C(20)—C(21)—C(27)	124.5 (5)	C(32)—C(31)—C(37)	99.5 (4)
C(22)—C(21)—C(26)	100.6 (5)	C(36)—C(31)—C(37)	102.4 (4)
C(22)—C(21)—C(27)	100.9 (4)	O(34)—C(32)—C(31)	126.8 (5)
C(26)—C(21)—C(27)	102.2 (5)	O(34)—C(32)—C(33)	126.2 (6)
O(24)—C(22)—C(21)	125.6 (5)	C(31)—C(32)—C(33)	106.9 (5)
O(24)—C(22)—C(23)	127.3 (6)	C(32)—C(33)—C(34)	102.4 (5)
C(21)—C(22)—C(23)	107.1 (5)	C(33)—C(34)—C(35)	107.3 (7)
C(22)—C(23)—C(24)	100.7 (5)	C(33)—C(34)—C(37)	102.5 (5)
C(23)—C(24)—C(25)	106.5 (6)	C(35)—C(34)—C(37)	101.6 (5)
C(23)—C(24)—C(27)	103.3 (6)	C(34)—C(35)—C(36)	103.1 (5)
C(25)—C(24)—C(27)	102.3 (5)	C(31)—C(36)—C(35)	104.2 (5)
C(24)—C(25)—C(26)	103.7 (6)	C(31)—C(37)—C(34)	93.5 (5)
C(21)—C(26)—C(25)	104.3 (6)	C(31)—C(37)—C(38)	114.6 (5)
C(21)—C(27)—C(24)	93.9 (4)	C(31)—C(37)—C(39)	114.3 (6)
C(21)—C(27)—C(28)	115.2 (5)	C(34)—C(37)—C(38)	112.1 (5)
C(21)—C(27)—C(29)	112.3 (5)	C(34)—C(37)—C(39)	113.5 (6)
C(24)—C(27)—C(28)	112.2 (5)	C(38)—C(37)—C(39)	108.4 (6)

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986) and difference Fourier synthesis using *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) and refined by block-diagonal least squares on *F*. Peaks around the S(30) atom, for one of the methyl 10-camphorsulfonate moieties, were grouped into three sets of O atoms defining reasonable geometry. The population of each group gave refined occupancy factors (fixed in the final least-squares cycle) of 0.40, 0.40 and 0.20 for the *X*, *Y* and *Z* sets, respectively. These O atoms were refined isotropically with all other non-H atoms being refined anisotropically. In the final cycles, H-atom coordinates were fixed (C—H = 0.95 Å) and their isotropic temperature factors were set to the $U_{\rm iso}$ value of the C atom to which they were attached. Note that no H atoms were found for C(31*m*). Real and imaginary parts of the anomalous-dispersion correction were taken from Cromer & Liberman (1970).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55914 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1024]

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Structure of an α-(Methyldiphenylsilyl)-γ-lactone

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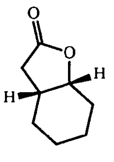
Abstract

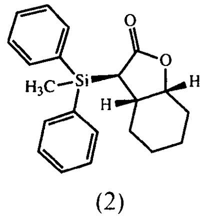
In the title compound, 3-methyl-3-(methyldiphenylsilyl)-3a,4,5,6,7,7a-hexahydro-1-benzofuran-2(3*H*)-one, the diphenylmethylsilyl group is *cis* to the cyclohexane ring, which is *cis*-fused to the lactone ring. The Si—C(lactone) bond length is 1.922 (2) Å, the Si—C(methyl) bond length is 1.866 (3) Å and the C(methyl)—Si—C—C(methyl) torsion angle is 152.8 (2)°.

Comment

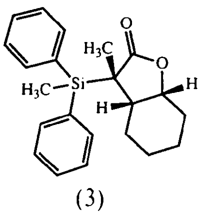
In the course of a study of the utility of α-(methyldiphenylsilyl)-γ-lactones in synthesis, we prepared the silylated lactone (2) (Betancourt de Perez, Fuentes, Larson, Barnes & Heeg, 1986). This material was formed by exclusive attack of methyldiphenylchlorosilane on the β-face of the lithium enolate of the lactone (1) (Grieco & Miyashita, 1974). We were interested in determining if this phenomenon of β-face attack would permit the placement of the bulky methyldiphenylsilyl group on the α-face of the molecule. Treatment of silylated lactone (2) with lithium diisopropylamide followed by methyl iodide yields (3). The crystal structure of title product (3) demonstrates that, not only can the bulky group occupy the α-position in (3), but also that the approach of an electrophile to the lithium enolate of lactone (1) is from the β-face, even under conditions which would seem to favor attack from the α-face.



(1)



(2)



(3)

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The Si—C1 distance, 1.922 (2) Å, is slightly longer than the corresponding distance in (2), 1.906 (3) Å (Betancourt de Perez *et al.*, 1986). The Si—C(methyl) distance and the Si—C(phenyl) distances agree well with those found in (2) and in other structures containing the methyldiphenylsilyl group (Eaborn, Hitchcock, Lickiss, Pidcock & Safa, 1984; Sharma, Vincenti, Vicari, Cervantes & Pannell, 1990; Barnes, Larson, Santiago & Rios Steiner, 1988; Daly & Sanz, 1974).

The two methyl groups on the molecule form a torsion angle about the Si—C1 bond of 152.8 (2)°. The lactone is in the envelope conformation with C3 in the flap position, while the cyclohexane ring is in a flattened chair conformation.

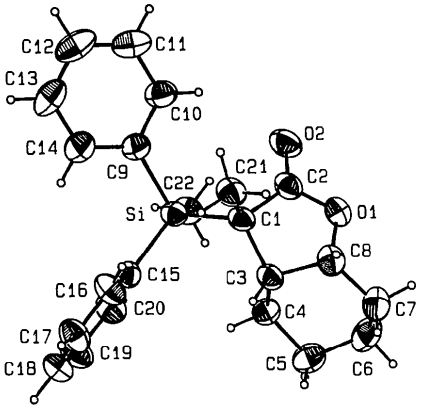

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title compound with thermal ellipsoids drawn at the 40% probability level.

Experimental

Crystal data

$C_{22}H_{26}O_2Si$
$M_r = 350.5$
Monoclinic
$P2_1/c$
$a = 13.436\ (2)$ Å
$b = 7.001\ (2)$ Å
$c = 20.698\ (3)$ Å
$\beta = 93.56\ (2)°$
$V = 1943.1\ (7)$ Å^3
$Z = 4$
$D_x = 1.198$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11\text{-}14°$
$\mu = 0.13$ mm^{-1}
$T = 299$ K
Rhombic prism
0.45 × 0.22 × 0.22 mm
Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: none

$R_{\rm int} = 0.021$
$\theta_{\rm max} = 26°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 8$
$l = -25 \rightarrow 25$

4307 measured reflections
3815 independent reflections
2725 observed reflections [$I > 0$]

3 standard reflections
frequency: 166.7 min
intensity variation: <2%

Refinement

Refinement on F
Final $R = 0.084$
$wR = 0.039$
$S = 1.262$
2725 reflections
330 parameters
All H-atom parameters refined

$w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$
$(\Delta/\sigma)_{\rm max} = 0.01$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$B_{\rm eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$
Si	0.22388 (5)	0.0737 (1)	0.10162 (3)	3.96 (1)
O1	0.3792 (1)	−0.0458 (3)	−0.05187 (7)	5.51 (4)
O2	0.3785 (1)	0.2299 (3)	0.00194 (8)	5.81 (4)
C1	0.3170 (2)	−0.0627 (4)	0.0520 (1)	3.80 (5)
C2	0.3604 (2)	0.0617 (4)	0.0005 (1)	4.52 (6)
C3	0.2789 (2)	−0.2342 (3)	0.0106 (1)	3.86 (5)
C4	0.1756 (2)	−0.2025 (4)	−0.0232 (1)	4.70 (6)
C5	0.1533 (2)	−0.3355 (4)	−0.0803 (1)	5.70 (7)
C6	0.2290 (2)	−0.3042 (4)	−0.1306 (1)	6.45 (8)
C7	0.3320 (2)	−0.3510 (4)	−0.1016 (1)	6.33 (7)
C8	0.3582 (2)	−0.2462 (4)	−0.0391 (1)	4.97 (6)
C9	0.2951 (2)	0.2064 (3)	0.1689 (1)	4.13 (6)
C10	0.3703 (2)	0.3354 (4)	0.1568 (1)	5.33 (7)
C11	0.4203 (2)	0.4362 (4)	0.2065 (1)	6.39 (7)
C12	0.3942 (2)	0.4139 (4)	0.2689 (1)	6.81 (7)
C13	0.3202 (2)	0.2894 (4)	0.2824 (1)	6.57 (8)
C14	0.2721 (2)	0.1881 (4)	0.2329 (1)	5.36 (7)
C15	0.1388 (2)	−0.1026 (3)	0.13855 (9)	3.70 (5)
C16	0.1722 (2)	−0.2512 (4)	0.1779 (1)	5.10 (6)
C17	0.1088 (2)	−0.3765 (4)	0.2056 (1)	5.84 (7)
C18	0.0083 (2)	−0.3576 (4)	0.1948 (1)	5.84 (7)
C19	−0.0280 (2)	−0.2130 (4)	0.1564 (1)	6.00 (7)
C20	0.0356 (2)	−0.0878 (4)	0.1287 (1)	5.16 (6)
C21	0.4055 (2)	−0.1271 (4)	0.0990 (1)	4.77 (6)
C22	0.1498 (2)	0.2521 (4)	0.0519 (1)	5.17 (6)

Table 2. *Geometric parameters* (Å, °)

Si—C1	1.922 (2)	C1—C21	1.556 (3)
Si—C9	1.885 (2)	C2—O2	1.202 (3)
Si—C15	1.877 (2)	C8—O1	1.458 (3)
Si—C22	1.866 (3)	C3—C8	1.528 (3)
C1—Si—C9	108.8 (1)	Si—C1—C3	118.6 (1)
C1—Si—C15	108.9 (1)	Si—C1—C2	112.4 (2)
C1—Si—C22	112.4 (1)	Si—C1—C21	107.9 (2)
C9—Si—C15	108.5 (1)	C2—C1—C3	100.6 (2)
C9—Si—C22	107.9 (1)	C2—C1—C21	107.1 (2)
C15—Si—C22	110.3 (1)	C3—C1—C21	109.7 (2)
C22—Si—C1—C21	152.8 (2)	C4—C3—C8—C7	−39.2 (3)
C8—O1—C2—C1	−4.1 (2)	C3—C4—C5—C6	−60.4 (3)
C2—O1—C8—C3	27.2 (2)	C5—C4—C3—C8	47.3 (3)
C3—C1—C2—O1	−20.3 (2)	C4—C5—C6—C7	61.8 (3)
C2—C1—C3—C8	35.0 (2)	C5—C6—C7—C8	−53.2 (3)
C1—C3—C8—O1	−38.2 (2)	C6—C7—C8—C3	43.5 (3)

Programs used include *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *MolEN* (Fair, 1990) and *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry, least-squares-planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71161 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1034]

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Structure of (3*R**,6*S**)-3,6-Bis(methoxymethoxy)-2,2,7,7-tetramethyl-4-octene

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Abstract

The structure of the title compound has been established by X-ray analysis. The molecule has an inversion center and the two chiral C atoms have the opposite configuration to each other.

Comment

It has been found that in the presence of trialkylchlorosilane, addition of a cuprate reagent, R_2CuLi, to α,β-unsaturated γ-alkoxy aldehydes takes place in 1,2-addition mode with good diastereoselectivity (Arai, Nemoto, Ohashi & Nakamura, 1992). In order to ascertain the chirality of the newly introduced chiral center when ^{t}Bu$_2$CuLi is used as the cuprate reagent, the crystal structure has been determined. The molecule has an inversion center and is located on a crystallographic inversion center as shown in Fig. 1. This means the absolute configuration of the introduced chiral group is opposite to that of the γ-C atom of the reactant, although the product with the same configuration as that of the γ-C was obtained when Ph$_2$CuLi was used as the cuprate reagent. The central olefinic moiety is planar. The torsion angles are 116.6 (3), −66.5 (3), −63.0 (3) and −67.4 (4)° for O1—C2—C1—C1$^{\mathrm{i}}$, C1—C2—O1—C3, C2—O1—C3—O2 and O1—C3—O2—C4, respectively.

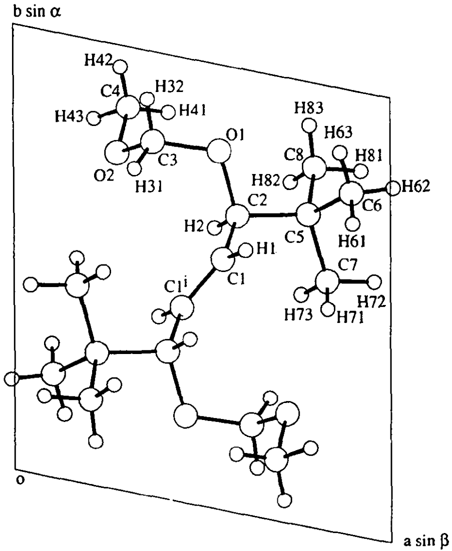

Fig. 1. Crystal structure viewed along the *c* axis with the numbering of the atoms. The C1$^{\mathrm{i}}$ atom is inverted by an inversion center at (1 − *x*, 1 − *y*, 1 − *z*).

Experimental

Crystal data

$C_{16}H_{32}O_4$
$M_r = 288.43$
Triclinic
$P\bar{1}$
$a = 8.087$ (3) Å
$b = 9.365$ (1) Å
$c = 6.200$ (1) Å
$\alpha = 98.45$ (1)°
$\beta = 98.19$ (3)°
$\gamma = 99.75$ (2)°
$V = 451.0$ (4) Å^3
$Z = 1$
$D_x = 1.06$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 20.80$–29.31°
$\mu = 0.69$ cm^{-1}
$T = 296$ K
Plate
0.4 × 0.3 × 0.25 mm
Colorless
Crystal source: AcOEt/CH$_2$Cl$_2$/hexane solution