Table 3. *Bond angles* (Å), *bond angles and torsion angles* (°) *with their e.s.d.'s for B*, $C_{14}H_{20}O_6$

C1—C2	1·524 (4)	C6—O5	1·347 (4)
C1—C8	1·541 (4)	C6—O6	1·201 (5)
C1—C11	1·507 (4)	C7—C8	1·546 (5)
C2—C3	1·514 (4)	C7—C17	1·532 (6)
C3—C4	1·553 (4)	C11—O1	1·207 (3)
C3—O3	1·440 (5)	C11—O2	1·346 (3)
C4—C5	1·517 (4)	C12—O2	1·442 (6)
C4—O4	1·422 (5)	C14—C15	1·494 (6)
C5—C8	1·552 (4)	C14—C16	1·531 (5)
C5—O5	1·452 (5)	C14—O3	1·416 (3)
C6—C7	1·498 (5)	C14—O4	1·427 (4)
C2—C1—C8	111·5 (2)	C8—C7—C17	120·6 (3)
C2—C1—C11	113·6 (2)	C1—C8—C5	110·8 (2)
C8—C1—C11	114·5 (2)	C1—C8—C7	118·7 (3)
C1—C2—C3	109·3 (2)	C5—C8—C7	101·9 (2)
C2—C3—C4	114·7 (2)	C1—C11—O1	126·1 (3)
C2—C3—O3	108·2 (2)	C1—C11—O2	110·6 (3)
C4—C3—O3	102·9 (2)	O1—C11—O2	123·3 (3)
C3—C4—C5	115·5 (3)	C15—C14—C16	113·7 (3)
C3—C4—O4	104·3 (2)	C15—C14—O3	109·0 (3)
C5—C4—O4	108·9 (3)	C15—C14—O4	109·2 (3)
C4—C5—C8	118·5 (3)	C16—C14—O3	109·4 (3)
C4—C5—O5	104·5 (2)	C16—C14—O4	111·1 (3)
C8—C5—O5	106·5 (2)	O3—C14—O4	103·9 (3)
C7—C6—O5	110·4 (3)	C11—O2—C12	116·2 (3)
C7—C6—O6	128·9 (3)	C3—O3—C14	108·6 (2)
O5—C6—O6	120·6 (3)	C4—O4—C14	105·9 (2)
C6—C7—C8	105·4 (3)	C5—O5—C6	111·7 (3)
C6—C7—C17	110·7 (3)		
C1—C2—C3—O3	−74·9 (3)	C4—C5—C8—C1	9·5 (4)
C1—C2—C3—C4	39·4 (3)	C4—C5—C8—C7	136·7 (3)
C1—C8—C5—O5	−107·8 (3)	C5—C8—C1—C11	173·9 (3)
C1—C8—C7—C17	−23·5 (5)	C5—O5—C6—C7	−0·3 (4)
C1—C11—O2—C1	173·8 (3)	C5—C8—C1—C2	43·2 (3)
C2—C3—C4—C5	11·5 (4)	C5—C8—C7—C17	−145·3 (3)
C3—O3—C14—O4	−33·1 (3)	C7—C8—C1—C2	−74·0 (3)
C3—O3—C14—C15	−149·4 (3)	C7—C8—C5—O5	19·4 (3)
C3—O3—C14—C16	85·6 (3)	C8—C1—C11—O1	−140·4 (3)
C3—C2—C1—C11	159·3 (3)	C8—C1—C11—O2	42·2 (3)
C3—C4—C5—C8	−37·6 (4)	C8—C5—O5—C6	−12·7 (3)
O3—C3—C4—O4	9·4 (3)	C8—C5—C4—O4	79·2 (3)
C4—O4—C14—C15	155·3 (3)	C8—C7—C6—O5	13·1 (4)
C4—O4—C14—C16	−78·4 (3)		

We thank 'Le Ministère de l'Education du Québec' for financial support and Professor A. L. Beauchamp for assistance in the collection of data and help in resolution of the structure.

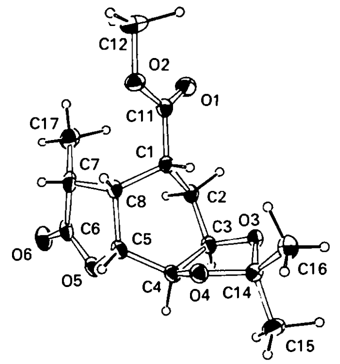

Fig. 2. An *ORTEP* diagram of isomer *B* with the H atoms and the atomic numbering. Ellipsoids represent 30% probability.

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Intramolecular Free-Radical Ring Closures. III. Structure of a Chiral δ-Lactone*

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Abstract. $C_{26}H_{34}O_5Si$, orthorhombic, $M_r = 454·64$, $P2_12_12_1$, $a = 7·425$ (3), $b = 10·491$ (4), $c = 32·882$ (12) Å, $V = 2561·4$ Å^3, $Z = 4$, $D_x = 1·179$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 1·05$ mm^{-1}, $F(000) = 976$, $T = 220$ K, $R = 0·052$ for 2075 observed reflections. A triphenyltin hydride-mediated intramolecular cyclization of a chloropropionate ester and an α,β-unsaturated ester gave a crystalline lactone. Although spectroscopic assignment based on ^{1}H NMR and nuclear Overhauser

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* Methyl (3*S*,4*R*,6*S*)-6-(*tert*-butyldiphenylsilyloxymethyl)-3-methyl-2-oxo-3,4,5,6-tetrahydro-4-pyranacetate.

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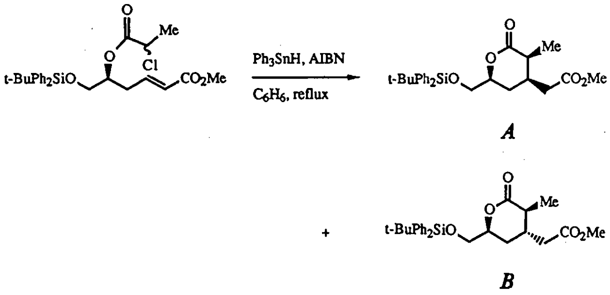
enhancement studies indicated the proposed structure, X-ray analysis was used for confirmation. The six-membered lactone exists in a twist-boat conformation with the substituents at C3 and C6 being pseudoequatorial and the substituent at C4 pseudoaxial.

Experimental. The reaction shown below produced two major lactones *A* and *B* in 62·5% yield and in a 3·5:1 ratio, one of which (*A*) was crystalline and suitable for X-ray analysis.



A colorless crystal of *A*, $C_{26}H_{34}O_5Si$, with dimensions 0·13 × 0·30 × 0·34 mm, was obtained from hexanes and mounted on an Enraf–Nonius CAD-4 diffractometer. Unit-cell dimensions from 25 well centered reflections in the range $20 < \theta < 25°$. Graphite-monochromatized Cu $K\alpha$ radiation was used, $2\theta_{\max} = 140·0°$. The data were collected in the ω-scan mode, $\Delta\omega = (1·00 + 0·14\tan\theta)°$. The orientation was checked every 200 measurements. The intensities of six reflections (checked every hour) presented a maximum fluctuation of less than 3·8%. 2665 reflections were measured, 2084 of which had $I > 1·96\sigma(I)$. Data corrected for Lp and uncorrected for absorption.

The structure was solved using *MULTAN*80,* refined on $|F_o|$ by the full-matrix least-squares method. Refinement anisotropic for C, O, Si atoms; H-atom coordinates were fixed at idealized positions ($d_{C—H} = 1·08$ Å) with $U_{iso} = 0·09$ and 0·16 Å^2 [H(6x) and H(9x)], $U_{iso} = 0·13$ Å^2 [H(12x), H(13x) and H(14x)] and $U_{iso} = 0·07$ Å^2 (others). Mirror enantiomer tested by separate least-squares refinements giving $R = 0·054$, $S = 1·07$.

Final $R = 0·052$, $wR = 0·050$ (unit weight, 9 reflections suffering extinction rejected), $S = 1·03$, (shift/σ) mean 0·010, max. 0·05. Residual electron density fluctuation on final difference Fourier synthesis: 2 peaks of 0·19 e Å^{-3} at 0·97–1·24 Å from Si, background ±0·17 e Å^{-3}.

Table 1. *Final atomic coordinates and their e.s.d.'s* (× 10^4, Si × 10^5) *and* U_{eq} *values* (Å^2 × 10^3) *for* $C_{26}H_{34}O_5Si$

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Si	10845 (18)	14163 (15)	63584 (4)	46
O(1)	1349 (4)	−1379 (3)	5532 (1)	48
O(2)	3087 (6)	−1880 (4)	5016 (1)	72
O(3)	3890 (7)	−4071 (4)	6690 (1)	79
O(4)	6442 (6)	−3042 (5)	6534 (1)	99
O(5)	683 (5)	−109 (3)	6276 (1)	50
C(1)	2247 (8)	−2249 (5)	5305 (1)	51
C(2)	2086 (7)	−3601 (5)	5445 (1)	50
C(3)	2422 (6)	−3653 (5)	5908 (1)	45
C(4)	1060 (8)	−2793 (5)	6123 (1)	49
C(5)	109 (7)	−1863 (5)	5836 (1)	45
C(6)	3266 (9)	−4504 (5)	5193 (2)	69
C(7)	4367 (7)	−3259 (6)	6008 (2)	61
C(8)	4842 (8)	−3521 (7)	6446 (2)	63
C(9)	7037 (10)	−3229 (10)	6952 (2)	129
C(10)	−683 (6)	−712 (5)	6051 (1)	47
C(11)	3602 (7)	1475 (6)	6419 (2)	62
C(12)	4540 (8)	1135 (8)	6020 (2)	87
C(13)	4129 (10)	471 (7)	6749 (2)	93
C(14)	4268 (9)	2796 (7)	6562 (2)	97
C(21)	−79 (7)	1872 (5)	6842 (1)	51
C(22)	−1023 (8)	978 (6)	7064 (1)	58
C(23)	−1897 (8)	1274 (7)	7428 (2)	70
C(24)	−1859 (9)	2516 (8)	7568 (2)	80
C(25)	−950 (9)	3428 (7)	7354 (2)	77
C(26)	−58 (9)	3123 (6)	6997 (2)	70
C(31)	205 (7)	2380 (5)	5926 (2)	49
C(32)	587 (8)	2041 (5)	5524 (1)	60
C(33)	−16 (9)	2738 (6)	5196 (2)	69
C(34)	−1070 (8)	3813 (5)	5258 (2)	64
C(35)	−1496 (8)	4150 (6)	5649 (2)	68
C(36)	−890 (7)	3462 (5)	5979 (2)	59

Table 2. *Bond distances* (Å), *bond angles and torsion angles* (°) *with their e.s.d.'s for* $C_{26}H_{34}O_5Si$

O(1)—C(1)	1·354 (6)	C(2)—C(3)	1·544 (6)
O(1)—C(5)	1·451 (6)	C(2)—C(6)	1·534 (8)
O(2)—C(1)	1·201 (6)	C(3)—C(4)	1·529 (7)
O(3)—C(8)	1·215 (7)	C(3)—C(7)	1·538 (7)
O(4)—C(8)	1·322 (7)	C(4)—C(5)	1·530 (7)
O(4)—C(9)	1·457 (8)	C(5)—C(10)	1·518 (7)
O(5)—C(10)	1·406 (6)	C(7)—C(8)	1·508 (8)
C(1)—C(2)	1·496 (7)		

C(1)—O(1)—C(5)	117·2 (4)	C(4)—C(3)—C(7)	111·3 (4)
C(8)—O(4)—C(9)	115·3 (5)	C(3)—C(4)—C(5)	113·4 (4)
Si—O(5)—C(10)	130·8 (3)	O(1)—C(5)—C(4)	110·8 (4)
O(1)—C(1)—O(2)	118·3 (5)	O(1)—C(5)—C(10)	106·8 (4)
O(1)—C(1)—C(2)	115·5 (4)	C(4)—C(5)—C(10)	113·5 (4)
O(2)—C(1)—C(2)	126·2 (5)	C(3)—C(7)—C(8)	112·0 (4)
C(1)—C(2)—C(3)	108·9 (4)	O(3)—C(8)—O(4)	124·0 (6)
C(1)—C(2)—C(6)	112·0 (4)	O(3)—C(8)—C(7)	125·5 (6)
C(3)—C(2)—C(6)	114·8 (4)	O(4)—C(8)—C(7)	110·5 (5)
C(2)—C(3)—C(4)	109·2 (4)	O(5)—C(10)—C(5)	109·9 (4)
C(2)—C(3)—C(7)	110·7 (4)		

O(1)—C(1)—C(2)—C(3)	−47·3 (6)	C(6)—C(2)—C(1)—O(1)	−175·2 (4)
C(1)—C(2)—C(3)—C(4)	58·2 (5)	C(6)—C(2)—C(3)—C(4)	−175·4 (4)
C(2)—C(3)—C(4)—C(5)	−15·5 (5)	C(6)—C(2)—C(3)—C(7)	61·7 (6)
C(3)—C(4)—C(5)—O(1)	−38·4 (5)	C(7)—C(3)—C(2)—C(1)	−64·7 (5)
C(4)—C(5)—O(1)—C(1)	54·8 (5)	C(7)—C(3)—C(4)—C(5)	107·0 (5)
C(5)—O(1)—C(1)—C(2)	−10·2 (6)	C(10)—C(5)—C(4)—C(3)	−158·5 (4)
O(2)—C(1)—O(1)—C(5)	169·9 (4)	C(10)—C(5)—O(1)—C(1)	178·9 (4)
O(2)—C(1)—C(2)—C(3)	132·6 (5)	O(5)—C(10)—C(5)—O(1)	−67·5 (4)
O(2)—C(1)—C(2)—C(6)	4·6 (7)	O(5)—C(10)—C(5)—C(4)	54·8 (5)
		Si—O(5)—C(10)—C(5)	142·3 (3)

The scattering factors were taken from Cromer & Mann (1968) for Si, O and C, and from Stewart, Davidson & Simpson (1965) for H.

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* The programs used here are modified versions of: *NRC*-2, data reduction, *NRC*-10, bond distances and angles and *NRC*-22, mean planes (Ahmed, Hall, Pippy & Huber, 1973); *MULTAN*80, multisolution program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); and *ORTEP* (Johnson, 1965).

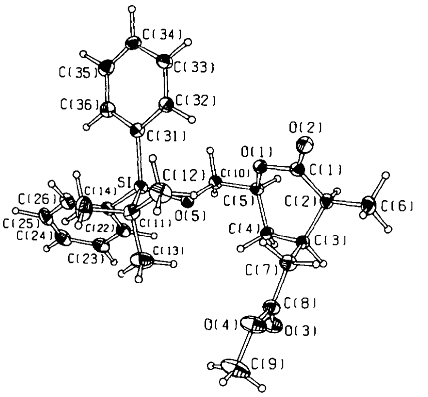

Fig. 1. An *ORTEP* diagram of the title compound with the H atoms and the atomic numbering. Ellipsoids are represented at the 30% probability level.

Atomic parameters are given in Table 1, selected bond distances and angles in Table 2.* Fig. 1 shows a thermal-ellipsoid plot with the atom numbering.

Related literature. The intramolecular cyclization of the chloropropionate ester shown above is a rare example of δ-lactone synthesis based on a radical process; see Surzur & Bertrand (1988), Curran (1988), Giese (1986) and Hanessian, Bennani & Di Fabio (1990).

We thank 'Le Ministère de l'Education du Québec' for financial support and Dr Michel Simard for assistance in collection of X-ray intensities and help in the elucidation of the structure.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, distances and angles related to the *tert*-butyldiphenylsilyl substituent, distances to the weighted least-squares planes for the phenyl groups and a stereoview of the unit cell have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52340 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 6-Methylene-4-pregnene-3,20-dione

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Abstract. $C_{22}H_{30}O_2$ (1), $M_r = 326{\cdot}47$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}662$ (3), $b = 23{\cdot}32$ (7), $c = 8{\cdot}167$ (2) Å, $V = 1840{\cdot}3$ (4) Å^3, $Z = 4$, $D_x = 1{\cdot}178$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 5{\cdot}34$ cm^{-1}, $F(000) = 712$, $T = 293$ K, $R = 0{\cdot}035$, $wR = 0{\cdot}044$, $S = 1{\cdot}954$ for 2147 unique observed reflections with $F_o > 2\sigma(F_o)$. Rings *B* and *C* have chair conformations, the *A* ring assumes an intermediate sofa–half-chair conformation, and the *D* ring is in the half-chair conformation. The progesterone side chain has the same con-

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