Pergamon

Tetrahedron Vol. 50, No. 48, pp. 13687-13696, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)00891-4

Direct Conversion of β,γ-Unsaturated Esters into Lactones Induced by TMS-I

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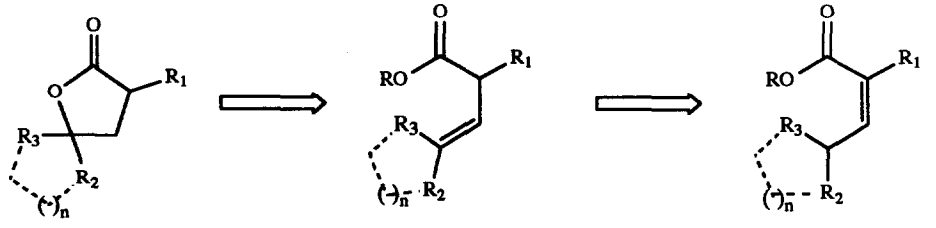
Abstract: *β,γ-unsaturated esters readily prepared by photodeconjugation are converted in one step into butanolides by treatment with TMS-I. The reaction has been extended to the access to α-alkylidene lactones.*

Due to the importance of the lactone framework in numerous natural products[1], much effort has been devoted to their access.[2] Among the plethora of syntheses already described, the conversion of alkenoates or unsaturated amides has indeed been achieved but requires in general a two step procedure. For example, iodolactonization[3] of unsaturated alkanoates or amides leads first to iodocompounds and needs a further reductive step with stannane hydrides.[4] Otherwise, selenolactonization presents the same inconveniance and generates toxic selenium derivatives. We anticipated that the cleavage of β,γ-unsaturated esters into the corresponding acids followed by a cationic lactonization procedure[5] could represent another efficient strategy.

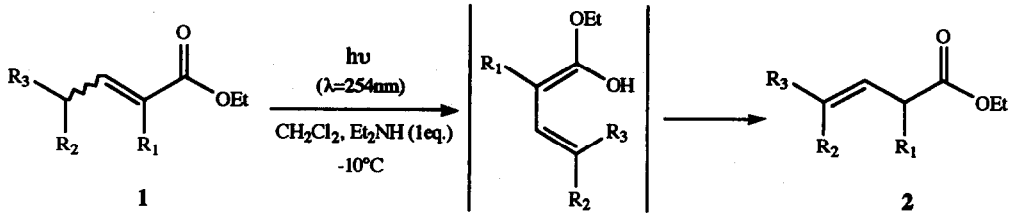
In connection with our previous work concerning the photodeconjugation of α,β-unsaturated esters[6,7] **1**, we have investigated the possibility of transforming β,γ-unsaturated carboxylic derivatives **2** into butanolides or spirolactones **3** whose the synthesis is presently of interest.[8] (Scheme 1).



scheme 1

The α,β-unsaturated esters **1**, readily prepared by a Wittig-Horner reaction[9] have been submitted to irradiation at 0°C in methylene chloride and in the presence of one equivalent of diethylamine. Diethylamine which is easily removable under vacuum constitutes a convenient base to promote the keto-enolic rearrangement of the photodienolic intermediate.[10] Under these conditions, the β,γ-unsaturated compounds **2** have been isolated in high yields (table 1).

Table 1: Preparation and photodeconjugation of α,β-unsaturated esters 1.



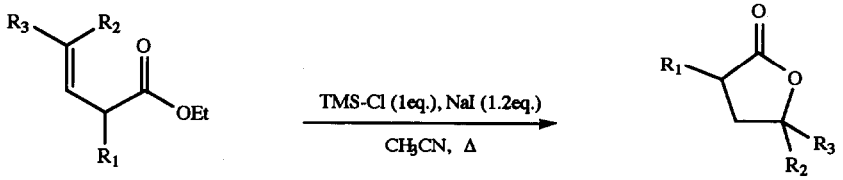
1 2

1	R_1	R_2	R_3	c.y.(%)	2	c.y. (%)
a	H	-$(CH_2)_5$-		88	a	92
b	H	Me	Me	65	b	73
c	Me	-$(CH_2)_4$-		68	c	61[a]
d	Me	-$(CH_2)_5$-		85	d	80
e	H	H	n-C_8H_{17}	94[b]	e	94

[a] reaction performed at 25°C. [b] mixture of E/Z isomers

To perform the first step without reconjugation of the substrates, alkaline conditions have to be avoided[11]. Trimethylsilyliodide (TMS-I), a powerful reagent for removing various protecting groups[12] is well known to allow the cleavage of esters into acids [13,14] and thus has been chosen for this purpose. Initially, ester **2a** was treated with TMS-I. To our surprise, the major product isolated was not the corresponding unsaturated acid but the spirolactone **3a** in 82% yield. This procedure was then tested on other esters **2** and the results are summarized in the following table .

Table 2: Conversion of esters **2** into butanolides **3**:

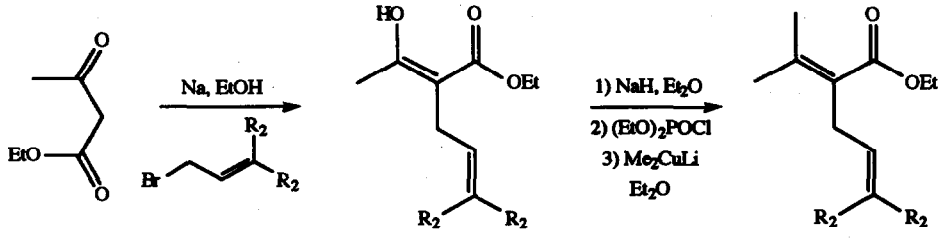


2 **3**

2	R_1	R_2	R_3	3	c.y. (%)
a	H	-$(CH_2)_5$-		a	82
b	H	Me	Me	b	87
c	Me	-$(CH_2)_4$-		c	75
d	Me	-$(CH_2)_5$-		d	67
e	H	H	n-C_8H_{17}	e	traces

The cyclization appears efficient for the majority of substrates tested, except for compound **2e** which bears only one substituent on the γ-carbon. In this case, only traces of the expected butyrolactone are observed, accompanied with a complex mixture of iodocompounds.

In addition, with the aim to gain rapid access to α-alkylidene lactones, which present interesting biological properties,[15] the reaction has been tested also on 2-(ω-alkenyl) acrylates **6a** and **6b**, prepared from ethyl acetoacetate.[16] (Scheme 2 and table 3).

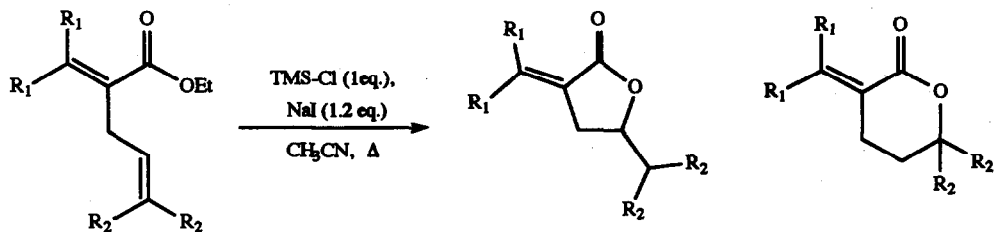


4a R_2 = Me
4b R_2 = H

6a 64%
6b 56%

Scheme 2

Table 3. Cyclization of substrates **6** into α-alkylidene lactones:

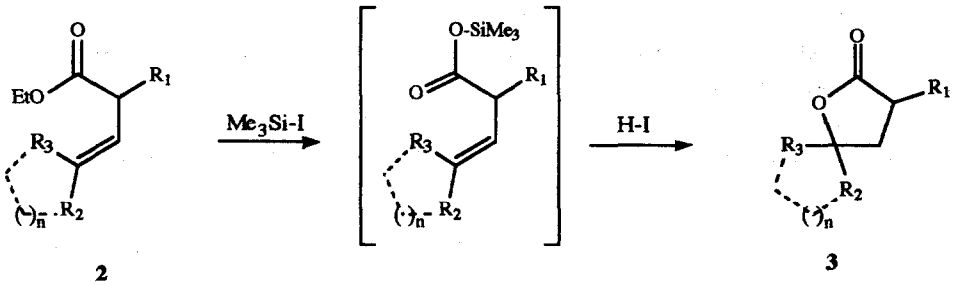


6 **7** **8**

6	R_1	R_2	**7**	**8**
a	Me	Me	**a** -	**a** 78%
b	Me	H	**b** 80%	**b** -

The cyclization occurs nicely for **6a** and **6b** leading respectively to the alkylidene hexanolide **8a** and the butyrolactone **7b** and the regioselectivity of the reaction follows that of cationic closure already described.[5a]

Mechanistically, the formation of lactones **3** could result from the cleavage of the ester by TMS-I, followed by a ring closure promoted itself by traces of hydroiodic acid. This explanation is supported by the previous observation of the formation of HI from trimethylsilyliodide[17] (Scheme 3). Furthermore, when the cyclization procedure for **2a** is performed in the presence of triethylamine, the lactonisation is totally inhibited and thus supports the above hypothesis. Moreover, the efficiency of this reaction is highly dependent on the γ-substitution or of the presence of existing ring in the substrate. These phenomena can be compared to similar results of cyclization strain and ring presence contraints for cationic closure of unsaturated acids.[5]



Scheme 3

In conclusion, this mild and novel procedure allows the easy and one step conversion of unsaturated esters into lactones in high yields and represent a new use of TMS-I in organic synthesis.

Experimental Section:

The NMR spectra were recorded in $CDCl_3$ using a Bruker AC 250 instrument. FT-IR spectra were carried out in $CHCl_3$ on a IR MIDAC spectrometer. Mass spectra were obtained on a D 300-JEOL apparatus at the UFR Pharmacy of the University of Reims. Elementary analyses were determined on a CHN 2400 Perkin Elmer Apparatus. Flash-chromatographies[18] were performed on silica gel Merck 60 (40-63 mesh).

Synthesis of α,β-unsaturated esters **1**. General procedure:

To a suspension of sodium hydride (12 mmol) in diethylether (150 ml) was added dropwise triethylphosphonoacetate (12 mmol). After 45 minutes at RT, a solution of the aldehyde (10mmol) in the same solvent (5 ml) was slowly added. The reaction mixture was stirred for an additional hour at RT and hydrolyzed carefully with brine. After extraction with ether (x3), the crude product was purified by flash-chromatography (Eluent: AcOEt / PE: 5/95).

(E)-Ethyl 3-cyclohexyl 2-propenoate: **1a**

C.y. = 88%.^{1}H NMR: 0.98-1.34 (m, 8H); 1.52-1.85 (m, 5H); 1.98-2.10 (m, 1H); 4.17 (q, 7.0 Hz, 2H); 5.73 (dd, 15.7 and 1.4 Hz, 1H); 6.87 (dd, 15.7 and 6.8 Hz, 1H). ^{13}C NMR: 14.1; 25.6; 25.8; 31.6; 40.3; 60.0; 118.8; 154.1; 166.9. IR: 2925, 2880, 1720, 1650, 1450, 1375, 1300, 1265, 1225, 1180, 1140, 1095. MS: 182 ($M^{+\cdot}$, 50); 137 (53); 136 (43); 107 (40); 73 (50); 67 (100).

Analysis: $C_{11}H_{18}O_2$: Calcd. C 72.49, H 9.95. Found: C 72.73, H 10.24.

(E)-Ethyl 4-methyl 2-pentenoate: **1b**

C.y. = 65%.^{1}H NMR: 1.05 (d, 6.8 Hz, 6H); 1.27 (t, 7.2 Hz, 3H); 2.44 (dtt, 6.5, 6.8 and 6.8 Hz, 1H); 4.15 (q, 7.2 Hz, 2H); 5.75 (dd, 0.9 and 15.6 Hz, 1H); 6.93 (dd, 6.5 and 15.6 Hz, 1H). ^{13}C NMR: 14.1; 21.1; 30.8; 59.9; 118.5; 155.1; 164.8. IR: 3000; 2950; 1680; 1640; 1375; 1295; 1240; 1200; 1260; 1030. MS: 142 ($M^{+\cdot}$, 24); 123 (16); 114 (46); 97 (88); 69 (100).

Analysis: $C_8H_{14}O_2$: Calcd. C 67.57, H 9.92. Found: C 67.67, H 10.15.

(E)-Ethyl 3-cyclopentyl, 2-methyl 2-propenoate: **1c**

C.y. = 68%.^{1}H NMR: 1.29 (t, 7.2 Hz, 3H); 1.56-1.83 (m, 8H); 1.85 (d, 1.3Hz, 3H); 2.74 (ddd, 7.7, 7.7 and 8.3 Hz, 1H); 4.18 (q, 7.2 Hz, 2H); 6.67 (dq, 8.3 and 1.3 Hz, 1H). ^{13}C NMR: 14.3; 20.7; 25.5; 33.7; 40.0; 60.0; 125.8; 147.9; 168.4. IR: 2960; 2860; 1695; 1640; 1385; 1365; 1280; 1240-1200; 1105; 1030. MS: 182 ($M^{+\cdot}$, 65); 153 (33); 137 (65); 115 (57); 109 (94); 108 (70); 87 (77); 67 (100).

Analysis: $C_{11}H_{18}O_2$: Calcd. C 72.49, H 9.95. Found: C 72.61, H 9.98.

(E)-Ethyl 3-cyclohexyl, 2-methyl 2-propenoate: **1d**

C.y. = 85%.^{1}H NMR: 0.86-2.02 (m, 10H); 1.30 (t, 7.0Hz, 3H); 1.85 (d, 1.5 Hz, 3H); 2.26 (m, 1H); 4.16 (q, 7.0 Hz, 2H); 6.58 (dq, 10 and 1.5Hz, 1H). ^{13}C NMR: 14.2; 20.7; 25.7; 25.9; 26.0; 32.6; 32.8; 38.1; 59.9; 125.3; 148.0; 168.1. IR: 2930; 2860; 1700; 1645; 1375; 1210; 1160; 1100; 1030. MS: 196 ($M^{+\cdot}$, 52); 150 (49); 121 (38); 115 (77); 95 (31); 93 (39); 87 (59); 81 (50); 79 (39); 69 (46); 67 (100): 55 (57).

Analysis: $C_{12}H_{20}O_2$: Calcd. C 73.46, H 10.27. Found: C 73.31, H 10.25.

*(E)-Ethyl 2-dodecenoate:***1e**

C.y. = 94%.^{1}H NMR: 0.87 (t, 6.9 Hz, 3H); 1.15-1.52 (m, 17H); 2.18 (ddt, 1.5, 6.9 and 6.9 Hz, 2H); 4.17 (q, 7.2 Hz, 2H); 5.76 (dt, 15.6 and 1.5 Hz, 1H); 6.95 (dt, 15.6 and 6.9 Hz, 1H). ^{13}C NMR: 14.0; 14.2; 22.6; 28.0; 29.1; 29.2; 29.3; 29.4; 31.8; 32.1; 60.0; 121.2; 166.7. IR: 2940, 2850, 1720, 1655, 1460, 1370, 1270. MS: 226 (M^+, 14); 171 (48); 138 (35); 101 (100); 89 (56); 73 (64).

Analysis: $C_{14}H_{26}O_2$: Calcd. C 74.28, H 11.57. Found: C 74.48, H 11.78.

Photodeconjugation of esters **1**: *General procedure.*

To a solution of the ester **1** (10 mmol) in methylene chloride (50 ml) is added diethylamine (10 mmol). The solution is poured into quartz tubes and deoxygenated by bubbling with argon. The tubes are placed around a quartz Dewar containing a short wave length OSRAM lamp. The irradiation is carried out at 0°C. After disappearance of the starting material (TLC control), the solvent is removed. The deconjugated ester is purified by flash-chromatography (Eluent AcOEt / Petrol ether: 5 / 95).

Ethyl 3-cyclohexylidene propanoate: **2a**

C.y = 92%.^{1}H NMR: 1.25 (t, 7.0 Hz, 3H); 1.46-1.60 (m, 6H); 2.05-2.15 (m, 4H); 3.00 (d, 7.2 Hz, 2H); 4.11 (q, 7.1 Hz, 2H); 5.22 (dt, 1.1 and 7.2 Hz, 1H). ^{13}C NMR: 14.1; 25.4; 26.6; 27.4; 28.3; 28.8; 32.3; 32.9; 36.9; 60.35; 112.4; 143.3; 172.5. IR: 2980; 2930; 2850; 1725; 1650; 1450; 1370; 1260; 1170; 1035. MS: 182 ($M^{+\cdot}$, 24); 152 (26); 135 (46); 107 (100); 81 (53); 67 (62).

Ethyl 4-methyl 3-pentenoate: **2b**

C.y = 73%. ^{1}H NMR: 1.23 (t, 7.1 Hz, 3H); 1.61 (s, 3H); 1.72 (s, 3H); 3.00 (d, 7.1 Hz, 2H); 4.10 (q, 7.1 Hz, 2H); 5.28 (tq, 7.1 and 1.4 Hz, 1H). ^{13}C NMR: 14.1; 17.8; 25.5; 33.8; 60.4; 115.9; 135.3; 172.4. IR: 2970; 2950; 1740; 1650; 1450; 1365; 1265; 1190; 1165. MS: 142 ($M^{+\cdot}$, 15); 124 (21); 105 (65); 91 (28); 68 (100).

Ethyl 3-cyclopentylidene 2-methyl propanoate: **2c**

C.y = 61%. ^{1}H NMR: 1.20 (d, 7.0 Hz, 3H); 1.24 (t, 7.0 Hz, 3H); 1.58-1.69 (m, 4H); 2.19-2.28 (m, 4H); 3.19 (dq, 9.2 and 7.0 Hz, 1H); 4.11 (q, 7.0 Hz, 2H); 5.27 (dt, 9.2 and 2.2 Hz, 1H). ^{13}C NMR: 14.4; 18.0; 26.4; 28.9; 33.8; 40.8; 60.4; 119.6; 145.9; 175.7. IR: 2960; 1720; 1375; 1255; 1185; 1165; 1045. MS: 182 ($M^{+\cdot}$, 7); 136 (21); 109 (100); 108 (41); 91 (35); 81 (42); 67 (82); 55 (39).

Ethyl 3-cyclohexylidene 2-methyl propanoate: **2d**

C.y = 80%. ^{1}H NMR: 1.19 (d, 7.0 Hz, 3H); 1.24 (t, 7.1 Hz, 3H); 1.45-1.66 (m, 6H); 2.08-2.22 (m, 4H); 3.34 (dq, 9.1 and 7.0 Hz, 1H); 4.11 (q, 7.1 Hz, 2H); 5.10 (d, 9.1 Hz, 1H). ^{13}C NMR: 14.4; 18.6; 26.9; 27.9; 28.7; 29.3; 37.2; 38.2; 60.5; 120.8; 142.1; 175.8. IR: 2940; 2860; 1720; 1375; 1210; 1180; 1045. MS: 196 ($M^{+\cdot}$, 8); 150 (19); 123 (61); 122 (26); 102 (37); 95 (47); 81 (100); 67 (57); 55 (73).

Ethyl 3-dodecenoate: **2e**

C.y = 93%.

^{1}H NMR: 0.88 (t, 6.4 Hz, 6H); 1.20-1.40 (m, 30H); 2.00-2.06 (m, 4H); 3.00 (d, 5.4 Hz, 2H), (E)-isomer; 3.08 (d, 5.4 Hz, 2H), (Z)-isomer; 4.12 (q, 7.1 Hz, 2H), (E)-isomer; 4.14 (q, 7.1 Hz, 2H), (Z)-isomer; 5.50-5.57 (m, 4H). ^{13}C NMR: 14.0; 14.1; 22.6; 27.3; 29.1; 29.2; 29.4; 31.8; 32.4; 33.0; 38.1; 60.4; 120.8 and 121.5; 133.4 and 134.7; 172.1. IR: 2930; 2845; 1740; 1465; 1250; 1165; 1030. MS: 227 ($M^{+\cdot}$+1, 7); 226 ($M^{+\cdot}$, 4); 170 (16); 137 (42); 101 (46); 87 (78); 69 (64).

Cyclization Procedure: Synthesis of butanolides **3**:

To a suspension of anhydrous sodium iodide (6 mmol) in freshly distilled acetonitrile (10 ml) is added under argon trimethylsilylchloride (6 mmol). The resulting mixture is stirred for 10 minutes at room temperature. The ester **2** (5 mmol) in acetonitrile (2 ml) is added and the solution is heated at 60°C until complete conversion (TLC control). After cooling, the solution is hydrolyzed with brine, extracted with methylene chloride. The organic layers are dried over $MgSO_4$, concentrated and the product is purified by flash-chromatography.

1-Oxaspiro[5,4]decan-2-one: **3a**[8f]

C.y = 82%. ^{1}H NMR: 1.40-1.70 (m, 10H); 1.98 (t, 8.1 Hz, 2H) 2.56 (t, 8.1 Hz, 2H). ^{13}C NMR: 22.5; 24.8; 28.5; 32.7; 36.8; 86.3; 176.7. IR: 2940; 2875; 1770; 1450; 1420; 1370; 1270; 1220; 1150; 1125; 1045. MS: 154 ($M^{+\cdot}$, 18); 153 (17); 112 (15); 111 (18); 98 (26).

4-Methyl ,4-pentanolide: **3b**[19]

C.y = 87%. ^{1}H NMR: 1.35 (s, 6H); 2.00 (t, 8.2 Hz, 2H); 2.52 (t, 8.2 Hz, 2H). ^{13}C NMR: 27.6; 29.6; 34.5; 84.4; 176.5. IR: 2980; 2880; 1760; 1460; 1385; 1375; 1270; 1145; 960. MS: 114 ($M^{+\cdot}$, 34); 98 (100); 55 (93).

3-Methyl, 1-oxaspiro[4,4] nonan-2-one: **3c**

C.y = 75%. ^{1}H NMR: 1.23 (d, 7.2 Hz, 3H); 1.55-2.10 (m, 9H); 2.32 (dd, 8.5 and 12.6 Hz, 1H); 2.73 (ddq, 8.5, 11.2 and 7.2 Hz, 1H). ^{13}C NMR: 15.3; 23.4; 23.9; 35.9; 38.2; 38.8; 40.9; 92.2; 179.2. IR: 2980; 2875; 1765; 1455; 1380; 1345; 1230; 1170; 1145; 1070; 980. MS: 154 ($M^{+\cdot}$, 25); 125 (74); 112 (32); 84 (21); 69 (27); 55 (100).

3-Methyl, 1-oxaspiro[4,5] decan-2-one: **3d**

C.y = 67%. ^{1}H NMR: 1.27 (d, 7.1 Hz, 3H); 1.32-1.90 (m, 11H); 2.34 (dd, 9.2 and 12.7 Hz, 1H); 2.79 (ddq, 9.2, 10.8 and 7.2 Hz, 1H). ^{13}C NMR: 15.8; 22.6; 24.9; 34.6; 35.9; 38.3; 41.6; 83.7; 179.2. IR: 3020; 2940; 2860; 1755; 1440; 1300; 1200; 965. MS: 168 ($M^{+\cdot}$, 15); 125 (100); 112 (38); 81 (41); 67 (27).

Analysis: $C_{10}H_{16}O_2$: Calcd. C 71.39, H 9.58. Found: C 70.97, H 9.82.

Preparation of compounds **6a** and **6b** [16]:

To a solution of sodium ethoxide (100 mmol) in EtOH (50ml) under argon, is slowly added ethyl acetoacetate (100 mmol) in the same solvent. After heating one hour at 80°C, the allylic bromide (120 mmol) is added dropwise and the solution is stirred for two additional hours. The solvent is removed by concentration and the reaction mixture is hydrolyzed with ice-water. After extraction with ether, the organic phases are dried over $MgSO_4$ and concentrated. The product **4a** or **4b** is then purified by flash-chromatography.

Ethyl 2-acetyl 5-methyl 4-hexenoate: **4a**

C.y =76%. ^{1}H NMR: 1.27 (t, 7.1 Hz, 3H); 1.62 (s, 3H); 1.67 (d, 1.3Hz, 3H); 2.22 (s, 3H); 2.53 (t, 7.4 Hz, 2H); 3.42 (t, 7.4 Hz, 1H); 4.18 (q, 7.1 Hz, 2H); 5.02 (tq, 7.5 Hz and 1.3 Hz, 1H). ^{13}C NMR: 13.9; 17.6; 25.6; 26.9; 28.9; 59.7; 61.1; 119.7; 134.6; 169.5; 202.8. IR: 2970; 2920; 1740; 1710; 1450; 1360; 1240; 1200; 1140. MS: 198 ($M^{+\cdot}$, 5); 156 (35); 125 (22); 109 (100); 81 (37); 69 (50).

Ethyl 2-acetyl 4-pentenoate: **4b**

C.y =79%. ^{1}H NMR: 1.25 (t, 7.2 Hz, 3H); 2.21 (s, 3H); 2.58 (dt, 6.9, 7.1 Hz, 2H); 3.50 (t, 7.1Hz, 1H); 4.16 (q, 7.2Hz, 2H); 5.00-5.12 (m, 2H); 5.72 (ddt, 10.2, 17.0, 6.9Hz, 1H). ^{13}C NMR: 14.0; 29.0; 32.1; 59.2; 61.3; 117.3; 134.1; 169.1; 202.3. IR: 2990, 2920, 1740, 1715, 1640, 1360, 1230, 1190, 1150, 1020. MS: 170 ($M^{+\cdot}$, <5); 156 (100); 127 (80; 99 (7).

To a suspension of NaH (90 mmol) in ether (100ml) is added at 0°C compound **4** (75 mmol). After one hour is added dropwise diethyl phosphoryloxychloride (90 mmol). The reaction mixture is stirred at RT until total conversion of the starting material (TLC control). Hydrolysis is performed with an aqueous saturated solution of NH_4Cl. After separation of the organic layer, the aqueous phase is twice extracted with Et_2O. Finally, the organic phases are washed successively with a saturated solution of $NaHCO_3$ and brine and dried over $MgSO_4$. The crude product is purified by flash-chromatography (AcOEt / PE: 50/50).

Ethyl 2-[1'-(diethoxyphosphoryloxy)ethylidene] 5-methyl 4-hexenoate: **5a**

C.y =99%. ^{1}H NMR: 0.88-1.46 (m, 9H); 1.64 (s, 3H); 1.68 (s, 3H); 2.13 (s, 3H); 2.94 (d, 6.6 Hz, 2H); 4.12-4.28 (m, 6H); 5.03 (t, 6.6 Hz, 1H). IR: 2980, 1695, 1440-1420, 1375, 1270, 1200, 1060, 1030, 980. MS: 334 ($M^{+\cdot}$, 3), 288 (10); 154 (100); 127 (30); 99 (32).

Ethyl 2-[1'-(diethoxyphosphoryloxy)ethylidene] 4-pentenoate: **5b**

C.y =71%. ^{1}H NMR: 1.22 (t, 7.3 Hz, 3H); 1.28 (t, 7.1 Hz, 3H); 1.29 (t, 7.1 Hz, 3H); 2.05 (s, 3H); 2.95 (d, 6.0 Hz, 2H); 4.07-4.19 (m, 6H); 4.94-5.05 (m, 2H); 5.72 (ddt, 10.0, 16.1 and 6.0Hz, 1H). ^{13}C NMR: 13.9;

15.8; 15.9; 17.7; 32.7; 60.3; 64.2; 64.3; 115.6; 116.6; 134.0; 150.4; 166.2. IR: 2980, 1720, 1450, 1385, 1280, 1195, 1150, 1025. MS: 306 ($M^{+\cdot}$, 15); 260 (40); 149 (100); 126 (50); 98 (65).

To CuI (110 mmol) in dried ether (150 ml) is added dropwise at 0°C, MeLi (220 mmol, 1.0M in Et_2O). The milky solution is cooled to -65°C and compound **5** (75 mmol) in ether (60 ml) is slowly added. The solution is stirred for 2h at this temperature and subsequently quenched with an aqueous saturated solution of ammonium chloride. After extraction three times with ether, the combined organic layers are dried over $MgSO_4$ and concentrated under vacuum. The product **6** is purified by flash-chromatography.

Ethyl 5-methyl 2-(1'-methylethylidene) 4-hexenoate: **6a**

C.y = 82%. ^1H NMR: 1.28 (t, 7.0 Hz, 3H); 1.65 (s, 3H); 1.67 (d, 1.1 Hz, 3H); 1.81 (s, 3H); 1.96 (s, 3H); 3.00 (d, 7.0 Hz, 2H); 4.17 (q, 7.0 Hz, 2H); 5.04 (tq, 7.0 Hz and 1.4 Hz, 1H). ^{13}C NMR: 14.2; 17.7; 21.7; 22.9; 25.6; 28.9; 59.9; 121.6; 127.2; 131.9; 141.5; 169.5. IR: 3000; 2980; 2920; 1680; 1450; 1410; 1375; 1270; 1220-1200; 1070. MS: 196 ($M^{+\cdot}$, 35); 151 (38); 123 (46); 107 (100); 95 (35); 81 (48).

Ethyl 2-(1'-methylethylidene) 4-pentenoate: **6b**

C.y = 90%. ^1H NMR: 1.21 (t, 6.9 Hz, 3H); 1.80 (s, 3H); 2.01 (s, 3H); 3.02 (d, 6.1 Hz, 2H); 4.16 (q, 7.1 Hz, 2H); 4.88-5.02 (m, 2H); 5.73 (ddt, 10.0, 17.1 and 6.1 Hz, 1H). ^{13}C NMR: 14.2; 23.0; 24.6; 34.0; 60.0; 114.9; 135.5; 140.4; 144.1; 171.7. IR: 2990, 2930, 1710, 1640, 1450, 1365, 1280, 1200, 1110, 1060, 1020. MS: 168 (M+., 35); 151 (38); 123 (46); 107 (100); 95 (35); 81 (48).

Analysis: $C_{10}H_{16}O_2$: Calcd. C 71.39, H 9.59. Found: C 71.40, H 9.66.

Cyclization of esters **6a** and **6b**:

2-[1'-methylethylidene] 5-methyl, 5-hexanolide: **8a**

C.y = 78%. ^1H NMR: 1.35 (s, 6H); 1.83 (t, 7.1 Hz, 2H); 1.86 (s, 3H); 2.23 (t, 1.9 Hz, 3H); 2.50 (tq, 7.0 and 1.9 Hz, 2H). ^{13}C NMR: 22.2; 23.8; 27.3; 33.4; 79.3; 118.9; 151.7; 166.3. IR: 2990; 2930; 1710; 1615; 1450; 1365; 1290; 1260; 1210; 1165; 1110; 1070; 960. MS: 168 (M+., 63); 153 (34); 125 (38); 111 (79); 94 (55); 57 (100).

Analysis: $C_{10}H_{16}O_2$: Calcd. C 71.39, H 9.58. Found: C 71.34, H 9.29.

2-[1'-methylethylidene] 4-pentanolide: **7b**

C.y = 80%. ^1H NMR: 1.31 (d, 6.2 Hz, 3H); 1.79 (s, 3H); 2.18 (s, 3H); 2.31-2.39 (m, 1H); 2.90 (m, 1H); 4.50 (ddq, 7.1 and 6.2 Hz, 1H). ^{13}C NMR: 19.5; 22.1; 24.3; 35.2; 72.29; 119.5; 149.8; 170.1. IR: 2960; 2930; 1740; 1665; 1440; 1380; 1340; 1265; 1190; 1060; 1030. MS: 140 ($M^{+\cdot}$, 100), 125 (33); 97 (26); 95 (25); 79 (33); 68 (48); 67 (43).

Analysis: $C_8H_{12}O_2$: Calcd. C 68.54, H 8.62. Found: C 68.13, H 9.01.

Acknowledgements: Professor J.P. Pete is thanked for his continual interest in this work. Dr T.G.C. Bird (Zeneca Pharma, Reims) is gratefully acknowledged for his help during the polishing of the text.

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(*Received in Belgium* 6 *June* 1994; *accepted* 10 *October* 1994)