Pergamon

Tetrahedron Vol. 51, No. 10, pp. 2939-2946, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4020/95 $9.50+0.00

0040-4020(95)00039-9

Synthesis of Substituted β-Lactones by a Reformatsky Reaction of Carbonyl Compounds, Phenyl α-Bromoalkanoates, and Indium[1]

Hans Schick,* Ralf Ludwig, Katharina Kleiner and Annamarie Kunath

Institut für Angewandte Chemie Berlin-Adlershof e.V., Rudower Chaussee 5, D-12489 Berlin,
Germany

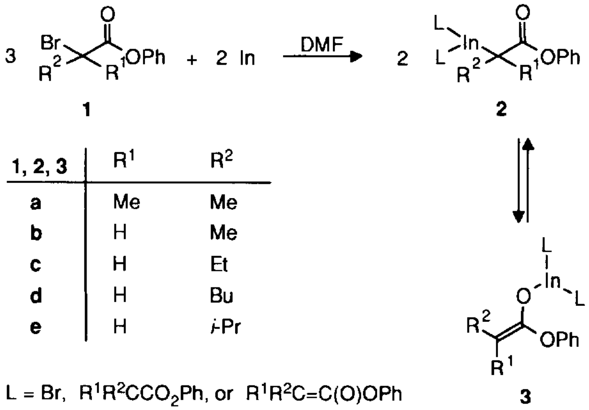
Abstract: Di-, tri-, and tetrasubstituted β-lactones are accessible in a one-step procedure by a Reformatsky reaction of phenyl α-bromoalkanoates with ketones or aldehydes at a sacrificial indium anode. With indium powder comparable results are obtained. The yield of β-lactones is significantly lower, if zinc is used instead of indium.

INTRODUCTION

The Reformatsky reaction of carbonyl compounds with alkyl α-bromoalkanoates and activated zinc has become one of the most often applied methods for the preparation of alkyl β-hydroxyalkanoates.[2] Magnesium,[3] cadmium,[4] nickel,[5] cerium,[6] manganese,[7] or indium[8] can be used instead of zinc without significant influence on the general outcome of the reaction. Recently, however, it has been demonstrated that α,α,β,β-tetrasubstituted β-lactones are formed in acceptable yields instead of the expected ethyl β-hydroxyalkanoates, when ketones and ethyl α-bromoisobutyrate were subjected to an electrochemically supported Reformatsky reaction with a sacrificial indium or zinc anode.[9] This β-lactone formation is not restricted to the electrochemical generation of the Reformatsky reagent. Also under the condition of the classical Reformatsky reaction these tetrasubstituted β-lactones are formed, when indium or zinc powder are used in a polar solvent, such as *N*,*N*-dimethylformamide.[1] A systematic investigation of this reaction revealed that it is limited to the formation of α,α,β,β-tetrasubstituted β-lactones. If the ketone is replaced by an aldehyde or the ethyl α-bromoisobutyrate by an unbranched ethyl α-bromoalkanoate, only ethyl β-hydroxyalkanoates are obtained. According to Scheme 2 the β-lactone formation is explained by the assumption that the intermediately formed *O*-metalated β-hydroxyalkanoate **5** (OEt instead of OPh) eliminates a metal alkoxide and cyclizes to the four-membered ring. This ring closure seems to be strongly dependent on the *gem*-dialkyl effect[10,11] and to occur only if all four hydrogen atoms of the cyclizing carbon chain are substituted by alkyl groups. In connection with our interest in the synthesis of less substituted β-lactones the question arose, whether a better leaving group in the *O*-metalated β-hydroxyalkanoate could compensate the diminished *gem*-dialkyl effect in the reaction of aldehydes with branched or unbranched α-bromoalkanoates. Here we report on the results with phenoxy instead of ethoxy as leaving group.

RESULTS AND DISCUSSION

When the phenyl ester **1a** was reacted in DMF with acetone **4a** and indium powder the tetrasubstituted β-lactone **6aa** was obtained in a yield of 62% (Table 1, entry 1). This orientating experiment revealed that the replacement of the ethyl ester by the phenyl ester caused indeed a reasonable improvement of the β-lactone formation. In earlier experiments with the corresponding ethyl ester only 11% of this β-lactone have been obtained.[1] This encouraged us to use phenoxy as leaving group in attempts to prepare trisubstituted β-lactones from phenyl α-bromoisobutyrate (**1a**) and aldehydes or from the α-unbranched phenyl α-bromoalkanoates **1b–e** and the ketones **4a–d** by a Reformatsky reaction with indium. The experiments were performed electrochemically at a sacrificial indium anode (method A) or under classical conditions with indium powder (method B). The details are given in the experimental part.



1, 2, 3	R^1	R^2
a	Me	Me
b	H	Me
c	H	Et
d	H	Bu
e	H	*i*-Pr

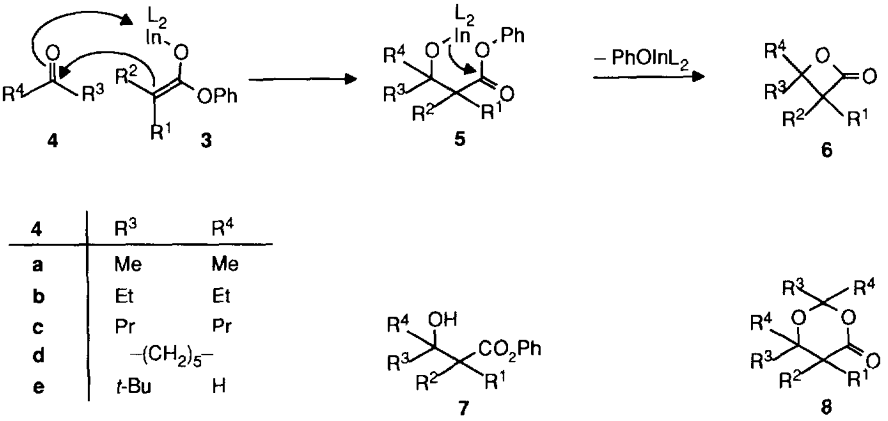
L = Br, $R^1R^2CCO_2Ph$, or $R^1R^2C{=}C(O)OPh$

Scheme 1

The reaction of the unbranched phenyl α-bromoalkanoates **1b–d** with the ketones **4b–d** afforded by both methods the corresponding α,β,β-trisubstituted lactones **6** in isolated yields of 50–80% (entries 3–5, 7–9, 11–13). The β-branched phenyl ester **1e**, however, gave only unsatisfying yields of the β-lactones **6e** with both methods (entries 15–17). There was only one exception. Method A allowed to obtain **6ed** from cyclohexanone **4d** in a yield of 56% (entry 17).

The α,α,β-trisubstituted β-lactone **6ae** could be obtained from the α-branched phenyl ester **1a** and pivalaldehyde (**4e**) in a yield of 45% according to method A and 59% according to method B (entry 2). α,β-Disubstituted β-lactones from the α-unbranched phenyl esters **1b–e** and the aldehyde **4e**, however, were accessible by both methods only in low yields (entries 6, 10, 14, 18).

The yields obtained by the electrochemically supported Reformatsky reaction (method A) and the Reformatsky reaction with indium powder (method B) were in almost all cases of the same order. For the electrochemically supported Reformatsky reaction the addition of indium(III) chloride to the reaction mixture had a beneficial influence on the β-lactone formation. With a sacrificial zinc anode or with zinc powder the yields of β-lactones were in all cases significantly lower compared with those of indium.



4	R^3	R^4
a	Me	Me
b	Et	Et
c	Pr	Pr
d	–(CH$_2$)$_5$–	
e	*t*-Bu	H

Scheme 2

Table 1. Synthesis of β-Lactones **6** via Electrochemically Supported or Classical Reformatsky Reaction of Phenyl α-Bromoalkanoates **1** and Carbonyl Compounds **4** with Indium

entry	β-lactone **6**	R^1	R^2	R^3	R^4	indium anode method A yield of **6** (%)	indium powder method B yield of **6** (%)
1	**6aa**	Me	Me	Me	Me	20	62
2	**6ae**	Me	Me	*t*-Bu	H	45	59
3	**6bb**	H	Me	Et	Et	75	81
4	**6bc**	H	Me	Pr	Pr	73	67
5	**6bd**	H	Me	–(CH$_2$)$_5$–		79	77
6	**6be**	H	Me	*t*-Bu	H	12	16
7	**6cb**	H	Et	Et	Et	72	51
8	**6cc**	H	Et	Pr	Pr	70	65
9	**6cd**	H	Et	–(CH$_2$)$_5$–		84	76
10	**6ce**	H	Et	*t*-Bu	H	20	18
11	**6db**	H	Bu	Et	Et	52	63
12	**6dc**	H	Bu	Pr	Pr	50	59
13	**6dd**	H	Bu	–(CH$_2$)$_5$–		78	78
14	**6de**	H	Bu	*t*-Bu	H	22	15
15	**6eb**	H	*i*-Pr	Et	Et	4	11
16	**6ec**	H	*i*-Pr	Pr	Pr	0	0
17	**6ed**	H	*i*-Pr	–(CH$_2$)$_5$–		56	10
18	**6ee**	H	*i*-Pr	*t*-Bu	H	27	37

The results compiled in Table 1 clearly reveal that the concept to use phenyl α-bromoalkanoates instead of the corresponding ethyl esters in order to get lower substituted β-lactones could be successfully applied to the synthesis of α,β,β-trisubstituted β-lactones from ketones and straight-chain phenyl α-bromoalkanoates as well as to the synthesis of α,α,β-trisubstituted β-lactones from aldehydes and α-branched phenyl α-bromoalkanoates. The phenyl β-hydroxyalkanoates **7** are formed in these cases only as by-products, which could be removed by flash chromatography. From the reactions of these straight-chain phenyl α-bromoalkanoates with aldehydes only the reactions with pivalaldehyde (**4e**) are included in Table 1. The α,β-disubstituted β-lactones thus obtained were *trans*-configurated as could be derived from their ^{1}H NMR spectra. According to the literature the coupling constants $J_{3,4}$ of the protons at C-3 and C-4 of *cis*- and *trans*-2-oxetanones are 6.5 and 4.5 Hz, respectively.[12] The reactions with other aliphatic aldehydes, such as 2-methylpropanal or pentanal, afforded the corresponding α,β-disubstituted β-lactones also in a yield of only 10%. In all cases, where aldehydes were applied, the main products were the corresponding 1,3-dioxan-4-ones **8**.[13]

In conclusion it has been shown that phenyl esters of α-bromoalkanoic acids generally react with ketones or aldehydes and indium in an electrochemically supported Reformatsky reaction as well as under classical Reformatsky conditions to afford trisubstituted β-lactones in good yields in a one-step procedure. The formation of β-lactones instead of β-hydroxyalkanoates in the very intensively exploited Reformatsky reaction is attributed to the use of phenyl instead of alkyl esters. It can be assumed that the application of other activated esters may broaden the scope of this β-lactone synthesis, which already now can well compete in many cases with the known methods.[13,14]

EXPERIMENTAL

All electrosyntheses were performed without a diaphragm under dry argon in a thermostatable beaker with a diameter of 4 cm and a height of 8 cm, equipped with a four-necked cover and a magnetic stirrer bar. A commercial dc voltage source (NTN 700M-350) was applied. The amount of electricity was measured with an electronic coulometer. A nickel net (4 × 4 cm) was used as cathode. An indium rod (Alfa) of a diameter of 0.5 cm served as sacrificial anode. DMF and THF, dried over molecular sieves, were purchased from Fluka. The other chemicals were purchased from Merck and used without further purification. Indium powder (200 micron) with a purity of 99.99% was supplied from Heraeus.

^{1}H NMR spectra were determined at 80 MHz on a Tesla BS 587 A spectrometer in $CDCl_3$ with tetramethylsilane as internal standard ($\delta_{TMS} = 0$). *J*-values are given in Hz. ^{13}C NMR spectra were measured at 75 MHz on a Varian Gemini 300 instrument in $CDCl_3$ with hexamethyldisiloxane as internal standard ($\delta_{HMDS} = 1.92$). IR spectra were recorded on a Specord 75 (Carl Zeiss, Jena).

General Procedure for the Synthesis of the Phenyl α-Bromoalkanoates 1

The corresponding 2-bromoalkanoyl bromide (100 mmol) was refluxed for 5 h in a solution of phenol (9.4 g, 100 mmol) in toluene (60 mL) and concentrated sulfuric acid (0.25 mL). After cooling the mixture was worked up by washing with water (2 × 50 mL), ice-cold aqueous NaOH (3%, 2 × 30 mL), water (4 × 30 mL), drying with Na_2SO_4, and removal of the solvent by distillation under reduced pressure. The residue was purified by kugelrohr distillation. According to this procedure the following phenyl esters **1** have been obtained.

***Phenyl 2-Bromo-2-methylpropanoate* (1a).**[15] Yield 19.3 g (79%); Colourless liquid, b.p. 190° C/1500 pa; δ_H 1.99 [6 H, s, $(CH_3)_2CH$], 7.03–7.36 (5 H, m, $H_{arom.}$); δ_C 30.5 [$(CH_3)_2C$], 55.4 (C-2), 120.9, 126.0, 129.4, and 150.7 ($C_{arom.}$), 170.0 (C-1).

***Phenyl 2-Bromopropanoate* (1b).**[15,16] Yield 20.6 g (90%); Colourless liquid, b.p. 190 °C/1700 pa; δ_H 1.88 (3 H, d, *J* 7, 3-H_3), 4.52 (1 H, q, *J* 7, 2-H), 7.04–7.38 (5 H, m, $H_{arom.}$); δ_C 21.4 (C-3), 39.6 (C-2), 121.0, 126.2, 129.5, and 150.4 ($C_{arom.}$), 168.7 (C-1).

***Phenyl 2-Bromobutanoate* (1c).**[15] Yield 20.6 g (84%); Colourless liquid, b.p. 70 °C/1 pa; δ_H 1.05 (3 H, t, *J* 7, 4-H_3), 1.97–2.22 (2 H, m, 3-H_2), 4.30 (1 H, t, *J* 7, 2-H), 7.03–7.36 (5 H, m, $H_{arom.}$); δ_C 11.9 (C-4), 28.2 (C-3), 47.2 (C-2), 121.0, 126.2, 129.5, and 150.4 ($C_{arom.}$), 168.2 (C-1).

***Phenyl 2-Bromohexanoate* (1d).** Yield 22.3 g (82%); Colourless liquid, b.p. 225 °C/1800 pa (Found: C, 53.15; H, 5.6. $C_{12}H_{15}O_2Br$ requires C, 53.2; H, 5.6); δ_H 0.87 (3 H, t, *J* 7, 6-H_3), 1.26–1.58 (4 H, m, 4-H_2 and 5-H_2), 1.95–2.26 (2 H, m, 3-H_2), 4.36 (1 H, t, *J* 7, 2-H), 7.02–7.41 (5 H, m, $H_{arom.}$); δ_C 13.8 (C-6), 22.0 , 29.4, and 34.4 $(CH_2)_3$, 45.6 (C-2), 121.0, 126.2, 129.4, and 150.4 ($C_{arom.}$), 168.3 (C-1).

***Phenyl 2-Bromo-3-methylbutanoate* (1e).**[15] Yield 19.8 g (77%); Colourless liquid, b.p. 220 °C/1700 pa; δ_H 1.08 (3 H, d, *J* 7, 3-CH_3), 1.12 (3 H, d, *J* 7, 4-H_3), 2.25–2.39 (1 H, m, 3-H), 4.16 (1 H, d, *J* 8, 2-H), 7.02–7.36 (5 H, m, $H_{arom.}$); δ_C 19.9 and 20.0 (C-4 and 3-CH_3), 32.3 (C-3), 54.0 (C-2), 121.1, 126.2, 129.5, and 150.4 ($C_{arom.}$), 167.9 (C-1).

*General Procedure for the Synthesis of the β-Lactones **6** by an Electrochemically Supported Reformatsky Reaction at a Sacrificial Indium Anode*

In the above described cell equipped with an indium anode, a solution of the carbonyl compound **4** (5 mmol), the α-bromo ester **1** (15 mmol), tetrabutylammonium bromide (322 mg, 1 mmol), and anhydrous indium(III) chloride (663 mg, 3 mmol) in DMF/THF (1 : 2, 15 mL) was electrolyzed at a temperature of 50 °C, an external voltage of 20–30 V and a current lower than 100 mA. If pivalaldehyde (**4e**) was used as carbonyl compound, the aldehyde was added dropwise within 2 h during the electrolysis. The course of the reaction was monitored by TLC. When 900 As were passed, the electrolysis was stopped and the reaction mixture was stirred for an additional 1 h. Then the reaction mixture was poured onto a mixture of aqueous HCl (3%, 50 mL) and ice (25 g) and extracted with ethyl acetate (5 × 20 mL). The further workup by washing with water (2 × 10 mL), ice-cold aqueous NaOH (3%, 2 × 15 mL), and water (4 × 10 mL), drying with Na_2SO_4, and removal of the solvent by distillation under reduced pressure afforded a crude product which was purified by flash chromatography on silica gel 60 with hexane/ethyl acetate (10 : 1) as eluent. The isolated yields of the β-lactones **6** are given in Table 1.

*General Procedure for the Synthesis of the β-Lactones **6** by a Reformatsky Reaction with Indium Powder*

Indium powder (574 mg, 5 mg atom) and some crystals of iodine were added to a solution of an α-bromo ester **1** (6 mmol) and a carbonyl compound **4** (5 mmol) in dry DMF (5 mL). If the exothermic reaction did not start spontaneously, the mixture was gently warmed to 60 °C. If pivalaldehyde (**4e**) was used as carbonyl compound, the aldehyde was added dropwise during 5 min after the start of the reaction. Thereafter stirring was continued for an additional 2 h without external heating. Then the reaction mixture was poured onto a mixture of aqueous HCl (3%, 50 mL) and ice (25 g) and extracted with ethyl acetate (5 × 20 mL). The further workup by washing with water (2 × 10 mL), ice-cold NaOH (3%, 2 × 15 mL), water (4 × 10 mL), drying with Na_2SO_4, and removal of the solvent by distillation under reduced pressure afforded a crude product which was purified by flash chromatography on silica gel 60 with hexane/ethyl acetate (10 : 1) as eluent. The isolated yields of the β-lactones **6** are given in Table 1. The following β-lactones **6** have been prepared according to the foregoing described general procedures.

***3,3,4,4-Tetramethyl-2-oxetanone* (6aa).**[17] Colourless crystals, m.p. 129–130 °C, ν_{max} 1805 cm^{-1} (β-lactone); δ_H 1.25 [6 H, s, $C(CH_3)_2$], 1.45 [6 H, s, $C(CH_3)_2$]; δ_C 19.3 and 24.0 (4 × CH_3), 54.6 (C-3), 83.8 (C-4), 176.1 (C-2).

(±)-*4-*tert*-Butyl-3,3-dimethyl-2-oxetanone* (6ae). Colourless crystals, m.p. 33–35 °C (Found: C, 69.2; H, 10.0. $C_9H_{16}O_2$ requires C, 69.2; H, 10.3); ν_{max} 1821 cm^{-1} (β-lactone); δ_H 0.99 [9 H, s, $C(CH_3)_3$], 1.33 (3 H, s, 3-CH_3), 1.37 (3 H, s, 3-CH_3), 3.88 (1 H, s, 4-H); δ_C 17.7, and 25.6 (2 × CH_3), 25.9 [(4-$CH_3)_3C$], 33.6 [4-$C(CH_3)_3$], 53.4 (C-3), 90.4 (C-4), 175.6 (C-2).

(±)-*4,4-Diethyl-3-methyl-2-oxetanone* (6bb). Colourless oil (Found: C, 67.3; H, 9.65. $C_8H_{14}O_2$ requires C, 67.6; H, 9.9); ν_{max} 1818 cm^{-1} (β-lactone); δ_H 0.84–0.96 (6 H, m, 4-CH_2CH_3), 1.21 (3 H, d, *J* 8, 3-CH_3), 1.64–1.96 (4 H, m, 4-CH_2CH_3), 3.26 (1 H, q, *J* 8, 3-H); δ_C 7.6, 8.0, and 8.7 (3 × CH_3), 24.6 and 29.2 (2 × CH_2), 51.4 (C-3), 84.9 (C-4), 172.6 (C-2).

(±)-*3-Methyl-4,4-dipropyl-2-oxetanone* (6bc). Colourless oil (Found: C, 67.3; H, 10.6. $C_{10}H_{18}O_2$ requires C, 70.55; H, 10.7); ν_{max} 1816 cm^{-1} (β-lactone); δ_H 0.87–0.95 (6 H, m, 4-$CH_2CH_2CH_3$), 1.20 (3 H, d, *J* = 8, 3-CH_3), 1.25–1.95 (8 H, m, 4-$CH_2CH_2CH_3$), 3.25 (1 H, q, *J* 8, 3-H); δ_C 8.7 (3-CH_3), 14.2 and 14.4 (2 × CH_3), 16.7, 17.4, 34.4, and 39.3 (2 × CH_2CH_2), 52.1 (C-3), 84.1 (C-4), 172.6 (C-2).

(±)-*3-Methyl-1-oxaspiro[3.5]nonan-2-one* (6bd).[13] Colourless solid, m.p. 25 °C; ν_{max} 1816 cm^{-1} (β-lactone); δ_H 1.22 (3 H, d, *J* 8, 3-CH_3), 1.31–1.98 [10 H, m, $(CH_2)_5$], 3.15 (1 H, q, *J* 8, 3-H); δ_C 8.4 (3-CH_3), 22.5, 23.1, 24.9, 31.1, and 37.1 (5 × CH_2), 52.5 (C-3), 82.1 (C-4), 172.6 (C-2).

(±)-trans-*4-*tert*-Butyl-3-methyl-2-oxetanone* (6be). Colourless oil (Found: C, 67.4; H, 9.8. $C_8H_{14}O_2$ requires C, 67.6; H, 9.9); ν_{max} 1823 cm^{-1} (β-lactone); δ_H 0.93 [9 H, s, 4-$C(CH_3)_3$], 1.31 (3 H, d, *J* 7, 3-CH_3), 3.21–3.34 (1 H, m, 3-H), 3.83 (1 H, d, *J* 4, 4-H); δ_C 13.1 (3-CH_3), 24.3 [4-$(CH_3)_3C$), 32.8 [4-$C(CH_3)_3$), 45.6 (C-3), 86.6 (C-4), 172.0 (C-2).

(±)-*3,4,4-Triethyl-2-oxetanone* (6cb). Colourless oil (Found: C, 68.9; H, 10.1. $C_9H_{16}O_2$: C, 69.2; H, 10.3); ν_{max} 1805 cm^{-1} (β-lactone); δ_H 0.83–1.03 (9 H, m, 3 × CH_3CH_2), 1.53–2.04 (6 H, m, 3 × CH_3CH_2), 3.04 (1 H, t, *J* 8, 3-H); δ_C 7.4, 8.1, and 12.5 (3 × CH_3), 17.9, 24.6, and 29.4 (3 × CH_2), 58.7 (C-3), 84.9 (C-4), 171.8 (C-2).

(±)-*3-Ethyl-4,4-dipropyl-2-oxetanone* (6cc). Colourless oil (Found: C, 71.6; H, 11.05. $C_{11}H_{20}O_2$ requires C, 71.7; H, 10.9).; ν_{max} 1816 cm^{-1} (β-lactone); δ_H 0.87–1.98 (19 H, m, $H_{aliph.}$), 3.04 (1H, t, *J* 8, 3-

H); δ_C 12.5, 14.3, and 14.4 (3 × CH_3), 16.5, 17.5, 17.7, 34.2, and 39.3 (5 × CH_2), 59.2 (C-3), 84.2 (C-4), 172.2 (C-2).

(±)-*3-Ethyl-1-oxaspiro[3.5]nonan-2-one* (6cd). Colourless oil (Found: C, 71.6; H, 9.9. $C_{10}H_{16}O_2$ requires C, 71.4; H, 9.6.; ν_{max} 1810 cm^{-1} (β-lactone); δ_H 1.00 (3 H, t, *J* 7, 3-CH_2CH_3), 1.26–1.83 (12 H, m, $H_{aliph.}$), 2.93 (1 H, t, *J* 8, 3-H); δ_C 12.3 (3-CH_3CH_2), 17.5 (3-CH_3CH_2), 22.2, 22.9, 24.9, 31.1, and 37.4 [$(CH_2)_5$], 59.7 (C-3), 82.1 (C-4), 172.1 (C-2).

(±)-trans-*4*-tert-*Butyl-3-ethyl-2-oxetanone* (6ce). Colourless oil (Found: C, 69.1; H, 10.1. $C_9H_{16}O_2$ requires C, 69.2; H, 10.3.; ν_{max} 1820 cm^{-1} (β-lactone); δ_H 0.93 [9 H, s, $C(CH_3)_3$], 0.98 (3 H, t, *J* 7, CH_3CH_2), 1.56–1.87 (2 H, m, CH_3CH_2), 3.13–3.22 (1 H, m, 3-H), 3.89 (1 H, d, *J* 4, 4-H); δ_C 11.4 (3-CH_3CH_2), 21.6 (3-CH_3CH_2), 24.4 [4-$(CH_3)_3C$], 32.7 [4-$C(CH_3)_3$], 52.3 (C-3), 84.7 (C-4), 171.5 (C-2).

(±)-*3-Butyl-4,4-diethyl-2-oxetanone* (6db). Colourless oil (Found: C, 71.7; H, 10.95. $C_{11}H_{20}O_2$ requires C, 71.7; H, 10.9); ν_{max} 1820 cm^{-1} (β-lactone); δ_H 0.82–1.04 (9 H, m, 3 × CH_3), 1.25–2.03 (10 H, m, $H_{aliph.}$), 3.11 (1 H, t, *J* 8, 3-H); δ_C 7.4, 8.2, and 13.8 (3 × CH_3), 22.5, 24.1, 24.5, 29.3, and 30.0 (5 × CH_2), 56.9 (C-3), 85.0 (C-4), 172.2 (C-2).

(±)-*3-Butyl-4,4-dipropyl-2-oxetanone* (6dc).[18] Colourless oil; ν_{max} 1815 cm^{-1}; δ_H 0.83–0.95 (9 H, m, 3 × CH_3), 1.13–1.97 (14 H, m, $H_{aliph.}$), 3.10 (1 H, t, *J* 8, 3-H); δ_C 13.8, 14.3, and 14.4 (3 × CH_3), 16.5, 17.5, 22.5, 24.0, 30.0, 34.3, and 39.3 (7 × CH_2), 57.6 (C-3), 84.2 (C-4), 172.3 (C-2).

(±)-*3-Butyl-1-oxaspiro[3.5]nonan-2-one* (6dd). Colourless solid, m.p. 19 °C (Found: C, 73.6; H, 10.2. $C_{12}H_{20}O_2$ requires C, 73.4; H, 10.3); ν_{max} 1816 cm^{-1} (β-lactone); δ_H 0.85 (3 H, t, *J* 7, CH_3), 1.21–1.84 (16 H, m, $H_{aliph.}$), 3.00 (1 H, t, *J* 8, 3-H); δ_C 13.8 (CH_3), 22.2, 22.5, 22.9, 23.7, 25.0, 29.9, 31.2, and 37.4 (8 × CH_2), 58.2 (C-3), 82.0 (C-9), 172.2 (C-2).

(±)-trans-*4*-tert-*Butyl-3-butyl-2-oxetanone* (6de). Colourless oil (Found: C, 71.4; H, 10.8. $C_{11}H_{20}O_2$ requires C, 71.7; H, 10.9); ν_{max} 1824 cm^{-1} (β-lactone); δ_H 0.85 (3 H, t, *J* 7, CH_3CH_2), 0.92 [9 H, s, $C(CH_3)_3$], 1.19–1.45 (4 H, m, $CH_3CH_2CH_2$), 1.51–1.75 (2 H, m, $C_3H_7CH_2$), 3.16–3.25 (1 H, m, 3-H), 3.87 (1 H, d, *J* 4, 4-H); δ_C 13.7 (CH_3), 22.4 (CH_2), 24.4 [4-$(CH_3)_3C$], 28.2 and 29.1 (2 × CH_2), 32.7 [4-$C(CH_3)_3$], 50.9 (C-3), 85.1 (C-4), 171.7 (C-2).

(±)-*4,4-Diethyl-3-isopropyl-2-oxetanone* (6eb). Colourless oil (Found: C, 70.3; H, 10.3. $C_{10}H_{18}O_2$ requires C, 70.55; H, 10.7); ν_{max} 1815 cm^{-1}; δ_H 0.83–1.12 (12 H, m, 4 × CH_3), 1.49–2.19 (5 H, m, $H_{aliph.}$), 2.79 (1 H, d, *J* 12, 3-H); δ_C 7.2 and 8.4 (2 × CH_3), 20.4 [$(CH_3)_2CH$], 22.5 [$CH(CH_3)_2$], 24.3 (CH_2), 24.7 [$(CH_3)_2CH$], 29.2 (CH_2), 64.0 (C-3), 85.3 (C-4), 171.4 4(C-2).

(±)-*3-Isopropyl-1-oxaspiro[3.5]nonan-2-one* (6ed). Colourless crystals, m.p. 45–47 °C (Found: C, 72.6; H, 10.1. $C_{11}H_{18}O_2$ requires C, 72.5; H, 9.95); ν_{max} 1817 cm^{-1} (β-lactone); δ_H 0.87 (3 H, d, *J* 6, CH_3CH), 1.07 (3 H, d, *J* 6, CH_3CH), 1.49–1.87 (10 H, m, $H_{aliph.}$), 2.00–2.16 [1 H, m, $(CH_3)_2CH$], 2.67 (1 H, d, *J* 11, 3-H); δ_C 20.2 [$(CH_3)_2CH$], 21.7 (CH_2), 22.2 [3-$CH(CH_3)_2$], 22.6 (CH_2), 24.4 [$(CH_3)_2CH$], 25.1, 31.2, and 37.6 (3 × CH_2), 65.6 (C-3), 82.4 (C-9), 171.4 (C-2).

(±)-trans-*4-tert-Butyl-3-isopropyl-2-oxetanone* (6ee). Colourless oil (Found: C, 70.4; H, 10.3. $C_{10}H_{18}O_2$ requires C, 70.55; H, 10.7); ν_{max} 1820 cm^{-1} (β-lactone); δ_H 0.87–1.05 (15 H, m, 5 × CH_3), 1.90–2.04 [1 H, m, $(CHCH_3)_2$], 2.97–3.03 (1 H, m, 3-H), 3.93 (1 H, d, *J* 4, 4-H); δ_C 19.9 and 20.6 [3-$(CH_3)_2CH$], 24.6 [4-$(CH_3)_3C$], 27.9 [3-$CH(CH_3)_2$], 32.7 [4-$C(CH_3)_3$], 57.7 (C-3), 83.0 (C-4), 171.0 (C-2).

Acknowledgements: Financial support by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* is gratefully acknowledged.

REFERENCES AND NOTES

1. Reactions of Electrochemically Generated Organometallics, Part 5. Part 4, Schick, H;. Ludwig, R.; Schwarz, K.-H.; Kleiner, K.; Kunath, A. *J. Org. Chem.* **1994**, *59*, 3161–3164.
2. (a) Fürstner, A. *Synthesis* **1989**, 571–590. (b) Rathke, M. W. *Org. React.* **1975**, *22*, 423–460. (c) Gaudemar, M. *Organomet. Chem. Rev. A* **1972**, *8*, 183–233. (d) Shriner, R. L. *Org. React.* **1942**, *1*, 1.
3. Moriwake, T. *J. Org. Chem.* **1966**, *31*, 983–985.
4. Burkhardt, E. R.; Rieke, R. D. *J. Org. Chem.* **1985**, *50*, 416–417.
5. Inaba, S. N.; Rieke, R. D. *Tetrahedron Lett.* **1985**, *26*, 155–156.
6. Imamoto, T.; Kusumoto, T.; Tawarayama, Y.; Sugiura, Y.; Mita, T.; Hatanaka, Y.; Yokoyama, M. *J. Org. Chem.* **1984**, *49*, 3904–3912.
7. Cahiez, G.; Chavant, P.-Y. *Tetrahedron Lett.* **1989**, *30*, 7373–7376.
8. (a) Chao, L.-C.; Rieke, R. D. *J. Org. Chem.* **1975**, *40*, 2253–2255. (b) Araki, S.; Ito, H.; Butsugan, Y. *Synth. Commun.* **1988**, *18*, 453–458. (c) Johar, P. S.; Araki, S.; Butsugan, Y. *J. Chem. Soc. Perkin Trans 1* **1992**, 711–713.
9. Schick, H.; Ludwig, R.; Schwarz, K.-H.; Kleiner, K.; Kunath, A. *Angew. Chem.* **1993**, *105*, 121831220; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1191–1193.
10. Jung, M. E.; Gervay, J. *J. Am. Chem. Soc.* **1991**, *113*, 224 and references cited therein.
11. Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183.
12. Mulzer, J.; Kerkmann, T. *J. Am. Chem. Soc.* **1980**, *102*, 3620.
13. Danheiser, R. L.; Nowick, J. S. *J. Org. Chem.* **1991**, *56*, 1176.
14. For recent reviews of β-lactone syntheses, see: (a) Mulzer, J. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I. Eds.; Pergamon: Oxford, 1991; Vol. 6, pp 342–350. (b) Pommier, A.; Pons, J. M. *Synthesis* **1993**, 441.
15. Bischoff, C. A. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 3830.
16. von Auwers, K.; Pötz, H.; Noll, W. *Liebigs Ann. Chem.* **1938**, *535*, 219, especially p 246.
17. Adam, W.; Rojas, C. I. *Synthesis* **1972**, 616.
18. Batandier, C.; Taillandier, G.; Boucherle, A.; Walrant, P. *Pharmazie* **1986**, *41*, 632.

(*Received in Germany* 2 *December* 1994; *accepted* 9 *January* 1995)