Crystal Structure and Synthesis of 6-(Phtalimidomethyltrimethylsilyl)-hexan-1-ol

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A key intermediate in the synthesis of original organosilicon ascorbic acid derivatives, 6-(phtalimidomethyltrimethylsilyl)hexan-1-ol crystallizes in a triclinic form, $P\bar{1}$. The unit-cell dimensions at 296 K are $a = 7.807(8)$, $b = 10.145(4)$, $c = 11.886(4)$ Å, $\alpha = 93.53(3)^\circ$, $\beta = 105.84(4)^\circ$, $\gamma = 89.77(5)^\circ$, $V = 903.8(10)$ Å³, $D_x = 1.174$ g/cm³, and $Z = 2$. The R value is 0.0657 for 2662 observed reflexions.

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As part of an ongoing study aimed at synthesizing organosilicon derivatives of L-ascorbic acid as potential bone remodeling agents,¹ we synthesized a series of silanol compounds **1a** – **d** that can be equally considered as interesting building blocks for the synthesis of organosilicon bioactive molecules (Scheme 1). Thus, the hydrosilylation of unsaturated acetates **4a** – **d** with chloromethyltrimethylsilane gave the saturated acetoxy derivatives **3a** – **d** in 80% average yield. The latter compounds were subjected to a transesterification in methanol to afford the silyl alcohols **2a** – **d** in almost quantitative yields, and then reacted with potassium phthalimide to yield compounds **1a** – **d**. Among them, 6-(phtalimidomethyltrimethylsilyl)hexan-1-ol (**1d**, $n = 4$) was isolated as an oil after silica-gel chromatography (hexane/ethyl acetate 6:4, 76% yield). Single crystals for X-ray crystallography were prepared by slow evaporation from hexane/ethyl acetate (6:4) at room temperature.

Unfortunately, no other phtalimido derivatives (namely **1a** – **c**) crystallized so easily, and we were not able to find a suitable solvent mixture to recrystallize them. Although crystal-structure data on hypervalent silicon derivatives (penta- or hexacoordinate complexes) are quite numerous (the subject was reviewed in 1986²) literature reports concerning X-ray determinations of simpler organosilicon compounds are sparse.

In this study, the crystal structure of compound **1d** was

analyzed.³ Crystal and experimental data are given in Table 1.

Lorentz and polarization corrections and an empirical absorption correction were applied. The positions of non-H atoms were easily determined by the program SHELXS-97, and the positions of the H atoms were deduced from the coordinates of the non-H atoms and confirmed by Fourier synthesis. The non-H atoms were refined with anisotropic temperature

Table 1 Crystal and experimental data

Formula: C ₁₇ H ₂₅ NO ₃ Si
Formula weight: 319.47
Crystal system: triclinic
Space group: $P\bar{1}$
$a = 7.807(8)$ Å
$b = 10.145(4)$ Å
$c = 11.886(4)$ Å
$\alpha = 93.53(3)^\circ$
$\beta = 105.84(4)^\circ$
$\gamma = 89.77(5)^\circ$
$V = 903.8(10)$ Å ³
Colorless
Crystal size: 0.40 × 0.30 × 0.25 mm ³
$D_x = 1.174$ Mg/m ³
$F(0\ 0\ 0) = 344$
$\mu = 1.239$ mm ⁻¹
Temperature = 296(2) K
$\theta_{\max} = 64.91^\circ$
Radiation: Cu K α ($\lambda = 1.54178$ Å)
No. of reflections used: 2662 [$I > 2\sigma(I)$]
$R = 0.0657$
$wR^2 = 0.1902$
Goodness-of-fit = 1.060
$(\Delta/\sigma)_{\max} = 0.012$
$(\Delta\rho)_{\max} = 0.504$ Å ⁻³
$(\Delta\rho)_{\min} = -0.370$ Å ⁻³
Measurement: Enraf-Nonius CAD4 ⁴
Structure determination: SHELXS-97 ⁵
Refinement: SHELXL-97 ⁶

Scheme 1

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Table 2 Final atomic coordinates and equivalent isotropic thermal parameters ($U_{eq}(\text{\AA}^2)$)

Atom	x	y	z	U_{eq}
C(1)	1.1716(3)	0.1225(2)	0.1168(2)	0.052(1)
C(2)	1.0567(3)	0.0478(2)	0.1578(2)	0.051(1)
C(3)	1.0968(4)	-0.0792(3)	0.1898(3)	0.065(1)
C(4)	1.2579(4)	-0.1290(3)	0.1787(3)	0.073(1)
C(5)	1.3729(4)	-0.0536(3)	0.1382(3)	0.071(1)
C(6)	1.3313(3)	0.0735(3)	0.1068(3)	0.065(1)
C(7)	1.0896(4)	0.2528(3)	0.0900(2)	0.058(1)
N(8)	0.9275(3)	0.2496(2)	0.1176(2)	0.055(1)
C(9)	0.8981(3)	0.1288(3)	0.1569(2)	0.056(1)
O(10)	1.1455(3)	0.3460(2)	0.0509(2)	0.087(1)
O(11)	0.7646(3)	0.0987(2)	0.1840(2)	0.082(1)
C(12)	0.7974(4)	0.3561(3)	0.0960(2)	0.064(1)
Si(13)	0.8157(1)	0.4846(1)	0.2208(1)	0.067(1)
C(14)	0.7795(5)	0.4098(3)	0.3512(3)	0.080(1)
C(15)	0.5960(5)	0.3544(4)	0.3383(3)	0.087(1)
C(16)	0.5711(6)	0.2952(4)	0.4464(3)	0.098(1)
C(17)	0.3940(6)	0.2329(5)	0.4322(3)	0.102(1)
C(18)	0.3666(8)	0.1771(6)	0.5401(4)	0.140(2)
C(19)	0.1862(12)	0.1189(8)	0.5256(6)	0.209(4)
O(20)	0.1679(12)	0.0777(17)	0.6217(9)	0.367(6)
C(21)	0.6423(6)	0.6075(4)	0.1627(3)	0.097(1)
C(22)	1.0419(5)	0.5604(4)	0.2584(4)	0.092(1)

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

Table 3 Selected torsion angles ($^\circ$)

Si(13)-C(14)-C(15)-C(16)	-179.6(3)
C(14)-C(15)-C(16)-C(17)	-176.3(4)
C(15)-C(16)-C(17)-C(18)	-178.4(4)
C(16)-C(17)-C(18)-C(19)	178.1(6)
C(17)-C(18)-C(19)-O(20)	-177.3(10)

Table 4 Selected bond distances ($^\circ$)

Si(13)-C(12)	1.889(3)
Si(13)-C(14)	1.855(4)
Si(13)-C(21)	1.856(5)
Si(13)-C(22)	1.857(5)

Table 5 Hydrogen-bonding geometry ($\text{\AA}$, $^\circ$) and van der Waals contact ($\text{\AA}$)

O20...O11(I)	2.941(14)
H20...O11(I)	2.574
O20-H20...O11(I)	108.6
C21...O10(II)	3.445(6)
H21...O10(II)	2.582
C21-H21...O10(II)	149.5
O11...C5(III)	3.326(5)
O11...C6(III)	3.261(5)
O20...C19(IV)	3.414(16)
C3...C7(V)	3.597(6)
C5...O11(VI)	3.326(5)
C6...O11(VI)	3.261(5)
C7...C3(V)	3.597(6)
C19...O20(IV)	3.414(16)

Symmetry codes: I (1-x, -y, 1-z); II (2-x, 1-y, -z); III (x-1, y, z); IV (-x, -y, 1-z); V (2-x, -y, -z); VI (1-x, -y, -z).

Fig. 1 Molecular structure with the numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

parameters. H atoms were inserted in calculated positions and not refined.

The structure of 6-(phthalimidomethyl)dimethylsilanylhexan-1-ol is illustrated in Fig. 1. It shows an open carbon chain as evidenced by the torsion angle values around 180° (Table 3). It must be noted that the silicon-carbon bond distances are in good agreement with the literature data ($d = 1.857 \text{ \AA}$ for C-Si)⁷ (Table 4).

The aromatic phthalimido moiety is quasi planar, as expected, with least-squares plane variations of 0.003 and 0.008 $\text{\AA}$ for the six and five-membered rings, respectively. The interplanar angle of the aromatic ring and the hexanol open chain is $65.0(4)^\circ$.

Additionally, intermolecular stacking is provided by two hydrogen bonds and several van der Waals contacts (Table 5).

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