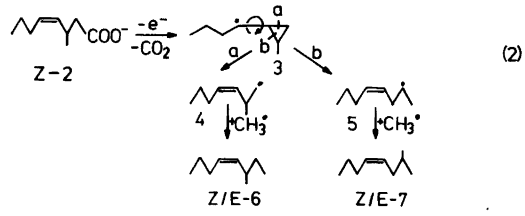
Z-4-Enoic acids partially isomerize to *E*-configurated products in the Kolbe electrolysis. The results from methyl and deuterium labelled carboxylic acids *2* and *16* support an isomerization *via* a reversible ring closure to cyclopropylcarbinyl radicals. The double bonds of *Z*-N-enoic acids with N≥5 fully retain their configuration in the Kolbe electrolysis; for N=6, 7 cyclic products are formed to some extent, which is in accord with the reactivity of 5- and 6-alkenyl radicals.

The Kolbe electrolysis has been successfully applied to the synthesis of pheromones.[2a–c] (for other pheromone syntheses, see Ref. 2d.). As the efficiency of synthetic pheromones to lure insects is very much influenced by the presence of the other geometric isomer,[3] it is the aim of every pheromone synthesis to obtain the olefins configurationally pure. Surprisingly, in the Kolbe syntheses of the *Cabbage looper* and the *Douglas fir tussock moths* pheromones: *Z*-7-dodecenyl acetate and *Z*-6-heneicosen-11-one, a double bond isomerization of the γ,δ-unsaturated carboxylic acid occurred.[4] Starting from pure monomethyl *Z*-4-octene dioate 6–15 % of *E*-configurated coupling products were found. As the recovered half ester was not isomerized, it was assumed that the *Z/E*-conversion occurred after the anodic decarboxylation at the alkenyl radical stage. The isomerization can only take place, when free rotation is possible by decoupling of the π-bond. The most plausible way for that is the reversible, intramolecular cyclization of the intermediate γ-alkenyl radical *1* (eqn. (1)). Such cyclizations have been found in Kolbe electrolyses [5a] (the coelectrolysis of *E*-4-nonen-6-ynoic acid with methyl glutarate afforded 33 % methyl 5-cyclopropyl-6-nonynoate [5b]) and are well known for alkenyl radicals generated from other sources.[6]



(1)



(2)

If a cyclopropylcarbinyl radical is an intermediate, it should be detectable by an appropriate labelling of the unsaturated carboxylic acid, *e.g.* by a β-methyl group in *2* (eqn, (2)). The ring opening of the cyclopropylcarbinyl radical *3*, which is now unsymmetrical, leads to a primary *4* and secondary radical *5*, depending on the position of the ring opening at *a* or *b*. *4* and *5* could be coupled with methyl radicals generated by coelectrolysis with acetic acid to afford *6* and *7*.

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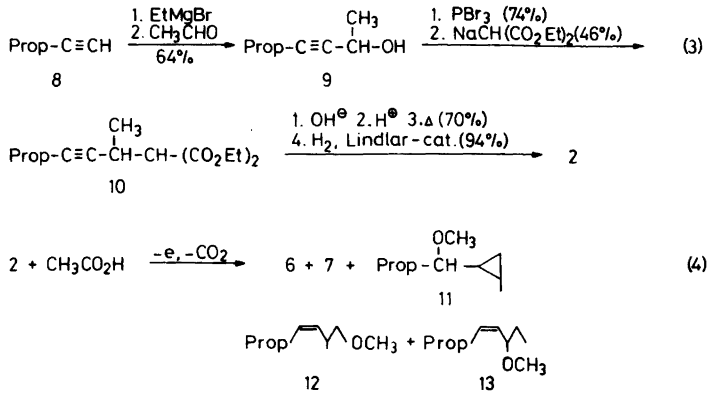


RESULTS

2 was prepared according to eqn. (3) from 1-pentyne (*8*). *8* was added to acetaldehyde to yield 64 % alcohol *9*, which was converted to the bromide and this substituted by sodio diethyl malonate to *10*. *10* was decarboxylated after hydrolysis and hydrogenated with a Lindlar catalyst to *2*. The overall yield of *2* was 14 %, the admixture of *E*-isomers was, as determined by capillary GLC, between 0–0.4 %. To make the product analysis simple, *2* was coelectrolyzed with an excess of acetic acid. This way only the unsymmetrical coupling products *6* and *7* should be yielded, besides ethane, whilst no dimers of *4* or *5* are expected because of the high methyl radical concentration. The electrolysis products (eqn. (4)) and their yields under different reaction conditions are summarized in Table 1.

The products were identified by capillary GLC-MS and ^{1}H NMR spectra or comparison with authentic reference compounds. After hydrogenation the four GLC peaks of *Z/E-6* and *7* merged to two isomeric methyloctanes. A reference sample for *7* was prepared by alkylation of lithio 1-pentyne with i-butylbromide to *14*, which was hydrogenated on a Lindlar catalyst to *Z-7*. *11* was obtained according to eqn. (5) by cyclopropanation of crotonaldehyde with the Simmons-

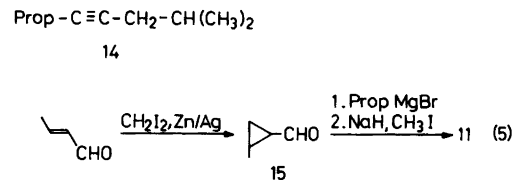
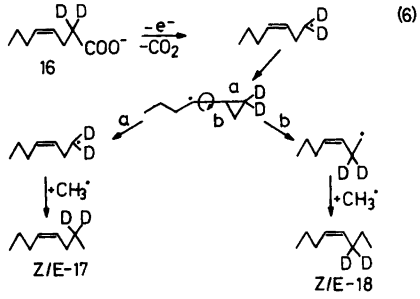


Table 1. Products of the mixed Kolbe electrolysis between *2* and acetic acid (molar ratio 1:10) at different conditions.

Current density (mA/cm^2) [a]	Temp. (°C)	Yield *6* (%)	*Z/E*-Ratio of *6*	Yield *7* (%)	Yield [b] *11* (%)
200	34	34	71/29	7	20
100	−16	35	91/9	2	18
120	0	19	88/12	2	31
120	0–5	21	90/10	2	30
250	25–27	46	85/15	8	7
200	25–30	50	85/15	8	5
200	40	38	79/21	8	16
250	40–43	42	80/20	12	10
200	44	37	75/25	12	14
110	46	40	70/30	21	7
250	60	43	78/22	16	7

[a] Degree of neutralization 5 %. [b] The yield of *12* and *13* was between 2 and 4 %.



(6)

Smith reagent. Subsequently the impure cyclopropanecarboxaldehyde *15*, which was too labile to purify by distillation, was added to propyl magnesiumbromide and the alcohol obtained was methylated with a 20-fold excess of sodium hydride and methyliodide to *11*.

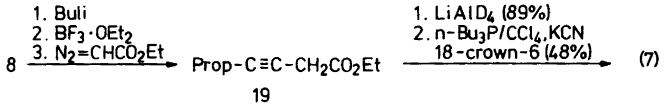
In order to exclude a possible influence of the methyl group in the ring opening of the cyclopropylcarbinyl radical,[7] the dideuterated carboxylic acid *16* (eqn. (6)) was coelectrolyzed with a 10-fold excess of acetic acid. Electrolysis products were to more than 85 % the alkenes *17* and *18* and contained, contrary to the electrolysis with *2*, only small amounts of methyl ethers. The ratio *17:18* was about 95:5; the portion of isomerized *E-17,18* is shown in Table 2. The amount of *18* was determined in two ways by MS and ^{1}H NMR spectroscopy. For the MS analysis *17, 18* were converted by ozonization, oxidative work-up and methylation to methyl butyrate; in the mass spectrometer this forms by a McLafferty rearrangement the fragment: $X_2C{=}C(OH){=}OCH_3^+$ as base peak: [*m/e*=74 (X=H), 76 (X=D)]. From the intensities of *m/e*=76, 74 the portion of *18* was calculated to be 5 %. From the integration of the ^{1}H NMR signals of a carefully purified sample of *17, 18* the ratio of *17:18* was determined to be 94:6. A control experiment confirmed that *16* did not exchange deuterium under the electrolysis conditions. *16* was prepared from 1-pentyne (*8*) according to eqn, (7). *8* was converted to tris(1-pentynyl)bor-

Table 2. Portion of *E-17/18* in the coelectrolysis of *16* with acetic acid (1:10) at different reaction conditions.

Temp. (°C)	Current density (mA/cm^2)	Portion of *E-17/18* (%)
37	200	5.0
39	120	5.8
45	160	8.7
48	170	9.5
52	180	11.5

ane which afforded with diazo ethyl acetate [8] 30 % ethyl 3-heptynoate (*19*). Subsequent reduction with $LiAlD_4$ and reaction with tributylphosphine/KCN under phase transfer conditions [9] yielded after column separation 48 % of the nitrile *20*, which was hydrolyzed and hydrogenated with a Lindlar catalyst to *16*, this *Z*-enoic acid had less than 1 % of the *E*-isomer admixed.

We were next interested in whether similar isomerizations, as found with *2* and *16*, occurred with *Z*-enoic acids *21*, where the distance between the double bond and the carboxyl group was increased. The electrolysis of *21* (*n*=3 to 7) with a 10-fold excess of acetic acid afforded the products *22–25* (eqn. (8), Table 3); the effect of the temperature is shown in Table 4. In all cases, no *Z/E*-isomerization was observed but cyclic products *23* were found for *21* (*n*=4, 5). The portion of Non-Kolbe products: *24, 25* increased with decreasing acidity of the electrolyte. For comparison with the *Z*-enoic acid *2 E-21* (*n*=2) was coelectrolyzed with acetic acid. It yielded 70 % 4-decene, which contained only 2 % of the *Z*-isomer. The products were identified by ^{1}H NMR and mass spectroscopy, *23* and *25* (*n*=4) by authentic reference compounds. Authentic *23* (*n*=4) was prepared by addition of cyclopentyl magnesiumbromide to 2-heptanone, dehydration of the alcohol and subsequent hydrogenation. *25* (*n*=4) could be obtained by reaction of cyclo-



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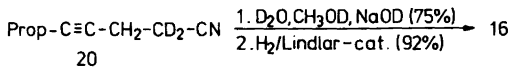
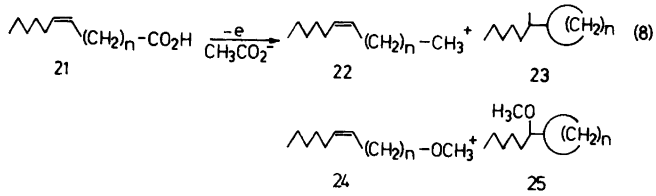




pentyl magnesiumbromide with hexanal and methylation of the alcohol. The carboxylic acids *21* were yielded by alkylation of 1-heptyne with 1,n-chlorobromoalkanes, subsequent substitution to the nitrile and its hydrolysis to the alkynoic acids *26* [*26* (*n*=3) 56 %; (*n*=4) 58 %]; furthermore by alkylation of 1-heptyne with 6-bromohexanoic acid [*26* (*n*=5) 70 %] or with 7-bromo-1-heptanol followed by CrO_3-oxidation [*26* (*n*=6) 34 %]. The alkynoic acids were then hydrogenated with a Lindlar catalyst to *21*.

DISCUSSION

The methyloctene *7* and the cyclopropylcarbinyl methyl ether *11* support the assumption that the double bond isomerization is caused by reversible cyclization of the intermediate alkenyl radical. A mechanism is proposed in eqn, (9).

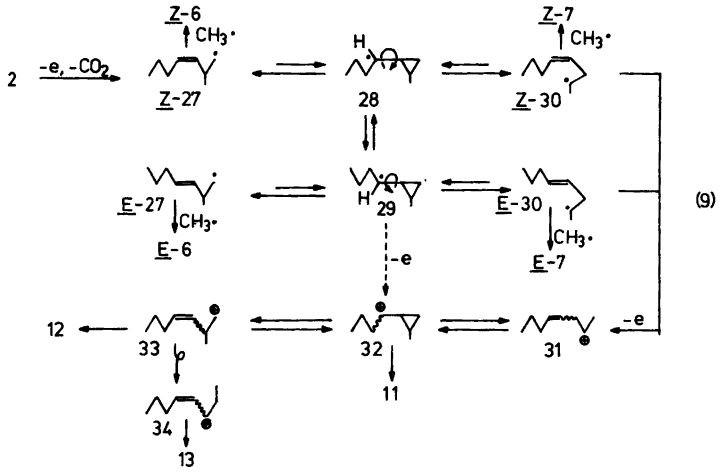
2 is decarboxylated to the alkenyl radical *Z-27*, which can couple with CH_3 to *Z-6* or cyclize to the cyclopropylcarbinyl radical *28*,[15a,b] free rotation around the single bond interconverts *28* and *29*, subsequent fast ring opening of the cyclopropylcarbinyl radicals [10b,11] yields *Z-27*, *30* and *E-27*, *30*, that react with the CH_3 radicals from acetic acid to *Z-6*, *7* and *E-6*, *7*. The *Z*:*E*-ratio of *7* (25:75) possibly reflects the thermodynamic equilibrium between *E*- and *Z-30*. The secondary alkenyl radicals *30* are to some extent oxidized to the alkenyl cation *31*, that can rearrange to *32* and *33*,[12] a subsequent methyl shift converts the primary cation *33* partly to its isomer *34*. *32*, *33*, *34* solvolyze to the methyl ethers *11*–*13*. The oxidation of *28*, *29* to *32* seems to be a less important reaction path to the Non-Kolbe products. With *16*, where only a cyclopropylcarbinyl- and a primary alkenyl radical are intermediates, the alkenes *17*, *18* are the

Table 3. Coelectrolysis of *Z-21* with acetic acid (1:10); reaction conditions and products.

Z-21 *n*	Current density [mA/cm^2]	*T* [°C]	Yield (%) *22*	*23*	*24*	*25*	Rates for ring closure [6b] (s^{-1})
3	200	53	68	–	9	–	7×10^{-1}
4	160	52	46	21	–	5	3.6×10^{5}
5	175	52	65	5	6	–	1.1×10^{4}
6	160	50	72	–	7	–	3.0×10^{2}
7	160	48	73	–	4	–	–

Table 4. Effect of temperature on the product distribution in the Kolbe electrolysis of *Z-21* (*n*=4) with acetic acid.

Temp. (°C)	Current density [mA/cm^2]	Rel. yield (%) *22*	*23*	*24*	*25*
18	100	75	18	2	5
49	170	62	29	1	8
52	160	64	29	–	7



predominant products, whilst the Non-Kolbe products are considerably decreased. Primary radicals, as *E,Z-27,* are normally not oxidized in a Kolbe electrolysis. From the mechanism, it is to be expected that there is a relation between the degree of *Z/E*-isomerization and the amount of *7* and, as Fig. 1 shows, this is indeed the case. Compared to the degree of isomerization the yield of *7* appears to be too low. This could be due to the oxidative drain: *30*→*31* and/or the sterically favoured, predominant cyclization to *trans-28,* that then mainly opens to the primary radical *27.*[7] The latter is suggested by the temperature dependence of the isomerization and of the formation of *7* (see Table 1). Lowering the temperature reduces the portion of *7* much more than the isomerization, which is predicted for *trans-28,* whose selectivity of ring opening to the primary alkenyl radical increases with decreasing temperature.[7] Coupling products of *28* with CH_3. radicals are not to be expected as the equilibrium [*k*(ring-opening) 1.3×10^8 s^{-1}, *k*(cyclization) 1.8×10^4 s^{-1} [6b, 10, 11]] strongly favours the acyclic radicals.

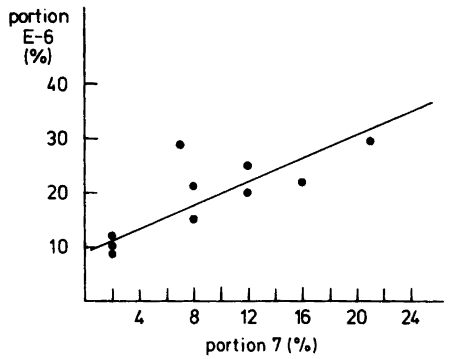
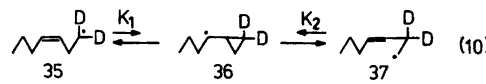
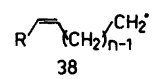


Fig. 1. Relation between double bond isomerization (*E-6*) and rearrangement (*7*).

The results with *2* are independently confirmed by those obtained with *16.* Here 5–11 % of double bond isomerization are accompanied by 4–8 % of rearranged products. As with *2* double bond isomerization increases with temperature. The effect of the methyl substituent in *2*, favouring the unrearranged product, is here excluded. The considerable decrease in Non-Kolbe products indicates that with *2* the secondary alkenyl radicals *30* are partly further oxidized, thus favouring the formation of *6* over this of *7.* With *2* the ratio *7*:*E-6* is 0.17 to 0.72 whilst with *16* the corresponding ratio *18*:*E-17, 18* is 0.72 to 0.8. If one assumes the same equilibrium constant for *35*⇄*36* and *37*⇄*36* (eqn. (10)) one can calculate from the ratio *18*:*E-17, 18* that about 40–30 % *Z-35, 37* and about 60–70 % *E-35, 37* alkenyl radicals are formed in the reversible cyclization. That the *E*-configurated radicals preponderate is also demonstrated by the results with *E-21* (*n*=2), where only 2 % isomerization to the





Z-alkene is found.

Extension of the Kolbe electrolyses to enoic acids *21*, with varying distances between the radical site and the double bond, shows that the *Z*/*E*-isomerization is limited to γ,δ-unsaturated carboxylic acids. For *21* ($n \geq 3$) no isomerization is found, except for a small to moderate portion of cyclic products with $n=5$, 4. These results are readily explained by the proposed mechanism [eqn. (9)]. The cyclization of the alkenyl radicals *38* ($n=3,6$) is 10^5 to 10^2 times slower than this of *38* ($n=2$),[6b] so it is sensible that the cyclization and thus the isomerization cannot compete with the Kolbe coupling. The radicals *38* ($n=4,5$) cyclize as fast as *38* ($n=2$), however, the ring opening of the cyclohexyl- and cyclopentylcarbinyl radicals is much slower, due to the lack of steric strain, than this of the cyclopropylcarbinyl radical,[13] so that the cyclic products are trapped by Kolbe coupling before ring opening.

The results demonstrate that the Kolbe electrolysis is a suitable method for the stereospecific introduction of olefinic units *via* enoic acids, except for γ,δ-unsaturated carboxylic acids, whose double bond can isomerize at the alkenyl radical stage by a reversible cyclization *via* cyclopropylcarbinyl radicals.

EXPERIMENTAL

IR spectra were recorded with the Perkin-Elmer spectrometers 177 and 441, the ^{1}H NMR spectra with the Jeol PMX 60, Varian HA 100 and Bruker WM 300 instruments, TMS was used as internal standard. Mass spectra were obtained with the Varian CH 7 model, the Varian GLC-MS System MAT 111 and for capillary GLC-mass spectroscopy the Varian MAT CH 7 A.

Gas chromatography. GLC analyses were done with the Varian Gaschromatograph 2740, combined with the Perkin-Elmer recorder 56, the Spectra Physics Integrator Vidar 6300 and the following columns; column 1: 1.7 m glass, Ø 2 mm, 4 % FFAP on Chromosorb W-DMCS; column 2: as 1 but with 4 % OV 225; column 3: 3 m glass, Ø 2 mm, 8 % SE 52 on Chromosorb W-DCMS. The *Z*/*E*-isomers were analyzed with the Varian Gaschromatograph 3700 combined with the Kipp and Zonen recorder BD 7, the Spectra Physics integrator Minigrator Autolab and the following capillary glass columns; column 4: 45 m, inner Ø 0.2 mm, outer Ø 0.8 mm, 0.3 % SE 52: as 4 but 36 m; nitrogen served as carrier gas. For preparative GLC the Varian instrument P-90 was used, combined with a Kontron recorder and the following columns; column 6: 3 m glass, Ø 8 mm, 15 % SE 30 on Chromosorb W-DMCS; column 7: 3 m, Ø 8 mm, 15 % FFAP on Chromosorb W-DMCS; carrier gas was hydrogen. For gas chromatographic analyses the carboxylic acids were converted to their methyl esters with diazomethane.[14]

The electrolysis cells were 50 and 150 ml double-walled glass vessels with reflux condenser and a Teflon plug with holes for the thermometer and the electrode feeders. The electrodes were 5 cm^2 platinum sheets (0.05 mm). Current was supplied by the Heri potentiostat/galvanostat TNS 300–1500. Cooling was achieved with the Hoco Kryostat Typ HM 60. All solvents were distilled and if necessary dried. The electrolyses were conducted in analytically pure methanol (Merck).

Preparation of Z-3-Methyl-4-octenoic acid (2). 3-Heptin-2-ol (9). In a 1 l three-necked flask with thermometer, dropping funnel, reflux condenser and gas inlet 14.5 g (0.6 mol) magnesium turnings in 50 ml ether were reacted with 64 g (0.59 mol) ethyl bromide, added dropwise in 400 ml ether. To this solution within 2 h and intense stirring 40 g (0.58 mol) 1-pentyne (*8*) were added and after standing overnight excess *8* was removed by distillation. Then with stirring 24 g (0.55 mol) acetaldehyde were added dropwise. After 1 h reflux it was hydrolyzed with ice and an NH_4Cl-solution, extracted with ether, the ether washed with an $NaHSO_3$- and an $NaHCO_3$-solution and dried (Na_2SO_4). Distillation afforded 41.4 g (64 %) *9*, b.p. 75–78 °C, 19 Torr, n_D^{25}=1.4455 (lit.[15] 1.4454). ^{1}H NMR ($CDCl_3$): δ 4.45 (q, 1H), 2.15 (s, 1H), 2.1 (t, 2H), 1.5 (m, 2H), 1.35 (d, 3H), 0.9 (t, 3H). MS: [*m*/*e* (%, rel. int.)]: 112 (4), 97 (98), 43 (100).

Diethyl-2-(3-heptynyl)-malonate (10). 30 g (0.27 mol) *9* in 50 ml ether were added slowly to 3.5 ml dry pyridine and 24.4 g (0.09 mol) PBr_3 in 300 ml dry ether cooled to −20 °C. After warming to room temperature, the ether was separated and distilled to yield 35 g (74 %) bromide; b.p. 62–64 °C, 15 Torr, n_D^{25}=1.4826 (lit.[15] n_D^{25}=1.4825). To a solution of 4.8 g (0.21 mol) sodium and 33 g (0.2 mol) diethyl malonate in 80 ml dry ethanol, 35 g (0.2 mol) of the bromide were added slowly under stirring and reflux. After 2 h ethanol is distilled off, water added and extracted with ether. Distillation yielded 23.5 g (46 %) *10*, b.p. 81–86 °C/0.1 Torr IR (film): 2960–2820, 2220, 1750–1720 cm^{-1}. ^{1}H NMR ($CDCl_3$); δ 4.2 (q, 4H), 3.3 (m, 1H), 2.1 (m, 1H), 1.7–1.2 (m, 4H), 1.2 (t, 6H), 1.15 (d, 3H), 0.9 (t, 3H). MS [*m*/*e* (%, rel. int.)]: 255 (0.5), 226 (3), 181 (88), 153 (100). Anal.

$C_{14}H_{22}O_4$: C, H.

2. 23.5 g (93 mmol) *10* and 18 g (0.32 mol) KOH in 22 ml water and 44 ml ethanol are refluxed for 4 h. Then ethanol was distilled off, acidified to pH 2 with HCl and extracted with ether (5×), the ether dried and evaporated to yield 15.6 g (85 %) malonic acid, which was heated for 4 h to 180 °C. Subsequent distillation afforded 10.0 g (82 %) ynoic acid, b.p. 149–151 °C, 15 Torr. IR (film): 3200–2500, 2960–2870, 2240 (weak), 1730–1700 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.8 (s, 1H), 2.45 (m, 2H), 1.4 (m, 4H), 1.15 (d, 3H), 0.9 (t, 3H). MS as ethylester [*m/e* (%, rel. int.)]: 182 (7), 167 (22), 154 (62), 95 (100).

2.0 g (12.6 mmol) ynoic acid and 50 mg Lindlar catalyst [16] in 20 ml heptane, to which three drops freshly distilled quinoline were added, were hydrogenated for 6 h at 0 °C. Bulb-to-bulb distillation afforded, after separation of the catalyst, at 110 °C, 14 Torr, 1.93 g (97 %) *2*, portion of *E*-isomer 0.3 % (column 4). IR (film): 3200–2500, 2960–2850, 1710 cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.15 (s, 1H, exchangeable with D_2O), 5.25 (m, 2H), 3.02 (m, 1H), 2.25 (d, 2H), 2.05 (m, 2H), 1.32 (m, 2H), 1.03 (d, 3H), 0.9 (t, 3H). MS, as methylester [*m/e* (%, rel. int.)]: 170 (2), 139 (5), 96 (65, McLafferty), 55 (100). Anal. $C_9H_{16}O_2$: C, H.

Electrolyses. 1.6–8.3 mmol *2* and a 10-fold excess of acetic acid, dissolved in 30 ml methanol and neutralized as indicated in Table 1 with KOH were electrolyzed until pH 8 was reached. The electrolyte was then extracted with pentane, the pentane extract washed with K_2CO_3-solution, then water and dried ($MgSO_4$). GLC analysis and GLC-MS combination was done with column 4. By preparative GLC *Z/E- 6, 7* could be separated from *11–13*.

Z/E-3-Methyl-4-octene (6). IR (film): 2980–2850, 1690, 1645, 1450, 1370, 960, 725 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.25 (m, 2H), 2.05 (m, 3H), 1.25 (m, 4H), 0.9 (m, 9H). MS [*m/e* (%, rel. int.)]: 126 (12, M), 111 (1), 97 (32), 55 (100). Anal. C_9H_{18}: C, H.

Z/E-2-Methyl-4-octene (7). MS [*m/e* (% rel. int.)]: 126 (15, M), 111 (13), 98 (7), 97 (6), 55 (100).

2-Methyl-1-methoxy-3-heptene (12). MS [*m/e* (%, rel. int.)]: 142 (2, M), 127 (50), 113 (8), 111 (7), 32 (100).

1-(1-Methoxybutyl)-2-methylcyclopropane (11). MS [*m/e* (%, rel. int.)]: 142 (0.5, M), 127 (8), 110 (4), 99 (100).

3-Methoxy-4-octene (13). MS [*m/e* (%, rel. int.)]: 142 (0.5, M), 113 (65), 110 (5), 99 (12), 32 (100). Anal. for the *11–13* mixture $C_9H_{18}O$: C, H.

Hydrogenation of the electrolysis products. The pentane extract was hydrogenated (10 mg 10 % Palladium on charcoal) 2 h at 0 °C and analyzed by GLC-MS (column 4, 80 °C).

3-Methyloctane from Z/E-6. MS [*m/e* (%, rel. int.)]: 128 (2, M), 113 (1), 99 (12), 57 (100).

2-Methyloctane from Z/E-7. MS [*m/e*, (%, rel. int.)]: 128 (1, M), 113 (2), 85 (13), 43 (100).

2-Methyl-1-methoxyheptane from 12. MS [*m/e* (%, rel. int.)]: 144 (0.1, M), 129 (4), 101 (20), 87 (30), 73 (100).

3-Methoxyoctane from 13. MS [*m/e* (%, rel. int.)]: 144 (0.1, M), 115 (20), 83 (38), 73 (100).

11 remained unchanged.

Preparation of Z-2,2-dideutero-4-octenoic acid (16). *Ethyl 3-heptynoate (19)*. To a solution of lithium-1-pentyne (from 0.25 mol 1-pentyne and 0.25 mol butyllithium in 100 ml tetrahydrofuran) held at −20 °C were added, gradually, 0.33 mol boron trifluoride etherate. The resulting mixture was stirred for 0.5 h at −20 °C and then 12.16 g (0.107 mol) ethyl diazoazetate [18] were slowly added. After stirring for 1.5 h water was added, the mixture stirred (*ca.* 20 min) then poured into ice water (200 ml). It was extracted with ether (3×100 ml), the extracts dried (Na_2SO_4), the solvent evaporated and distilled to afford 4.0 g (0.026 mol, 24 %) ethyl 3-heptynoate,[19] b.p. 83–84 °C/14 Torr. (lit.[19] 83–85 °C/15 Torr), n_D^{25}=1.4465 (lit.[19] n_D^{25}=1.4470). IR (film): 2950–2850, 2220, 1780–1720 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.2 (q, 2H), 3.2 (s, 2H), 2.17 (m, 2H), 1.5 (m, 2H), 1.25 (t, 3H), 0.9 (t, 3H). MS [*m/e* (%, rel. int.)]: 154 (10, M), 126 (80, McLafferty), 125 (42), 109 (25), 79 (100).

1,1-Dideutero-3-heptyn-1-ol. To a solution of 200 mg (4.76 mmol) of lithium aluminium deuteride in 30 ml of ether were introduced at a rate such as to produce gentle reflux 1 g (6.5 mmol) *19*. Then water was added dropwise, the mixture was poured into 100 ml of ice water acidified with 50 ml of 10 % sulfuric acid. The usual work-up yielded 0.741 g (89 %) 1,1-dideutero-3-heptyn-1-ol, b.p. 85–90 °C/14 Torr. IR (film): 3600–3200, 2960–2800, 2200, 2100, 1150–1040 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.2 (s, 1H), 2.4 (s, 2H), 2.15 (m, 2H), 1.5 (m, 2H), 0.95 (t, 3H). MS [*m/e* (%, rel. int.)]: 114 (7, M), 99 (4), 95 (3), 67 (100).

1,1-Dideutero-1-cyano-3-heptyne (20). To a mixture of 10.5 g (0.161 mol) potassium cyanide and 1.7 g (6.5 mmol) 18-crown-6 in 40 ml acetonitrile 3.68 g (32.3 mmol) 1,1-dideutero-3-heptyn-1-ol and 7.18 g (35.5 mmol) tributylphosphine in 20 ml acetonitrile are added, followed under cooling in dry ice methanol by the dropwise addition of a solution of 5.5 g (35.5 mmol) carbon tetrachloride in 10 ml acetonitrile. The mixture is stirred at room temperature for 24 h,

diluted with diethyl ether (300 ml) and washed with 70 ml aqueous 10 % nitric acid. After the addition of 10 ml carbon tetrachloride, the mixture is washed with water (2×100 ml), saturated aqueous sodium chloride (100 ml) and dried (Na_2SO_4). The crude product is purified by TLC on silica gel (Merck, CH_2Cl_2/CH_3CCO_2Et, 8:1) to yield 1.9 g (48 %) *20*. IR (film): 2960–2850, 2220, 2120 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.5 (s, 2H), 2.17 (m, 2H), 1.5 (m, 2H), 0.9 (t, 3H). MS [*m/e* (%, rel. int.)]: 124 (2, M), 123 (20), 122 (40), 108 (48), 79 (100).

2,2-Dideutero-4-octynoic acid. A mixture of 1.9 g (15,4 mmol) *20*, 4.2 g of 30 % sodium hydroxide-d_1 and 5 ml of methanol-d_4 was refluxed for 96 h. Then the solvent was evaporated to dryness, the residue dissolved in 20 % aqueous ethanol and twice extracted with ether. After acidification of the aqueous layer with dilute hydrochloric acid the precipitated organic acid was extracted with ether. Distillation afforded 1.53 g (70 %) 2,2-dideutero-4-octynoic acid, b.p. 138 °C/14 Torr. IR (film): 3500–2500, 2960–2850, 2200 2130–2070, 1740–1670 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.5 (s, 1H), 2.48 (s, 2H), 2.05 (m, 2H), 1.5 (m, 2H), 0.9 (t, 3H). MS [*m/e* (%, rel. int.)]: 156 (0.6, M), 141 (3), 128 (33), 125 (10), 99 (100). Anal. $C_8H_{12}D_2O_2$: C, H+D.

Z-2,2-Dideutero-4-octenoic acid (Z-16). 720 mg (5 mmol) 2,2-dideutero-4-octynoic acid and 30 mg Lindlar catalyst [16] in 15 ml heptane, to which three drops freshly distilled quinoline were added, were hydrogenated for 2 h at 0 °C. Bulb-to-bulb distillation afforded after separation of the catalyst at 130 °C, 14 Torr, 710 mg (97 %) *Z-16*, portion of *E*-isomer *ca.* 0.1 % (column 4). IR (film): 3200–2500, 2960–2850, 1720–1690, 1680–1650 cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.1 (s, 1H), 5.35 (m, 2H), 2.35 (d, 2H), 2.05 (q, 2H), 1.4 (m, 2H), 0.9 (t, 3H). MS, as methylester [*m/e* (%, rel. int.)]: 158 (3, M), 127 (20), 126 (56), 82 (65, McLafferty), 76 (100).

Electrolyses of Z-16. 1.2–2.1 mmol *Z-16* and 10-fold excess of acetic acid, dissolved in 25 ml methanol and to 5 % neutralized with KOH were electrolyzed until pH 8 was reached. The electrolyte was then extracted with pentane, the pentane extract washed with K_2CO_3-solution, water and dried ($MgSO_4$). GLC analysis and GLC-MS combination was done with column 4. By preparative GLC the mixture of *17* and *18* was purified for ^1H NMR. ^1H NMR ($CDCl_3$): δ 5.35 (m, 2H), 2.0 (m, 3.88 H, portion of D 6 %), 1.36 (m, 2.12 H, portion of D 94 %), 0.9 (t, 6H). MS [*m/e* (%, rel. int.)]: 114 (10, M), 99 (1), 85 (14), 83 (9), 41 (100).

Ozonization of Z/E-17, 18. The *Z/E*-mixture was treated in 5 ml pentane and 5 ml methanol at −40 °C with 2 mmol ozone. Work-up with CrO_3 in acetone afforded butyric acids, which were esterified with diazomethane. The methyl butyrates were analyzed with the capillary GLC-MS combination. From the ratio of the peaks *m/e*=-74/74 (McLafferty) the ratio *17/18* was calculated to be 95/5.

Control experiment for deuterium-exchange of Z-16. A mixture of 20 mg (0.14 mmol) *Z*-16 and 84 mg acetic acid (1.4 mmol) in 15 ml methanol, neutralized to 5 % with KOH, was stirred for 1.5 h. The GLC-MS analysis showed for the reisolated *Z-16* no reduced deuterium content.

Preparation of Z-21 (n=*3–7*). Z-21, n=*3,4*. To a solution of 9.6 g (0.1 mol) 1-heptyne in 100 ml dry tetrahydrofuran and 10 ml HMPT, cooled to −20 °C, 0.1 mol *n*-butyllithium in hexane were injected under stirring. After 40 min 0.1 mol 1-bromo-4-chlorobutane (*n*=3) or 1-bromo-5-chloropentane (*n*=4), respectively, were added dropwise, hydrolyzed (150 ml water) after 12 h and extracted with ether (3×100 ml). Distillation at 78 °C/0.4 Torr afforded for *n*=3 8.5 g (65 %) chloride and at 81 °C/0.3 Torr for *n*=4 13.3 g (71 %) chloride, respectively. The products contained *ca.* 8 % of bromide. MS for *n*=3 [*m/e* (%, rel. int.)]: 174/172 (0.5 M), 159/157 (3), 145/143 (10), 81 (100). MS for *n*=4 [*m/e*, (%, rel. int.)]: 188/186 (0.5, M), 173/171 (2), 159/157 (18), 67 (100).

A mixture of 49 mmol chloride (*n*=3) and 8 g sodium cyanide or 60 mmol chloride (*n*=4) and 9.8 g sodium cyanide in 20 ml of water and 120 ml ethanol was stirred and refluxed for 48 h. The residue was filtered off and 100 ml solvent evaporated. To the solution of 1-cyano-4-decyne (*n*=3) or 1-cyano-5-undecyne (*n*=4) in 50 ml ethanol was added 0.15 mol sodium hydroxide and refluxed for 96 h. The usual work-up and distillation afforded 6.9 g (78 %) ynoic acid (*n*=3) at 138 °C/0.3 Torr or 9.8 g (83 %) ynoic acid (*n*=4) at 145 °C/0.3 Torr.

Ynoic acid, *n*=3: IR (film): 3200–2500, 2950–2820, 1720–1690 cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.1 (s, 1H), 2.15 (m, 6H), 1.4 (m, 8H), 0.9 (t, 3H). MS, as methylester, [*m/e* (%, rel. int.)]: 196 (3, M), 181 (4), 165 (4), 164 (3), 122 (18), 80 (100).

Ynoic acid, *n*=4: IR (film): 3200–2500, 2950–2820, 1720–1690 cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.6 (s, 1H), 2.15 (m, 6H), 1.4 (m, 10H), 0.9 (t, 3H). MS, as methylester, [*m/e* (%, rel. int.)]: 210 (0.5, M), 195 (1), 179 (3), 178 (4), 136 (15), 80 (100). The hydrogenation with Lindlar catalyst afforded 91 % *Z-21 n*=3 and 97 % *Z-21 n*=4.

Z-21, n=3: B.p. 130 °C/0.3 Torr. IR (film): 3200–2500, 2950–2850, 1725–1690, 730–675 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.8 (s, 1H), 5.35 (m,

2H), 2.35 (t, 2H), 2.05 (m, 4H), 1.7 (m, 2H), 1.25 (m, 6H), 0.9 (t, 3H). MS, as methylester, [*m/e* (%, rel. int.)]: 198 (2, M), 166 (11), 124 (28), 74 (100). Anal. $C_{11}H_{20}O_2$: C, H.

Z-21, n=4: B.p. 138 °C/0.3 Torr. IR (film): 3200–2500, 2950–2850, 1725–1690, 730–675 cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.0 (s, 1H), 5.25 (m, 2H), 2.35 (t, 2H), 2.05 (m, 4H), 1.65 (m, 2H), 1.4–1.2 (m, 8H), 0.9 (t, 3H). MS, as methylester, [*m/e* (%, rel. int.)]: 212 (4, M), 181 (10), 180 (18), 138 (28), 74 (100). Anal. $C_{12}H_{22}O_2$: C, H.

Z-21, n=*5*: 3.84 g (40 mmol) 1-heptyne was added to a stirred suspension of 40 mmol lithiumamide in 100 ml liquid ammonia and the mixture was stirred under reflux for 1 h. After addition of 10 mmol 6-bromohexanoic acid in 30 ml tetrahydrofuran, the mixture was refluxed for 8 h and then allowed to evaporate. Dilute hydrochloric acid was added and the mixture was extracted with ether. The washed and dried (Na_2SO_4) solution was evaporated under reduced pressure and the residue distilled at b.p. 160 °C/0.3 Torr to afford 1.47 g (70 %) ynoic acid.

IR (film) 3200–2500, 2950–2820, 1720–1690. ^1H NMR ($CDCl_3$): δ 10.0 (s, 1H), 2.37 (t, 2H), 2.15 (m, 4H), 1.68 (m, 2H), 1.40 (m, 10H), 0.9 (t, 3H). MS, as methylester [*m/e* (%, rel. int.)]: 224 (2, M), 193 (6), 192 (6), 150 (27), 94 (100).

The hydrogenation with Lindlar catalyst [16] afforded 99 % *Z-7*-tridecenoic acid-(*Z-21, n=5*), b.p. 150–154 °C/0.1 Torr, n_D^{27}=1.4522 (lit.[20] n_D^{27}=1.4526). IR (film): 3200–2500, 2960–2850, 1730–1670. ^1H NMR ($CDCl_3$) δ=11.0 (s, 1H), 5.35 (m, 2H), 2.35 (t, 2H), 2.05 (m, 4H), 1.65 (m, 2H), 1.4–1.2 (m, 10H), 0.9 (t, 3H). MS, as methylesters [*m/e* (%, rel. int.)]: 226 (1, M), 195 (5), 194 (7), 152 (15), 55 (100).

Z-21, n=*6*. *7-Bromoheptan-1-ol*. A mixture of 10 g heptane-1,7-diol and 50 ml 48 % HBr in 15 ml water was kept at 70–80 °C and extracted continuously with toluene for 16 h. From the extract 10.9 g (74 %) of 7-bromoheptan-1-ol, b.p. 75 °C/0.05 Torr (lit.[21] 111–112 °C/4 Torr) were yielded. IR (film) 3600–3100, 2930–2860, 1455–1425, 1245, 1050, 750–725 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.6 (t, 2H), 3.4 (t, 2H), 2.55 (s, 2H), 1.85 (m, 2H), 1.6–1.36 (m, 8H). MS [*m/e* (%, rel. int.)]: 178/176 (0.1, M), 150/148 (20), 55 (100).

8-Tetradecyn-1-ol. 5.2 g (60 mmol) 1-heptyne in 30 ml tetrahydrofuran were added to 0.12 mol lithiumamide in 100 ml liquid ammonia. After stirring for 1 h 5.85 g (30 mmol) 7-bromoheptan-1-ol in 30 ml tetrahydrofuran were added. The mixture was stirred under reflux for 8 h and then allowed to evaporate. Addition of dilute hydrochloric acid and extraction with ether gave by bulb-to-bulb distillation 4.07 g (65 %) alcohol, b.p. 120 °C/0.03 Torr. IR (film) 3600–3100, 2960–2850, 2200 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.6 (t, 2H), 2.06 (m, 4H), 1.8 (s, 1H), 1.6–1.2 (m, 16 H), 0.9 (t, 3H). MS [*m/e* (%, rel. int.)]: 210 (0.5, M), 192 (1), 67 (100).

8-Tetradecynoic acid. 4 g (19 mmol) 8-tetradecyn-1-ol in 57 mol acetic acid were stirred at 15–20 °C while a chromic acid solution (5.7 g, CrO_3 in 50 ml acetic acid) was gradually added. The acetic acid was evaporated under reduced pressure and water (100 ml) was added. The ether extracts were extracted with a sodium hydrogen carbonate solution. Acidification and distillation gave 2.26 g (53 %) ynoic acid, b.p. 155 °C/0.05 Torr. IR (film) 3200–2500, 2960–2850, 1730–1680. ^1H NMR ($CDCl_3$): δ=11.00 (s, 1H), 2.35 (t, 2H), 2.16 (m, 4H), 1.65 (m, 2H), 1.5–1.2 (m, 12H), 0.9 (t, 3H). MS, as methylester [*m/e* (%, rel. int.)]: 238 (0.5 M), 207 (2), 206 (2), 164 (17), 81 (100).

The hydrogenation with Lindlar [16] catalyst afforded 99 % (*Z*)-8-tetradecenoic acid (*Z-21, n=6*), b.p. 160 °C/0.1 Torr. IR (film) 3200–2500, 2960–2850, 1730–1670. ^1H NMR ($CDCl_3$): δ=11.0 (s, 1H), 5.35 (m, 2H), 2.37 (t, 2H), 2.05 (m, 4H), 1.62 (m, 2H), 1.4–1.2 (m, 12H), 0.9 (t, 3H). MS, as methylester, [*m/e* (%, rel. int.)]: 240 (3, M), 209 (18), 208 (23), 166 (27), 55 (100). Anal. $C_{14}H_{26}O_2$: C, H.

Z-21, n=*7*, oleic acid was purchased from Fa. Fluka.

Electrolyses of 21. 0.5 to 6.0 mmol *21* and a 10-fold excess of acetic acid, dissolved in 30 ml methanol and neutralized to 5 % with KOH were electrolyzed until pH 8 was reached. The electrolyte was then extracted with ether, the ether extract washed with K_2CO_3-solution and water and dried (Na_2SO_4). GLC analysis and GLC-MS combination was done with column 4, preparative GLC with column 6.

5-Undecene (Z-22, n=*3*). n_D^{20}=1.4296 (lit.[22] n_D^{20}=1.4285). IR (film): 2980–2830, 1640, 1450, 720–670 cm^{-1}. ^1H NMR ($CDCl_3$) δ=5.35 (m, 2H), 2.0 (m, 4H), 1.3 (m, 10H), 0.9 (t, 6H). MS [*m/e* (%, rel. int.)]: 154 (6, M), 125 (5), 111 (12), 55 (100).

Products of Z-21, n=*4*. 6-Dodecene (*Z-22, n=4*): n_D^{20}=1.4329 (lit.[23] n_D^{20}=1.4334). IR (film): 2980–2830, 1450, 720–670. ^1H NMR ($CDCl_3$): δ=5.37 (2H, m), 2.05 (m, 4H), 1.30 (m, 12H), 0.9 (t, 6H). MS [*m/e* (%, rel. int.)]: 168 (28, M), 140 (2), 139 (1), 125 (4), 55 (100).

2-Cyclopentylheptane (23, n=*4*). MS [*m/e* (%, rel. int.)]: 168 (4 M), 153 (1), 97 (100).

1-Cyclopentyl-1-methoxyhexane (25, n=*4*). MS [*m/e*, (%, rel. int.)]: 184 (6, M), 153 (7), 152 (18), 115 (100), 113 (75).

Products of 21, n=*5*. *6-Tridecene* (Z-22, n=*5*).

n_D^{20}=1.4368 (lit.[24] n_D^{20}=1.4367). IR (film): 2980–2830, 1640, 720–670 cm^{-1}. ^1H NMR ($CDCl_3$): δ=5.35 (m, 2H), 2.03 (m, 4H), 1.3 (m, 14H), 0.9 (t, 6H). MS [*m/e* (%, rel. int.)]: 182 (40, M), 154 (7), 139 (2), 74 (100).

2-Cyclohexylheptane (23, n=*5*). MS [*m/e* (%, rel. int.)]: 182 (25, M), 167 (1), 111 (37), 83 (70), 82 (100).

1-Methoxy-6-dodecene (24, n=*5*). MS [*m/e* (%, rel. int.)]: 198 (2, M), 169 (10), 167 (8), 166 (40), 73 (100).

6-Tetradecene (Z-22, n=*6*). IR (film): 2980–2830, 1720–1690, 1460–1430, 720 cm^{-1}. ^1H NMR ($CDCl_3$): δ=5.35 (m, 2H), 2.05 (m, 4H), 1.3 (m, 16H), 0.9 (t, 6H). MS [*m/e* (%, rel. int.)]: 196 (8, M), 168 (1), 153 (1), 55 (100). Anal. $C_{14}H_{28}$: C, H.

9-Octadecene (Z-22, n=*7*). IR (film): 2980–2830, 1460–1430, 720 cm^{-1}. ^1H NMR ($CDCl_3$): δ=5.35 (m, 2H), 2.05 (m, 4H), 1.3 (m, 24 H), 0.9 (t, 6H). MS [*m/e* (%, rel. int.)]: 252 (9, M), 224 (2), 209 (1), 83 (100). Anal. $C_{18}H_{36}$: C, H.

Preparation of E-*4-octenoic acid* (E-21, n=*2*). A mixture of 4.88 g (48.8 mmol) 1-hexen-3-ol (prepared from 0.2 mol 2-propenone-1 and 0.2 mol 1-bromopropane under Grignard conditions) and 0.13 ml propanoic acid in 60 ml triethyl orthoacetate was heated at 120 °C for 12 h in a water separator. After evaporation of the triethylorthoacetate, the residue was hydrolyzed with 0.15 mol potassium hydroxide in 100 ml methanol. The bulb-to-bulb distillation afforded 4.7 g (67 %) *E*-4-octenoic acid. B.p. 132 °C/15 Torr (lit.[25] 93 °C/1.5 Torr). n_D^{20}=1.4440 (lit.[25] n_D^{20}=1.4441). IR (film): 3300–2500, 2960–2840, 1720–1690, 960 cm^{-1}. ^1H NMR: δ 11.5 (s, 1H), 5.47 (m, 2H), 2.40 (m, 2H), 2.32 (t, 2H), 1.96 (m, 2H), 1.38 (m, 2H), 0.9 (t, 3H). MS [*m/e* (%, rel. int.)]: 156 (3, M), 141 (1), 125 (15), 124 (41), 82 (58), 74 (100).

Electrolysis of E-21, n=*2*. *E-21* (*n*=2) was electrolyzed as *Z-16*.

Products were analyzed by GLC-MS and comparison with authentic *E*-4-octene (Fa. Fluka).

Preparation of reference compounds.

Z-2-Methyl-4-octen (*7*). To 4.76 g (0.07 mol) 1-pentyne in 30 ml dry HPMT under stirring 70 mmol *n*-butyllithium in hexane were injected, after 35 min the hexane was distilled off at reduced pressure and the solution cooled to 0 °C. Then 9.59 g (70 mmol) *i*-butyl bromide were added, hydrolyzed (150 ml water) after 12 h and extracted with pentane (4×75 ml). Distillation at b.p. 66 °C/400 Torr afforded 2.94 g 2-methyl-4-octyne (*14*). n_D^{20}=1.4267. IR (film): 2980–2840, 1470–1430 cm^{-1}. ^1H NMR ($CDCl_3$) δ=2.15 (m, 4H), 1.8–1.2 (m, 3H), 0.9 (m, 9H). MS [*m/e* (%, rel. int.)]: 124 (20, M), 109 (11), 95 (22), 81 (52), 57 (100). Anal. C_9H_{16}: C, H).

200 mg (1.6 mmol) *14* are hydrogenated in 20 ml pentane with the Lindlar catalyst, which was deactivated with 2 drops quinoline. After purification by preparative GLC 0.14 g (70 %) *7* were obtained. n_D^{20}=1.4180 (lit.[17] n_D^{20}=1.4181). IR (film): 2980–2850, 1450, 725 cm^{-1}. ^1H NMR ($CDCl_3$): δ=5.4 (m, 2H), 2.05 (m, 3H), 1.7–1.2 (m, 3H), 0.95 (m, 9H). MS [*m/e* (%, rel. int.)]: 126 (22, M), 111 (11), 98 (10), 97 (4), 84 (12), 83 (15), 55 (100). Anal. C_9H_{18}: C, H.

Isomerization of Z-7. 200 mg *Z-7* were added slowly with intense stirring to a mixture of 5 ml 2n HCl and 250 mg $NaNO_2$. After 5 min it was hydrolyzed and extracted with ether. The product consisted of a 1:1-mixture of *Z*/*E-7*.

1-(1-Methoxybutyl)-2-methylcyclopropan (*11*). *2-Methylcyclopropane carboxaldehyde* (*15*). To the zinc-silver-couple (prepared from 17 g zinc and 100 mg silver acetate in 100 ml acetic acid) in ether were first added 7 g (0.1 mol) crotonaldehyde and then dropwise 34 g (0.13 mol) diiodmethane. For work-up ether and pyridine were added, the precipitate removed by filtration and the ether evaporated to yield 4.7 g (56 %) *15* that contained unreacted crotonaldehyde, which could not be removed by distillation or TLC. MS [*m/e* (%, rel. int.)]: 84 (18, M), 83 (68), 70 (5), 55 (100); it corresponded to the MS in lit.[26]

1-(1-Methoxybutyl)-2-methylcyclopropan (*11*). 4 g of impure *15* were added to *n*-propyl magnesiumbromide (55 mmol Mg, 6.76 g (55 mmol) 1-bromopropan) in 50 ml ether. After heating for 2 h under reflux, hydrolysis with NH_4Cl and usual work-up 3 g (49 %) cyclopropylcarbinol containing heptenol, were obtained.

1-(1-Hydroxybutyl)-2-methylcyclopropan: IR (film): 3500–3200, 3050, 2990, 2950–2860 cm^{-1}. ^1H NMR ($CDCl_3$): δ=2.9 (m, 1H), 1.6–1.4 (m, 4H), 1.4 (s, 1H), 1.02 (m, 3H), 0.9 (m, 3H), 0.6 (m, 2H), 0.4–0.2 (m, 2H). MS [*m/e* (%, rel. int.)]: 128 (0.5, M), 110 (6), 85 (100), 81 (12). Anal. $C_8H_{16}O$: C, H.

500 mg (3.9 mmol) of impure cyclopropylcarbinol, after being distilled from sodium, were reacted in 20 ml tetrahydrofuran with 3 g (80 %) sodium hydride. After 1 h 35 g (0.25 mol) methyliodide were added and stirred for 24 h. After the usual work-up *11* was isolated by preparative GLC (column 6, 90 °C iso.). IR (film): 3050, 2990, 2950–2860, 1090–1140 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.35 (s, 3H), 2.45 (m, 1H), 1.7–1.2 (m, 4H), 1.05 (m, 3H), 0.9 (m, 3H), 0.7–0.2 (m, 4H). MS [*m/e* (%, rel. int.)]: 142

(0.5, M), 127 (1), 110 (2), 99 (100). Anal. $C_9H_{18}O$: C, H.

2-Cyclopentylheptane (23, n=6). 10 g (67 mmol) cyclopentylbromide were reacted under Grignard conditions with 2-heptanone to the tertiary alcohol, which was dehydrated giving two isomers. The hydrogenation with 10 % palladium/charcoal afforded 2-cyclopentylheptane, which was purified by preparative GLC. IR (film): 2960–2840, 1460–1430, 1365 cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.8–1.1 (m, 18H), 0.9 (m, 6H). MS [*m/e* (%, rel. int.)]: 168 (2, M), 153 (1), 97 (100). Anal. $C_{12}H_{24}$: C, H.

1-Cyclopentyl-1-methoxyhexane (24, n=4). The Grignard reaction of 7.5 g (50 mmol) cyclopentylbromide and of 4.0 g (40 mmol) hexanal afforded 5.0 g (74 %) 1-cyclopentylhexanol-1, b.p. 140 °C/20 Torr. IR (film): 3500–3200, 2960–2850 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.4 (m, 1H), 1.9 (m, 1H), 1.57 (m, 8H), 1.5 (s, 1H), 1.3 (m, 8H), 0.9 (t, 3H). MS [*m/e* (%, rel. int.)]: 169 (1), 152 (3), 81 (100). 200 mg (1.2 mmol) of cyclopentylhexanol-1 in 10 ml ether were added to a suspension of 1 g (30 mmol) sodium hydride in 10 ml dry ether. After 1 h 5 ml methyliodide were added. The suspension was stirred for 6 h, hydrolyzed and extracted with ether. The bulb-to-bulb distillation gave 160 mg (72.5 %) 1-cyclopentyl-1-methoxyhexane, b.p. 138 °C/18 Torr. IR (film): 2960–2830, 2810, 1170–1150 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.35 (s, 3H), 3.0 (m, 1H), 2.0 (m, 1H), 1.5 (m, 8H), 1.2 (m, 8H), 0.9 (t, 3H), – MS [*m/e* (%, rel. int.)]: 184 (1, M), 153 (1), 152 (2), 115 (100), 113 (82). Anal. $C_{12}H_{24}O$: C, H.

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