saponification of its diethyl ester,[18] in 120 mL dimethylformamide/acetic acid (5:1) was added under nitrogen 15.1 g (34 mmol) of lead tetraacetate and the solution degassed again. The mixture was stirred and slowly warmed to 100 °C. Carbon dioxide started to evolve at 75 °C, and a white precipitate appeared after 15 min at 100 °C. After 1.5 h, when the reaction mixture had turned into a brownish yellow solution, it was cooled to room temperature, poured into 250 mL of water, and extracted with methylene chloride (5 × 50 mL). The combined organic phases were washed with sodium bicarbonate solution (3 × 5 mL) and 50 mL of saturated sodium bisulfite solution and then dried over magnesium sulfate. The solvent was removed on a rotatory evaporator and the residue purified by sublimation [50 °C (0.1 torr)] to give 960 mg (35%) of **2**-Cl: ^{1}H NMR (100 MHz, $CDCl_3$) δ 2.17 (s, 12 H); ^{13}C NMR (25.4 MHz, $CDCl_3$) δ 63.8 (s), 37.9 (t).

Preparation of Carbocations. To freshly distilled SbF_5 dissolved in a twofold excess of SO_2ClF or SO_2 was added at −80 to −90 °C with vigorous stirring a cooled slurry or solution of the appropriate precursor in SO_2ClF or SO_2 resulting in an approximately 10–15% solution of the cation. In one laboratory (Hamburg), the solid **2**-Cl was added to the precooled (−80 to −100 °C) SbF_5/SO_2ClF in small portions with occasional vigorous shaking on a VORTEX vibrator. In one case, only 1 mg of **2**-Cl was added to 0.5 mL SbF_5/SO_2ClF and the cation ^{13}C NMR spectrum recorded on a Bruker WH 400 spectrometer. Ionizations in AsF_5 were carried out in a well-ventilated hood at −90 °C. AsF_5 should be handled very carefully as it is volatile (bp −53 °C) and highly toxic.

(18) Roberts, J. D.; Moreland, W. T., Jr.; Frazer, W. *J. Am. Chem. Soc.* **1953**, *75*, 637.

^{13}C NMR spectra were obtained on Varian Models FT-80, XL-100, XL-200 as well as Bruker WH-270 and WH-400 spectrometers equipped with low-temperature broad band probes. The ^{13}C chemical shifts are referenced from external capillary tetramethylsilane.

Quenching Experiment. A cation solution was prepared from 100 mg (0.56 mmol) of dichloride **2**-Cl and 1.2 g of SbF_5 in 3 mL of SO_2ClF at −110 to −90 °C and checked by ^{13}C NMR spectroscopy to contain the species **3**-Cl. The solution was transferred with a precooled pipet into a vigorously stirred suspension of 7 g of K_2CO_3 in 100 mL of methanol kept at −78 °C and the mixture stirred at this temperature for 4 h. After warming to room temperature it was worked up in the usual way (addition of H_2O, extraction with ether, removal of solvent from dried solution). The product was isolated by preparative gas chromatography (1.5 m 10% FFAP on Chromosorb W 60-80), yielding 30 mg (30%) of 4-chloro-1-bicyclo[2.2.2]octyl methyl ether (**11**): mp 45 °C; ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.02 (s, 3 H, OCH_3), 2.07 (m, 6 H), 1.72 (m, 6 H); ^{13}C NMR (25.4 MHz, $CDCl_3$) δ 71.1 (s), 65.1 (s), 49.2 (q), 36.8 (t), 31.0 (t). Anal. Calcd for $C_9H_{15}ClO$: C, 61.89; H, 8.66; Cl, 20.30; O, 9.16. Found: C, 61.99; H, 8.74; Cl, 20.30.

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Registry No. **2** (X = Cl), 1123-39-3; **2** (X = F), 20277-40-1; **3** (X = Cl→SbFs), 98922-12-4; **3** (X = F→SbFs), 98922-13-5; **7**, 98922-10-2; **11**, 98922-14-6; *N*-chlorosuccinimide, 128-09-6; 1,4-bicyclo[2.2.2]octanedicarboxylic acid, 711-02-4.

A Two-Step Preparation of α-Alkylidene γ-Lactones from γ-Lactones: A Synthesis of (±)-Ancepsenolide[1]

Gerald L. Larson* and Rosa M. Betancourt de Perez[2]

Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931

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γ-Butyrolactone, γ-valerolactone, and the cis lactone of 2-hydroxycyclohexaneacetic acid have been C-silylated via their respective lithium enolates with diphenylmethylchlorosilane. The resulting α-silylated γ-lactones can be deprotonated and condensed with aldehydes and ketones to give α-alkylidene γ-lactones in moderate to excellent yield. The enolate of the α-diphenylmethylsilyl cis lactone of 2-hydroxycyclohexaneacetic acid condensed with 1-butanal but not with benzaldehyde or acetaldehyde.

Although α-silyl acetates and their derivatives have been used in the preparation of α,β-unsaturated esters,[3] α-silyl lactones have been reported as precursors to α-alkylidene lactones in only two instances.[4] We have reported that the lithium enolates of esters and γ-lactones can be cleanly C-silylated with diphenylmethylchlorosilane as opposed to the more common O-silylation observed with trialkylchlorosilanes.[5] Due to their ease of preparation and potential differences in the reactivity of the α-diphenylmethylsilyl γ-lactones from that of the α-trimethylsilyl lactones we were interested to see if the α-diphenylmethylsilyl γ-lactones were viable precursors to α-alkyl-

(1) The Chemistry of α-Silyl Carbonyl Compounds. 10.

(2) Graduate student supported by the NIH-MBRS program (RR-8102-10).

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(5) Larson, G. L.; Fuentes, L. *J. Am. Chem. Soc.* **1981**, *103*, 2418.

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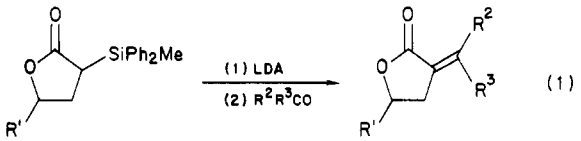
Table I. α-Ylidene γ-Lactones from α-Diphenylmethylsilyl γ-Lactones

entry	lactone	aldehyde/ketone	product 4 R^2	product 4 R^3	% yield[a]	E:Z ratio[b]
1	1	PhCHO	H	Ph	89	100:0
2	1	i-C_3H_7CHO	H	i-C_3H_7	74	100:0
3	1	CH_2=CHCHO	H	CH_2=CH	50	72:28
4	1	CH_3CHO	H	CH_3	25	0:100
5	1	n-C_3H_7CHO	H	n-C_3H_7	74	80:20
6	1	$(CH_2O)_n$	*d*	*d*	*d*	
7	1	$(CH_3)_2CO$	CH_3	CH_3	32	
8	1	cyclohexanone			60	
9	1	$PhCOCH_3$	CH_3	Ph	50	100:0
10	1	cholestenone	5	see eq 4		
11	1	cyclopentanone[c]				
12	2	PhCHO	H	Ph	76	100:0
13	2	dodecanedialdehyde		see Scheme I		
14	3	n-C_3H_7CHO		see eq 5		

[a] Isolated yields. [b] Determined by ^1H NMR. [c] Self-condensation of cyclopentanone occurred in 32% yield. [d] None of the desired product.

idene γ-lactones according to eq 1. We are pleased to report herein that this is indeed the case.

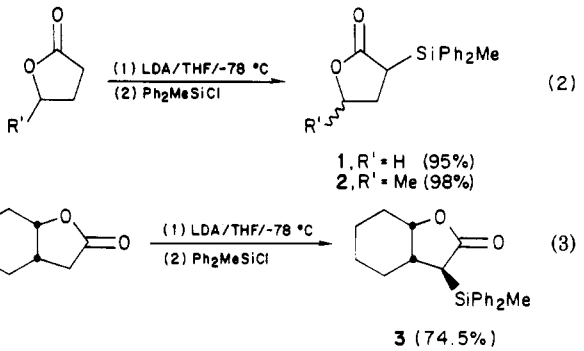


(1)

1, R' = H
2, R' = Me

4

The α-silyl lactones **1**, **2**, and **3** were prepared as shown.[7] Lactone **3** was prepared as a single diastereomer with the diphenylmethylsilyl group assumed to occupy an exo position, consistent with the results of Grieco and Miyashita.[8]



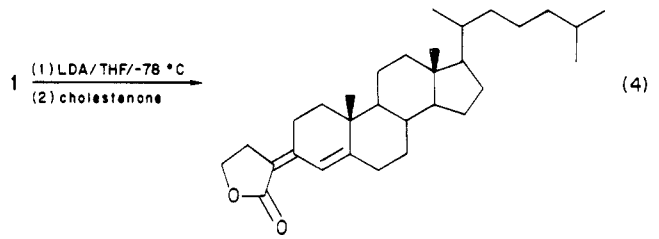
(2)

(3)

Treatment of **1** with a slight excess of lithium diisopropylamine (LDA) in THF at −78 °C followed by the addition of benzaldehyde gave (*E*)-α-benzylidene-γ-butyrolactone in 89% yield, providing excellent evidence that the reaction proceeds as desired. Further results are shown in Table I. Regarding the scope of the reaction the enolate of **1** could be condensed with both aldehydes and ketones. Reaction of the enolate of **1** with *p*-formaldehyde gave none of the desired product and mostly recovered starting **1**. Acetaldehyde produced only a moderate yield of α-ethylidene-γ-butyrolactone (entry 4). Acrolein reacts in a 1,2 fashion (entry 3) as does cholestenone (entry 10). The highly enolizable cyclopentanone is deprotonated by the enolate of **1** leading to the self-condensation product of cyclopentanone, α-cyclopentylidenecyclopentanone (entry 10), whereas another readily enolizable ketone, acetophenone, gives the desired product (entry 9).

The reaction occurs stereoselectively to produce the *E* isomer as the major product. Indeed with benzaldehyde (entries 1 and 11) and the hindered isobutyraldehyde (entry 2) the *E* isomer is formed exclusively. This is consistent with the results of Yamamoto and co-workers.[6k] Interestingly, the enolate of **1** reacts with acetaldehyde to give the *Z* isomer, albeit in low yield and mixed with γ-butyrolactone. This is in contrast with the report of Grieco and co-workers[4a] who found the *E* isomer from the reaction of the enolate of α-(trimethylsilyl)-γ-butyrolactone and acetaldehyde. No explanation for this difference in stereoselectivity is apparent.

The enolate of **1** reacts with cholestenone to give a single diastereomer, which we have assigned the *E* geometry as shown in **5** (eq 4). In support of this assignment is the

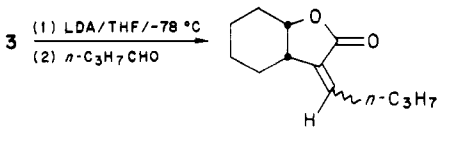


(4)

5

fact that the vinyl proton appears as a singlet at 7.39 ppm in chloroform-*d* and at 7.97 ppm in benzene-d_6, consistent with this proton being cis to the carbonyl of the lactone.[6b] Acetophenone reacts with the enolate of **1** to give the *E* isomer as the only isolated product. Consistent with the assignment of the *E* geometry to this product is the 2.16 ppm resonance for the methyl protons and the 24.9 ppm resonance for the methyl carbon.

The enolate of **3** did not react with benzaldehyde, even when the reaction mixture was warmed to room temperature and brought about condensation of acetaldehyde. It did, however, condense with *n*-butyraldehyde to give a 55:45 mixture of (*E*)- and (*Z*)-**6** in 40% yield (eq 5). These



(5)

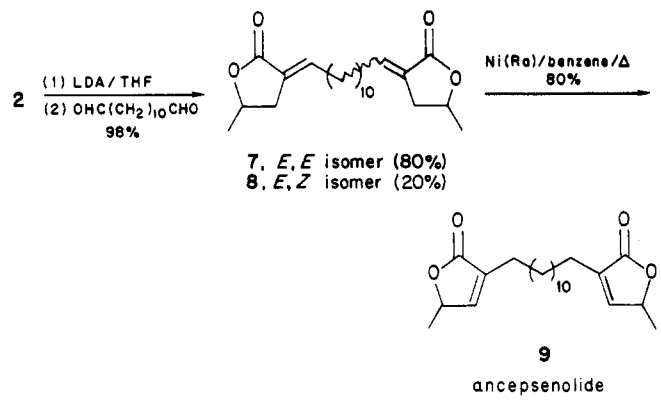
6

isomers did not separate when subjected to silica gel chromatography and were analyzed as the mixture, with the vinyl proton of the *E* isomer resonating at 6.59 ppm

(7) With both γ-valerolactone and γ-caprolactone mixtures of C- and O-silylation were observed. Heating of these mixtures leads to conversion to the C-silylated lactones accompanied by decomposition. Our initial work, which was reported to give clean C-silylation with γ-valerolactone, appears to be in error since all subsequent attempts at this preparation have given predominantly O-silylated isomer.

(8) Grieco, P. A.; Miyashita, M. *J. Org. Chem.* **1974**, *39*, 120.

Scheme I



and that of the Z isomer at 6.03 ppm.

Application of this alkylidenation to the synthesis of (±)-ancepsenolide, a bisbutenolide of marine origin isolated from the gorgonians Pterogorgia anceps (Pallas) and from Xiphigorgia anceps (Bimini),[9] was accomplished as shown in Scheme I. Treatment of 2.2 equiv of **2** with LDA and then dodecanedialdehyde gave a 4:1 mixture of the E,E diastereomer **7** and the E,Z diastereomer **8** in 98% total yield. Isomerization of this mixture with Raney nickel[10] in benzene gave (±)-ancepsenolide in 80% yield (Scheme I).

Experimental Section

All reactions were carried out in a standard apparatus and flame dried under nitrogen, with magnetic stirring, and under a nitrogen atmosphere. Infrared spectra were recorded with a Perkin-Elmer 283 spectrophotometer, ^1H and ^{13}C NMR spectra on a JEOL FX-90Q spectrophotometer in $CDCl_3$, and internal Me_4Si and mass spectra on a Hewlett-Packard 5995A GC–MS spectrophotometer. MS data are reported as m/e (relative abundance). Aldehydes and ketones were distilled prior to use. Dodecanedialdehyde was prepared by pyridinium chlorochromate oxidation of 1,12-dodecanediol. The cis lactone of 2-hydroxycyclohexaneacetic acid was prepared according to the procedure of Klein.[11] Solvents were dried by accepted procedures.

α-(Diphenylmethylsilyl)-γ-butyrolactone (1). This material was prepared in 95% yield by our published procedure.[5] The spectral data are reported therein.

α-(Diphenylmethylsilyl)-γ-valerolactone (2). To a solution of 60 mmol of LDA in 50 mL of THF was added 4.73 mL (50 mmol) of γ-valerolactone in 30 mL of THF at −78 °C. This solution was stirred for 30 min, and 10.3 mL (50 mmol) of diphenylmethylchlorosilane in 10 mL of THF was added. After the reaction mixture was stirred at −78 °C for 1 h, it was allowed to warm to room temperature where it was stirred for an additional 1 h. After the addition of 100 mL of hexane, the organic layer was washed with cold water (2 × 100 mL) and dried over magnesium sulfate. Solvent removal at reduced pressure gave 15.2 g (98%) of a viscous liquid which soldified in the refrigerator. This material is a mixture of isomers, which were not separated, mp 63–64 °C: IR (neat) 1745 cm^{-1}; ^1H NMR δ 7.7–7.16 (m, 10 H), 4.5 (tq, 1 H, J = 6.2, 2 Hz), 3.9 (tq, 1 H, J = 6.2, 2 Hz), 2.9–1.6 (m, 3 H) 1.25 (d, 3 H, J = 6.1 Hz), 1.15 (d, 3 H, J = 6.1 Hz), 0.7 (s, 3 H); ^{13}C NMR δ 178.3, 135.1, 135.0, 134.2, 133.9, 130.1, 129.8, 128.1, 128.0, 76.5, 33.1, 30.5, 30.2, 21.4, 21.0, −4.5, −4.9; MS, m/e 296 (13), 197 (100).

α-Diphenylmethylsilyl Cis Lactone of 2-Hydroxycyclohexaneacetic Acid (3). Following the procedure above, 0.98 g (7 mmol) of the cis lactone of 2-hydroxycyclohexaneacetic acid was deprotonated with 8.05 mmol of LDA, and the enolate anion was quenched with 1.44 mL (1.63 g, 7 mmol) of diphenylmethylchlorosilane to give, after crystallization (ether:hexane), 1.75 g (75%) of the title compound mp 83–84 °C: IR 1745 cm^{-1}; ^1H NMR δ 7.70–7.20 (m, 10 H), 3.97–3.77 (m, 1 H), 2.35–1.06 (m, 10 H), 0.72 (s, 3 H); ^{13}C NMR δ 177.1, 134.6, 133.9, 133.8, 130.0, 129.9, 128.1, 127.7, 41.5, 38.2, 30.3, 27.4, 23.1, 19.5, −3.9; MS, m/e 337 (13), 336 (45), 294 (5), 293 (21), 199 (12), 198 (18), 197 (100), 195 (7), 181 (6), 178 (7), 165 (5), 137 (10), 121 (5), 119 (5), 105 (12), 55 (5), 53 (5). Anal. Calcd for $C_{21}H_{24}OSi$: C, 74.94; H, 7.19. Found: C, 74.82; H, 7.21.

(E)-α-Benzylidene-γ-butyrolactone (Representative Procedure). A 50-mL, two-necked flask equipped with condenser, septum, magnetic stirrer, and a nitrogen inlet was charged with 0.8 mL (5.75 mmol) of diisopropylamine and 5 mL of THF. This was converted to LDA with n-butyllithium and 1.41 g (5 mmol) of α-(diphenylmethylsilyl)-γ-butyrolactone in 5 mL of THF added dropwise at −78 °C followed by stirring for 0.5 h at that temperature and then the addition of 0.5 mL (5 mmol) of benzaldehyde. The solution was allowed to reach room temperature and refluxed for 15 min, and 0.9 mL (7.5 mmol) of trimethylchlorosilane was added to silylate the lithium diphenylmethylsiloxide formed and thereby facilitate product purification. The reaction mixture was diluted with hexane (10 mL), washed with water (2 × 10 mL) and 10% ammonium chloride (10 mL), and dried over magnesium sulfate. After solvent removal at reduced pressure, the product was purified by column chromatography on alumina, eluting with 5% dichloromethane/hexane, to yield 0.77 g (89%) of the title compound: mp 115–117 °C (hexane) (lit.[12] mp 116–117 °C); IR (neat) 1740 and 1655 cm^{-1}; ^1H NMR δ 7.48 (t, 1 H, J = 3.0 Hz), 7.3–7.2 (m, 5 H), 4.37 (t, 2 H, J = 7.61 Hz), 3.1 (dt, 2 H, J = 7.6, 3.0 Hz); ^{13}C NMR δ 172.40, 136.71, 134.74, 129.97, 129.79, 128.90, 123.60, 65.37, 27.48.

(E)-α-Benzylidene-γ-valerolactone. This material was produced in 76% yield and showed the following properties: IR (neat) 1750 and 1650 cm^{-1}; ^1H NMR δ 7.6–7.1 (m, 6 H), 4.59 (m, 1 H), 3.26 (ddd, 1 H, J = 17.6, 7.6, 2.9 Hz), 2.65 (ddd, 1 H, J = 17.6, 5.6, 3.2 Hz), 1.34, (d, 3 H, J = 6.1 Hz); ^{13}C NMR δ 172.10, 136.55, 133.90, 129.85, 129.68, 127.76, 74.07, 35.20, 22.24; MS, m/e 214 (9), 116 (100).

(E and Z)-α-Propenylidene-γ-butyrolactone. This material was produced in 50% yield as a 72:28 E/Z mixture and showed the following properties: IR (neat) 1745, 1650, and 1600 cm^{-1}; ^1H NMR δ 7.1 (dt, 1 H, J = 11.1, 2.7 Hz O=CC=CH of E isomer), 6.56 (dd, 1 H, J = 11.1, 9.4 Hz, O=CC=CHC*H*=CH_2 of Z isomer), 6.37 (dd, 1 H, J = 11.2, 9.7 Hz O=CC=C*H*=CH_2 of E isomer), 5.80–5.62 (m, 1 H, O=CC=C*H* of Z isomer), 5.62–5.48 (m, 2 H, C=CH_2 of E isomer), 5.43–5.36 (m, 2 H, C=CH_2 of Z isomer), 4.36 (t, 2 H, J = 7.4 Hz OCH_2 of Z isomer), 2.99 (dt, 4 H, J = 7.4, 2.7 Hz); ^{13}C NMR δ 171.6, 139.3, 135.8, 132.3, 131.5, 126.6, 125.4, 124.7, 65.4, 29.0, 25.5; MS, m/e (E isomer) 125 (9), 124 (100), (Z isomer) 125 (8), 124 (100).

(Z)-α-Ethylidene-γ-butyrolactone. This material was prepared in 25% yield contaminated with γ-butyrolactone and showed the following properties: IR 1750, 1675 cm^{-1}; ^1H NMR δ 6.31 (tq, 1 H, J = 7.2, 2.4 Hz), 4.30 (t, 2 H, J = 7.4 Hz), 3.02–2.71 (m, 2 H), 2.17 (dt, 3 H, J = 7.4, 2.4 Hz); ^{13}C NMR δ 170.5, 138.6, 127.7, 65.2, 29.1, 13.9.

α-Propylidene-γ-butyrolactone. This material was produced in 32% yield and showed the following properties: IR 1740, 1660 cm^{-1}; ^1H NMR δ 4.29 (t, 2 H, J = 7.5 Hz), 3.05–2.69 (m, 2 H), 2.25 (t, 3 H, J = 2.2 Hz), 1.89 (t, 3 H, J = 1.6 Hz); ^{13}C NMR δ 170.3, 149.9, 118.3, 63.9, 27.4, 24.3, 19.4; MS, m/e 126 (100).

(E)-α-Isobutylidene-γ-butyrolactone. This material was produced in 76% yield and showed the following properties: IR (neat) 1755 and 1675 cm^{-1}; ^1H NMR δ 6.47 (dt, 1 H, J = 9.8, 2.7 Hz), 4.28 (t, 2 H, J = 7.4 Hz), 2.79 (dt, 2 H, J = 7.4, 2.7 Hz), 2.35 (m, 1 H), 0.98 (d, 6 H, J = 6.8 Hz); ^{13}C NMR δ 171.45, 146.54, 122.89, 65.20, 29.51, 24.44, 21.16; MS, m/e 140 (21), 67 (100).

α-Butylidene-γ-butyrolactone. The reaction produced the title compound as a mixture of E and Z isomers in 74% yield. Chromatography gave 14.8% of the Z isomer eluting first and showing the following: IR (neat) 1740 and 1665 cm^{-1}; ^1H NMR δ 6.24 (tt, 1 H, J = 7.8, 2.2 Hz), 4.32 (t, 2 H, J = 7.3 Hz), 2.82 (m, 4 H), 1.42 (sextet, 2 H, J = 7.0 Hz), 0.95 (t, 3 H, J = 7.0 Hz); ^{13}C NMR δ 170.06, 144.04, 123.74, 65.22, 29.32, 29.03, 22.25, and

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(10) Martin S. F.; Moore, D. R. *Tetrahedron Lett.* **1976**, 4459.
(11) Klein, J. *J. Am. Chem. Soc.* **1959**, *81*, 3611.
(12) Pinder, A. R. *J. Chem. Soc.* **1952**, 2236.

13.64; MS, m/e 140 (82), 125 (100). The E isomer eluted second in 59.2% yield and showed the following: IR (neat) 1740 and 1670 cm^{-1}; ^1H NMR δ 6.66 (tt, 1 H, J = 7.3, 2.9 Hz), 4.30 (t, 2 H, J = 7.4 Hz), 2.79 (m, 2 H), 2.15 (m, 2 H), 1.40 (sextet, 2 H, J = 7.0 Hz), 0.88 (t, 3 H, J = 7.2 Hz); ^{13}C NMR δ 171.10, 140.42, 125.20, 65.22, 31.96, 24.84, 21.22, 13.58; MS, m/e 140 (33), 99 (100).

α-Cyclohexylidene-γ-butyrolactone. This material was prepared in 60% yield and showed the following properties: IR (neat) 1740 and 1655 cm^{-1}; ^1H NMR δ 4.22 (t, 2 H, J = 7.3 Hz), 2.82 (bt, 2 H, J = 7.1 Hz), 2.15 (m, 2 H), 1.56 (m, 6 H), 1.19 (m 1 H), 0.82 (m, 1 H); ^{13}C NMR δ 170.58, 157.62, 115.09, 64.21, 34.18, 28.32, 27.81, 27.65, 27.13, 25.95; MS, m/e 166 (100).

(*E*)-α-(α-Methylbenzylidene)-γ-butyrolactone. This material was prepared in 50% yield and showed the following properties: IR 1748, 1645 cm^{-1}; ^1H NMR δ 7.45–7.09 (m, 5 H), 4.33 (t, 2 H, J = 7.5 Hz), 3.01 (tq, 2 H, J = 7.5, 1.8 Hz), 2.16 (t, 3 H, J = 1.8 Hz); ^{13}C NMR δ 168.5, 150.2, 139.8, 127.8, 127.7, 127.3, 119.9, 63.8, 28.2, 24.9; MS, m/e 189 (14), 188 (100). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.59; H, 6.38. Found: C, 76.63; H, 6.44.

α-Butylidene of Cis Lactone of 2-Hydroxycyclohexaneacetic Acid. Following the general procedure above, 0.2 g (0.6 mmol) of **3** was deprotonated with 0.7 mmol of LDA, and the resulting enolate anion was quenched with 0.10 mL (0.085 g; 1.18 mmol) of n-butyraldehyde to give, after alumina chromatography, 0.052 g (39.7%) of a 55:45 E:Z mixture of the title compound: IR 1745, 1675 cm^{-1}; ^1H NMR δ 6.59 (dt, J = 7.7, 1.3 Hz, vinyl proton of E isomer), 6.03 (dt, J = 7.7, 1.8 Hz, vinyl proton of Z isomer), 4.58–4.26 (m, $^1/_2$ H), 3.08–2.75 (m, $^1/_2$ H), 2.63 (dt, J = 7.5, 1.3 Hz), 2.22 (t, J = 6.8 Hz), 2.14 (t, J = 7.5 Hz), 1.95–1.08 (m, 10 H), 0.94 (t, 3 H, J = 6.8 Hz); ^{13}C NMR δ 171.5, 170.5, 141.4, 138.0, 134.3, 127.7, 76.4, 40.7, 37.3, 31.4, 29.3, 28.5, 27.3, 27.2, 26.9, 22.7, 22.4, 21.9, 21.4, 20.4, 19.2, 13.7, 13.6, GC–MS Z isomer (retention time 9.44 min) 195 (13), 194 (100); E isomer (retention time 10.26 min) 195 (15), 194 (100).

Reaction of 1 with 4-Cholesten-3-one: Preparation of 5. Following the general procedure above, 1.41 g (5 mmol) of **1** was deprotonated with 5.75 mmol of LDA, and the enolate was quenched with 1.92 g (5 mmol) of 4-cholesten-3-one to give, after crystallization from hexane, 0.67 g (30%) of the title product: IR 1728, 1620 cm^{-1}; ^1H NMR δ 7.39 (s, 1 H), 4.30 (t, 2 H, J = 7.7 Hz), 2.88 (t, 1 H, J = 7.7 Hz), 2.44–2.12 (m, 3 H), 2.12–1.10 (m, 26 H), 1.07 (s, 3 H,), 0.94 (s, 3 H), 0.89 (s, 3 H), 0.69 (s, 3 H); ^1H NMR (benzene-d_6) δ 7.97 (s, 1 H), 3.64 (t, 2 H, J = 7.7 Hz), 2.27 –1.87 (m, 4 H), 1.87–1.12 (m, 26 H), 0.97 (s, 3 H), 0.93 (s, 3 H), 0.90 (s, 3 H), 0.68 (s, 3 H); ^{13}C NMR δ 170.6, 157.5, 148.0, 117.6, 113.2, 64.5, 56.2, 56.1, 54.1, 42.4, 39.8, 39.5, 37.8, 36.2, 35.8, 33.0, 32.6, 28.2, 28.0, 27.6, 26.1, 24.2, 23.8, 22.8, 22.5, 21.2, 18.7, 17.8, 11.9: MS, m/e 454 (33), 453 (100). Anal. Calcd for $C_{31}H_{48}O_2$: C, 82.18; H, 10.59. Found: C, 82.04; H, 10.75.

Reaction of 2 with Dodecanedialdehyde. Preparation of 7 and 8. A standard apparatus of 100-mL capacity was charged with 1.7 mL (12 mmol) of diisopropylamine and 20 mL of THF. This was converted to LDA with 12 mmol of n-butyllithium and 3.2 g (10.8 mmol) of **2** in 10 mL of THF was added dropwise at −78 °C followed by stirring at that temperature for 45 min and then the addition of 0.99 g (5 mmol) of dodecanedialdehyde. The solution was allowed to reach room temperature and was refluxed for 15 min, and 6.38 mL (50 mmol) of trimethylchlorosilane was added to silylate the diphenylmethylsiloxide produced. The reaction mixture was then diluted with hexane (10 mL), washed with water (2 × 15 mL), and dried over magnesium sulfate. After solvent removal at reduce pressure, the product was purified by column chromatography on alumina, eluting with hexane followed by 5% dichloromethane, to yield 1.81 g (98%) of **7** and **8**, which were crystallized from ether/hexane. The E,Z diastereomer (20% of the mixture) eluted first and showed the following: IR (neat) 1755 and 1675 cm^{-1}; ^1H NMR δ 6.72 (tt, 1 H, J = 7.5, 2.9 Hz), 6.17 (tt, 1 H, J = 7.8, 2 Hz), 4.9–4.4 (m, 1 H), 3.2–2.8 (m, 4 H), 2.7–2.4 (m, 4 H), 2.3–1.3 (m, 16 H), 1.4 (d, 3 H), J = 6.4 Hz), 1.38 (d, 3 H, J = 6.4 Hz); ^{13}C NMR δ 170.88, 169.75, 144.01, 140.76, 126.46, 124.73, 73.91, 73.64, 36.86, 32.90, 29.33, 28.08, 27.54, 22.23, 21.74; MS, m/e 110 (100), 182 (45). The E,E diastereomer (80%) eluted second and showed the following: IR (neat) 1755 and 1680 cm^{-1}; ^1H NMR δ 6.72 (tt, 1 H, J = 7.5, 2.9 Hz), 4.9–4.4 (m, 1 H), 3.2–2.8 (m, 2 H), 2.7–2.4 (m, 2 H), 2.3–1.3 (m, 8 H), 1.4 (d, 3 H, J = 6.2 Hz); ^{13}C NMR δ 170.92, 140.79, 126.53, 73.96, 32.94, 30.17, 29.35, 28.13, 22.27; MS, m/e 110 (100), 182 (45). Anal. Calcd for $C_{22}H_{34}O_4$: C, 72.99; H, 9.39. Found: C, 72.70; H, 9.47.

Preparation of (±)-Ancepsenolide (9). A standard apparatus of 50-mL capacity was charged with 0.02 g (0.17 mequiv of Ni) of Raney nickel and 10 mL of benzene. This was refluxed for 3 h to deactivate it somewhat and 0.02 g (0.06 mmol) of **7** added in 5 mL of benzene and this solution refluxed for 20 h. The Raney nickel was washed with hot benzene, and the solution was evaporated to give a solid, which was crytallized from methanol to give 0.16 g (80%) of the title compound. The synthetic material was identical in all respects with the natural material.

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Reaction of α-Silyl Esters with Grignard Reagents: A Synthesis of β-Keto Silanes and Ketones. Preparation of the Douglas Fir Tussock Moth Pheromone[1]

Gerald L. Larson,* David Hernandez,[2] Ingrid Montes de Lopez-Cepero,[3] and Luz E. Torres[4]

Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931

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A variety of α-diphenylmethylsilyl esters have been prepared and reacted with Grignard reagents. The reaction is relatively slow in refluxing THF and can be controlled to allow the addition of 1 equiv of the Grignard reagent, providing the corresponding β-keto silane. Protiodesilylation of the β-keto silane results in the overall conversion of an ester to a ketone. This ester to ketone methodology has been applied to a two-step synthesis of the pheromone of the Douglas fir tussock moth. The β-keto silanes are viable precursors to regioselectively generated enol silyl ethers. The reaction of ethyl 2-methyl-2-(diphenylmethylsilyl)propionate with vinylmagnesium bromide or 2-methyl-1-propenylmagnesium bromide results in the addition of 2 equiv of the Grignard reagent, the second in a Michael fashion.

The preparation of ketones via the reaction of organometallic reagents and carboxylic acid derivatives represents a logical, but not always trouble-free, transformation.[5] Although enolization and reduction of the ketone resulting

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