

# Synthesis of $\gamma$ -lactones and unsaturated bis $\gamma$ -lactones via Cu–Fe-mediated reductive cyclization of di- and tri- $\alpha$ -halogenated carboxylic esters

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Received 28 October 1999; received in revised form 15 January 2000

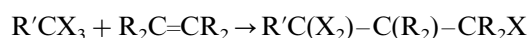
## Abstract

A new synthetic route to  $\gamma$ -substituted  $\gamma$ -butyrolactones from alkenes and  $\alpha$ -dichloro ester, in the presence of CuCl (catalytic) and Fe(0) (stoichiometric) in acetonitrile, was established. A study of this reaction has demonstrated that the overall process consists of the following reaction steps: (a) addition of the dichloro ester to the olefin via CuCl catalysis; (b) selective reduction of the  $\alpha$ -chloro atom in the resulting adduct by Fe(0); (c) cyclization of the resulting  $\gamma$ -chloro ester to  $\gamma$ -butyrolactone. Yields were improved by first carrying out step (a), then steps (b) and (c) in one pot. Selectivity was improved in the presence of a small amount of water.  $\alpha$ -Trichloro esters also generated the  $\gamma$ -substituted  $\gamma$ -butyrolactone, albeit in lower yields and selectivity. The latter reaction gave rise to the formation of interesting by-products, namely new unsaturated bis-lactones. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:**  $\gamma$ -Butyrolactones; Bis-lactones;  $\alpha$ -Chloro esters; Cu; Fe; Reductive cyclization

## 1. Introduction

The 1,2-addition reaction of  $\alpha$ -poly halides to olefins is formulated below:

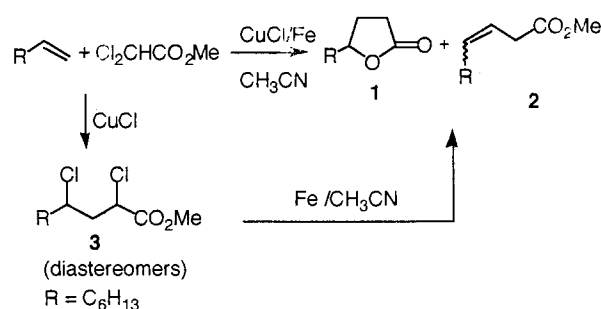


The reaction is known to be catalyzed by metal salts [1] and metal complexes [2], as well as by free radical initiators (Kharasch reaction [3]). Some of the reactive catalysts are: Cu(I),  $RuCl_2(PPh_3)_3$ ,  $[CpMo(CO)_3]_2$ ,  $[CpFe(CO)_2]_2$ ,  $Co_2(CO)_8$ , and Pd. While the peroxide-initiated Kharasch reaction is frequently accompanied by telomerization [4] of the olefins used, the metal-catalyzed reactions are usually more selective. Taken together, this is a simple and useful one-step C–C bond-forming reaction, valuable in organic synthesis.

The addition of several of  $\alpha$ -dichloro methyl esters to various terminal olefins, resulting in  $\alpha,\gamma$ -dichloro-substituted esters in moderate to good yields, has been

recently reported [5]. The above reaction was promoted by *catalytic* amounts of Fe(0).

The addition of  $\alpha$ -bromoalkanoic acids to various alkenes, initiated by peroxides, have also been studied [6]. In this case, the resulting addition products cyclized to give  $\gamma$ -butyrolactones in moderate to good yields. Various radical initiators were used; however, CuCl was found to be inactive with the above bromoalkanoic acid substrates.



Scheme 1.

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Table 1  
Experimental data for the reaction of **3** with various reagents and stainless steel (SS-304)<sup>a</sup>

Experiment	SS-304 (g)	CuCl (mol%)	bipy (mol%)	Water (mol%)	Time (h)	Conv. (%)	GC area (%) (1)	GC area (%) (2)
0	0	5	5		21	0		
1	0.5	5	5	–	21	100	37	45
2	0.5	–	5	–	21	100	51	28
3	0.66	–	–	–	22.5	100	43	42
4	–	–	–	–	18	0	0	0
5	0.5	–	–	570	23.5	100	84	2

<sup>a</sup> Reaction conditions: all reactions were performed in acetonitrile (15 ml) in a glass-lined, magnetically-stirred, closed reactor (25 ml) in an oil bath at 140°C. [3] = 1.8 M.

Table 2  
Experimental data for the reaction of **3** with Fe(0) in acetonitrile

Experiment	3:Fe (mol ratio)	[3] (M)	Water (mol%)	Time (h)	Temperature (°C)	Conv. (%)	GC area (%) (1)	GC area (%) (2)
1	1:1	1.8	622	23.5	141	100	94	2
2	1.3:1	1.6	649	24	140	100	93	1
3	2:1	1.6	622	23	140	90	82	1

## 2. Results and discussion

Extensive corrosion of metal parts of a *stainless-steel reactor* was noted at the end of a reaction of methyl dichloroacetate with 1-octene in the presence of CuCl in acetonitrile at 140°C. The crude reaction mixture, which had a strong peach odor, was distilled to yield 4-hexyl butyrolactone (**1**) (40%), and methyl-3-hexenoate (**2**) (11%). The former is a commercial peach odor fragrance.

As shown in Scheme 1, we presume that it must be **3**, generated by Cu(I)-catalyzed addition of the dichloro ester to 1-octene, that has reacted with the reactor's metal, to give the lactone (**1**) and the ester (**2**). Compound **3** was, therefore, independently prepared in a glass vessel, isolated, identified, and then exposed to stainless-steel shavings in a glass vessel in acetonitrile under a variety of reaction conditions (Table 1).

The experiments presented in Table 1 clearly demonstrate that it is the stainless steel that is responsible for the formation of **1** and **2** from **3**. Significantly, no lactone formation occurred prior to the reduction of the  $\alpha$  C–Cl bond by the stainless steel, which was absent in experiment 0. Noteworthy is the result of experiment 5, whereby the added water substantially suppressed the formation of the alkenoic acid ester (**2**). Interim analyses at 4.5 h of the reaction mixtures in experiments 3 and 5, revealed 90% and 22% conversion, respectively. Thus, although water imparts better selectivity toward lactone formation, it does slow the reaction rate. It has been claimed that a water molecule in the coordination sphere of an iron complex intermediate suppresses the reduction rate (see Ref. [7]).

The results of experiments in which the stainless steel was replaced with iron powder are compiled in Table 2.

The data (Table 2) reveal that it is the iron in the stainless steel that has reacted with **3**, thus generating the butyrolactone (**1**). Here too, the presence of water gave rise to high selectivity towards the lactone (**1**), as only traces of **2** were observed in all experiments. Practically quantitative conversions were realized with a 3:Fe molar ratio range of 1–1.3.

At this stage it was realized that 4-substituted butyrolactones, of importance to the fragrance industry, can be readily prepared from simple starting materials, either by a one-step reaction in the presence of both Cu(I) (catalytic) and Fe(0) (stoichiometric), or by a two-step sequence, reacting the pre-prepared ester **3** with a stoichiometric amount of Fe(0).

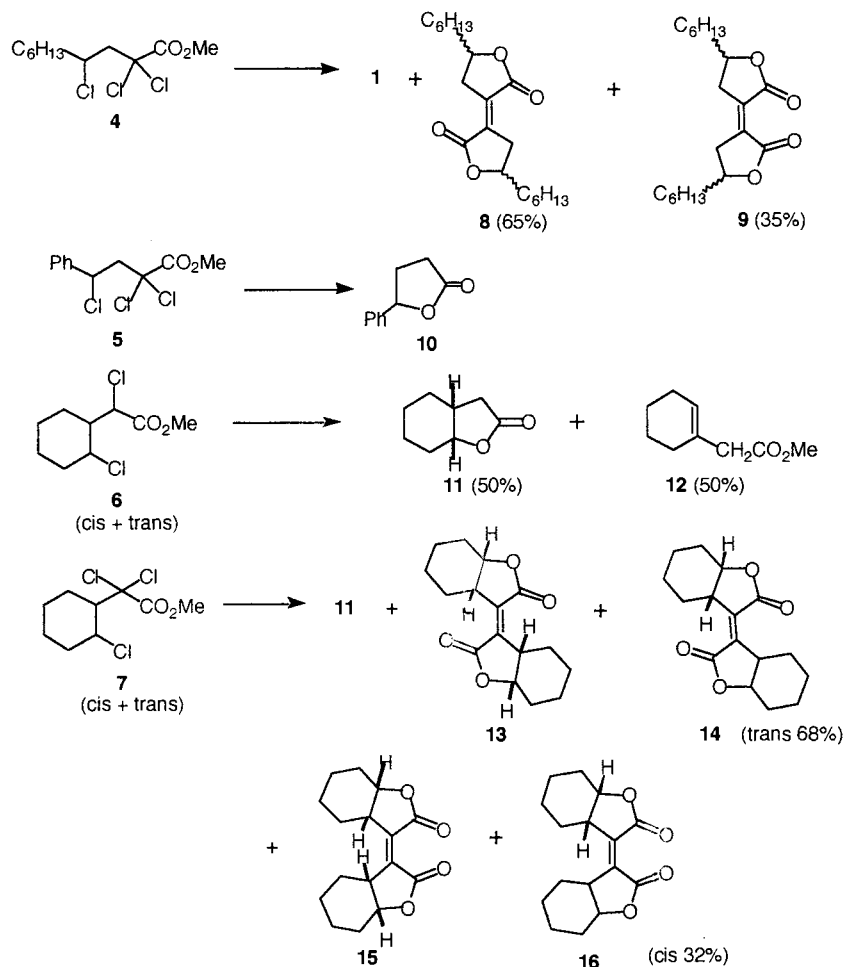
## 3. Reaction scope

In light of the above results, we have decided to study the scope of the reaction. To that end, several esters of type **3** were prepared by adding methyl dichloroacetate, or methyl trichloroacetate, to various alkenes in the presence of CuCl (catalytic). The addition products were isolated, purified, identified, and then subjected to the reducing conditions of Fe(0) in CH<sub>3</sub>CN, in the presence of traces of water. These reactions were studied with esters **4–7** (Scheme 2). The experimental conditions and the results of the Fe promoted reduction reactions are presented in Table 3. In all cases  $\gamma$ -butyrolactones were obtained.

It should be pointed out that esters **3**, **6**, and **7** were obtained as diastereomeric mixtures, as indicated by the close multiplicity of their GC signals, and were reacted with Fe–acetonitrile as such. The results, presented in Table 3 and Scheme 2, are discussed below.

4-Hexyl-butyrolactone (**1**) was obtained in a good yield and selectivity (Table 3) from methyl dichloroacetate (**3**). Although, methyl trichloroacetate (**4**) gave the

same lactone (**1**), it was in substantially lower yield and selectivity. In this experiment, a mixture of bis-lactones, **8** and **9**, accompanied **1**. The bis-lactone mixture was readily separated from lactone (**1**) by column chromatography. Their structure was established as **8** and **9** by elemental analysis, MS, IR and NMR spectra. While lactones **8** and **9** were not previously reported, the *unsubstituted trans* isomer was prepared in 20% yield

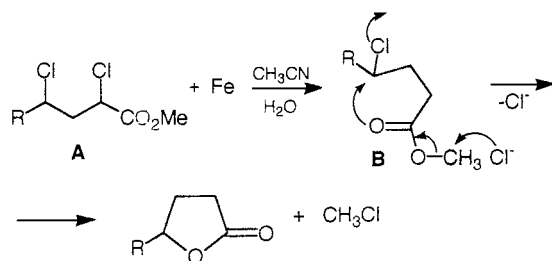


Scheme 2. All the reactions in this were promoted by Fe filings in acetonitrile–water solution. The yields are given in Table 3.

Table 3  
Experimental data for synthesis of butyrolactones from esters **3–7**<sup>a</sup>

Ester (mmol)	Water (mmol)	CH <sub>3</sub> CN (ml)	Time (h)	Conv. (%)	Products	GC area (%)	Yields (%)
<b>3</b> (9.8)	61.1	5.5	21.5	100	<b>1</b>	97	71
<b>4</b> (3.47)	36.0	3.0	5.5	98	<b>1</b> <b>8+9</b>	37 40	15 16
<b>5</b> (7.09)	72.2	6.0	20	100	<b>10</b>	86	42
<b>6</b> (8.93)	53.6	5.0	21.5	100	<b>11</b> <b>12</b>	50 50	23 22
<b>7</b> (7.75)	72	6.0	42.5	100	<b>11</b> <b>13–16</b>	66 15	10 5

<sup>a</sup> All reactions were carried out in sealed glass ampoules at an oil bath temperature of 140°C with a Fe:substrate molar ratio of 1:1. Coarse iron filings were used.



Scheme 3.

from  $\alpha$ -diazo- $\gamma$ -butyrolactone [8]. In its  $^1\text{H-NMR}$  spectrum, the allylic ring H atoms were found to resonate as multiplets at 3.54 ppm. Since the mixture of **8** and **9** exhibited two multiplets at 2.25–3.01 and 3.51–3.63 ppm (allylic H atoms), the latter signal can be assigned to the *trans* isomer, in analogy with the above unsubstituted *trans* bis-lactone. No attempt was made to separate the two isomers of the bis-lactones.

4-Phenyl-butyrolactone (**10**) was obtained with very good selectivity but in modest yield (42%) from **5** (Table 3).

The cyclohexene adduct **6** possesses three stereocenters. According to GC analysis, four diastereomers, in the ratio of 22:13:33:32, were formed. During the reductive cyclization reaction of the mixture, one stereocenter ( $\alpha$ -Cl C atom) is lost. The intramolecular cyclization is an  $\text{S}_{\text{N}}2$  type reaction (vide infra) [9]. Therefore only the *trans* isomer of **6** can cyclize to give the lactone, *cis*-7-oxabicyclo[4.3.0]nonan-8-one (**11**). Compound **12** is the HCl elimination product of *cis*-**6**, which due to the kinetic stereochemical constraints mentioned above, is incapable of undergoing cyclization [9].

Upon subjecting the *trichloro* ester **7** (diastereomeric mixture) to the reducing conditions ( $\text{Fe-CH}_3\text{CN}$ ), the expected bicyclic lactone **11** (identical to that obtained from **6**) was obtained, however in lower yield. It was accompanied again by butyrolactone dimers, to which structures **13–16** were assigned (Scheme 2), on the basis of elemental analysis, MS, IR and NMR spectra. The dimer mixture (GC), was separated from the bicyclic lactone **11** by column chromatography and was obtained as a colorless solid. No attempt was made to separate this mixture. We propose the following stereochemical analysis for the four isomeric bis-lactones **13–16** in the purified mixture.

1. The lactone and the cyclohexane rings in *all* isomers must be *cis*-fused due to the kinetic stereochemical constraints of the cyclization reaction, as previously explained.
2. Such a situation generates four diastereomers, two *meso*, **14** and **15**, and two racemates, **13** and **16**, which are depicted in Scheme 2. It should be noted that while **14** has point symmetry, **15** possesses a

plane of symmetry. Indeed, GC analysis of the purified bis-lactones mixture gave rise to four signals, in agreement with the above argument.

3. The  $^1\text{H-NMR}$  chemical shifts of the ring junction allylic H atoms in the various isomers may serve as indicators for the double-bond configuration (see Section 2 for the stereochemistry of **8** and **9**). Two  $^1\text{H-NMR}$  signals at  $\delta = 3.6$  and 3.9 ppm were assigned to two *trans* isomers, **13** and **14**. An additional broad signal at  $\delta = 2.8$  ppm was assigned to the *cis* isomers, **15** and **16**.

Obviously, the formation of lactone dimers disturbs the selectivity towards the bicyclic lactone **11**, when using the trichloro ester **7**. Better yield of **11** could be obtained from the dichloro ester **6** (Table 3). Nevertheless, the *one-step synthesis* of these novel bis-lactone compounds from simple starting materials is attractive in its own right.  $\gamma$ -Butyrolactone are known for their biological activity [10].

#### 4. Mechanism aspects

The mechanism of the reductive cyclization reaction, described in Scheme 3, can be readily rationalized. The  $\text{CuCl}$ -catalyzed addition of methyl dichloro acetate to an alkene yields the  $\alpha,\gamma$ -dichloro ester **A**. Reaction of **A** with  $\text{Fe-CH}_3\text{CN}$  (stoichiometric) results in the selective reduction of the  $\alpha$ -Cl atom (**B**). Such a reduction may proceed via oxidative addition of Fe to the more reactive  $\alpha$  C–Cl bond, and coordination of a water molecule to the Fe atom [7]. With the  $\gamma$ -Cl atom being intact, a well-known neighboring group displacement reaction (thermal) of the  $\gamma$ -Cl atom by the ester carbonyl group ensues [11]. The products (Scheme 3) are a lactone and MeCl (identified). Reduction must precede cyclization, as methyl 4-chlorooctanoate, identified by GC–MS, was observed as a transient reaction intermediate. This must be due to the diminished basicity of the  $\alpha$ -chloro ester carbonyl group in **A**, which functions as a nucleophile in the cyclization reaction.

In the absence of added water the Fe reduction reaction mixture was found to generate methyl chloride, which was collected in chloroform from the gas phase of the reaction mixture, and identified by NMR. However, in the presence of water, no MeCl could be detected, and instead, methanol only was observed in the reaction mixture (NMR). It stands to reason that the methanol was generated during the reaction (140°C) by hydrolysis of the methyl ester (rather than MeCl hydrolysis). The carboxylic acid formed in the presence of water must cyclize faster than the ester in the absence of water. Therefore, the improved selectivity towards lactone formation versus HCl elimination (in the presence of water) may now be ascribed to the above differential rate effect, i.e. the cyclization rate increased relative to elimination.

The source of H atoms that participate in the reduction of the C–Cl bond prior to cyclization was briefly studied. Reductive cyclization of **3** in the presence of added D<sub>2</sub>O resulted in the formation of  $\alpha$ -d<sub>1</sub>-4-hexyl- $\gamma$ -butyrolactone. Its <sup>1</sup>H-NMR spectrum was compared to that of 4-hexyl- $\gamma$ -butyrolactone (see Section 5). A signal at  $\delta = 2.5$  ppm, with a different multiplicity, clearly indicated the presence of only one H atom  $\alpha$  to a carbonyl. In a second experiment, cyclization of **3** was carried out (no added water) with Fe and CD<sub>3</sub>CN as solvent (dried over molecular sieves). No deuterium incorporation into lactone **1** could be detected by <sup>1</sup>NMR. Thus, the  $\alpha$ -H atoms of acetonitrile do not participate in the reduction of the  $\alpha$ -C–Cl bond of the esters in the presence of Fe. Therefore, when present, water serves as H donor for the above Fe promoted reduction, when absent, the source of H atom for the reduction reaction is presently unclear.

The proposed mode of formation of the bis-lactone compounds is outlined in Scheme 4. It should be noted that only adducts of methyl trichloroacetate, such as **17**, generated significant quantities of the bis-lactones. This can be attributed to the greater stability of the chloro substituted radical intermediate **18** versus H substituted radical, generated from methyl dichloroacetate, in the reaction with Fe(0). Radical **18** may undergo intermolecular coupling to give **19**, followed by iron promoted vicinal elimination of Cl atoms, generating *cis*- and *trans*-**20**. The resulting maleate–fumarate intermediate (**20**) then undergoes cyclization, as previously described, to the bis-lactone (**21**), with the elimination of MeCl (Scheme 4).

In conclusion, a new simple synthetic route to  $\gamma$ -butyrolactones from simple starting materials was found. Furthermore, novel unsaturated bis-lactones can now be readily prepared from  $\alpha$ -trichloro esters, albeit in low yields (no optimization was attempted). The low yield of the bis-lactones may be attributed to the multi-step process, involving free radical intermediates, associated with their formation, as depicted in Scheme 4. The simple *one-step* synthesis access to these rather

complex bis-lactone structures is an attractive synthetic route, in spite of the low yield.

## 5. Experimental

### 5.1. Preparation of esters **3–7**

Methyl 2,4-dichlorodecanoate (**3**) [2], methyl 2,2,4-trichlorodecanoate (**4**) [2], methyl 4-phenyl-2,2,4-trichlorobutanoate (**5**) [12] are known compounds.

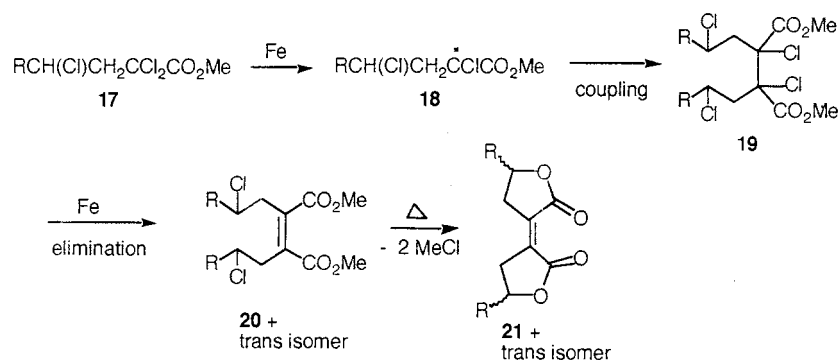
All reactions were carried out under a nitrogen blanket.

### 5.2. Methyl 2-chloro-2-(2-chlorocyclohexyl) acetate (**6**)

Cyclohexene (15.0 g, 0.183 mol), methyl dichloroacetate (dist. 26.1 g, 0.183 mol), benzonitrile (30 ml), 2,2'-bipyridine (1.426 g, 9.13 mmol) and CuCl (0.904 g, 9.13 mmol) were placed in a 100 ml glass vessel and heated at 130°C and stirred under reflux for 23 h. A total of 80 ml of CCl<sub>4</sub> were added to the cooled solution, and the catalyst was filtered. The filtrate was subjected to evaporator distillation. Benzonitrile was distilled at 72–76°C/15 mmHg followed by the product (**6**), b.p. 95–100°C/1 mmHg, 6.07 g (15%). <sup>1</sup>H-NMR ( $\delta$ ): 1.19–2.34 (m, 9H), 3.80, 3.81, 3.82 (3s, 3H), 3.87–5.13 (m, 2H). MS: *m/z* (%): 189 (M<sup>+</sup>–35) (2), 108 (100), 81 (47). IR  $\nu$  (neat): 1748 cm<sup>-1</sup>.

### 5.3. Methyl 2,2-dichloro-2-(2-chlorocyclohexyl) acetate (**7**)

Cyclohexene (6.15 g, 0.075 mol), methyl trichloroacetate (dist. 13.3 g, 0.075 mol), benzonitrile (12 ml), 2,2'-bipyridine (0.585 g, 3.75 mmol) and CuCl (0.371 g, 3.75 mmol) were placed in a 50 ml glass vessel in an oil bath at 140°C under reflux with stirring for 22 h. The reaction mixture was worked up as described above for **6**. A liquid (**7**) was obtained, b.p. 110°C/0.2 mmHg, 5.64 g (29%). <sup>1</sup>H-NMR ( $\delta$ ): 1.3–2.8 (m, 9H, (CH<sub>2</sub>)<sub>4</sub>CH),



Scheme 4.

3.87 (s, 3H, OCH<sub>3</sub>), 3.9–4.0 (m, 1H, CHCl. IR  $\nu$  (neat): 1750, 1764 cm<sup>-1</sup>. MS:  $m/z$  (%): 257 [M<sup>+</sup>-H] (1), 223 [M<sup>+</sup>-Cl] (10), 199 [M<sup>+</sup>-CO<sub>2</sub>CH<sub>3</sub>] (13), 185 (64), 163 (45), 142 (87), 68 (100).

#### 5.4. Reductive cyclization reactions (general procedure)

Methyl 2,4-dichlorooctanoate (**3**) (2.5 g, 9.8 mmol), water (1.1 ml, 61.1 mmol), acetonitrile (5.5 ml), and coarse iron filings (0.549g, 9.8 mmol) were charged into a 20 ml glass sleeve with a magnetic bar. The sleeve was placed in an stainless steel reactor, which was tightly closed and placed in an oil bath. The reaction mixture was kept at 141°C for 21.5 h with stirring. (The reaction conditions and specific quantities of reactants for the reductive cyclization of esters **4**–**7** are presented in Table 3.) After cooling, the reactor's content was taken up with CCl<sub>4</sub> (25 ml), the mixture filtered, the solvent evaporated, and the residue chromatographed on silica with CH<sub>2</sub>Cl<sub>2</sub>-petroleum ether (1:1). An oil was obtained (1.18 g, 71%), identified as 4-hexylbutyrolactone (**1**) [13].

The lactones **1** [13], **10** [14], **11** [15] and the ester **12** [16] are known compounds, and their properties (MS, IR, NMR) were in agreement with the literature data.

<sup>1</sup>H-NMR ( $\delta$ ): 0.89 (t, 3H, CH<sub>3</sub>) 1.29–1.90 (m, 11H, 5CH<sub>2</sub> + 1H $\beta$  to CO), 2.27–2.40 (m, 1H $\beta$  to CO), 2.49–2.57 (m, 2H, CH<sub>2</sub>CO), 4.41–4.54 (m, 1H, OCH).

A product with an identical <sup>1</sup>H-NMR spectrum was obtained by repeating the above reaction with CD<sub>3</sub>CN as solvent, previously dried over molecular sieves.

#### 5.5. 2-*d*<sub>1</sub>-4-Hexyl- $\gamma$ -butyrolactone

The above procedure was repeated, replacing the water with 1.1 ml of D<sub>2</sub>O. After heating for the specified period and workup as described above, the crude product was chromatographed on silica. The product emerged from the column with methylene chloride-petroleum ether (1:1), 1.213 g (73%).

<sup>1</sup>H-NMR ( $\delta$ ): 0.89 (t, 3H, CH<sub>3</sub>) 1.29–1.88 (m, 11H, 5CH<sub>2</sub> + 1H $\beta$  to CO), 2.27–2.39 (m, 1H $\beta$  to CO), 2.47–2.54 (ddt, 9 Hz, 5 Hz, 3 Hz, 1H, CHD), 4.42–4.56 (m, 1H, OCH).

#### 5.6. Bis-lactones **8** and **9**

Methyl 2,2,4-trichlorooctanoate (**4**) (1.0 g, 3.47 mmol), acetonitrile (3 ml), water (0.648 g, 36 mmol) and coarse iron filings (0.194 g, 3.47 mmol) were charged into a 20 ml glass sleeve, placed in a stainless-steel reactor, closed tightly and placed in an oil bath at 145°C for 5.5 h. After cooling, the reactor's content was taken up with CCl<sub>4</sub> (25 ml), the mixture filtered, the solvent evaporated, and the residue chromatographed on silica with CH<sub>2</sub>Cl<sub>2</sub>-petroleum ether (1:1). A white

solid (0.1 g, 16%) (**8** + **9**) was obtained which was washed with cyclohexane, m.p. 112–118°C, followed by 0.09 g of **1**, identical to that obtained using ester (**3**) as starting material.

Elemental analysis for C<sub>20</sub>H<sub>32</sub>O<sub>4</sub> (**8** + **9**). Anal. Found: C, 71.12; H, 9.70. Calc.: C, 71.39; H, 9.59%. Spectral data for the **8** + **9** mixture: <sup>1</sup>H-NMR ( $\delta$ ): 0.89 (t, 6H, CH<sub>3</sub>), 1.30–1.91 (m, 20H, CH<sub>2</sub>), 2.25–3.01 (m, =CCH<sub>2</sub>-, cis isomer), 3.51–3.63 (m, =CCH<sub>2</sub>-, trans isomer), 4.38–4.52 (m, -OCH-, cis isomer), 4.59–4.65 (m, -OCH-, trans isomer). <sup>13</sup>C-NMR ( $\delta$ ): 14.0, 22.5, 24.6, 27.1, 27.9, 28.9, 31.5, 33.5, 34.6, 36.3 (CH<sub>2</sub>/CH<sub>3</sub>), 78.2, 78.6, 79.1 (C-O), 133.4, 136.1, 136.5 (C=C), 163.9, 164.1, 170.0 (C=O). MS:  $m/z$  (%): 336 [M<sup>+</sup>] (51), 251 [M<sup>+</sup>-C<sub>6</sub>H<sub>13</sub>] (100), 222 (96), 153 [M<sup>+</sup>/2-CH<sub>3</sub>] (48). IR  $\nu$  (CH<sub>2</sub>Cl<sub>2</sub>): 1720, 1746 cm<sup>-1</sup>.

#### 5.7. Bis-lactones **13**–**16**

Methyl 2,2-dichloro-2-(2-chlorocyclohexyl)acetate (**7**) (2.0 g, 7.75 mmol), iron powder (0.434 g, 7.75 mmol) and water (1.30 g, 72.0 mmol) in acetonitrile (6 ml), were heated at 140°C for 42.5 h and then treated as described in the above procedure. Chromatography on silica with methylene chloride-petroleum ether (3:1) gave first a white solid, mixture of the dimers (**13**–**16**) (0.054 g, 5%), that was purified by washing with cyclohexane, m.p. 193–198°C. Elemental analysis for C<sub>16</sub>H<sub>20</sub>O<sub>4</sub>. Anal. Found: C, 69.38; H, 7.45. Calc. C, 69.55; H, 7.30%. <sup>1</sup>H-NMR ( $\delta$ ): 1.02–2.31 (m, 16H), 2.83–2.92 (m, cis isomer, =CCH), 3.56–3.68 and 3.85–3.95 (m, trans isomer, =CCH), 4.50 (m, 2H, OCH). MS:  $m/z$  (%): 277 [MH<sup>+</sup>] (100). IR  $\nu$  (KBr): 1718, 1752 cm<sup>-1</sup>.

The next emerging compound was the bicyclic lactone (**11**) (0.11g, 10%), identical with that obtained from the reductive cyclization of **6**.

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