

A bicyclo[3.3.0]octan-2-ylcyclopentanone

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Key indicators

Single-crystal X-ray study
 $T = 223$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 Disorder in main residue
 R factor = 0.041
 wR factor = 0.115
 Data-to-parameter ratio = 16.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, *rel*-(2*R*,3*S*,1'*R*,2'*S*,5'*S*,7'*S*)-3-allyl-2-(2'-hydroxy-7'-trimethylsilylbicyclo[3.3.0]octan-2'-yl)cyclopentanone, $\text{C}_{19}\text{H}_{32}\text{O}_2\text{Si}$, the two rings of the bicyclo[3.3.0]octane unit adopt an envelope conformation and the cyclopentanone ring is in a twist conformation. In the crystal, molecules related by a center of symmetry are hydrogen bonded to form dimers.

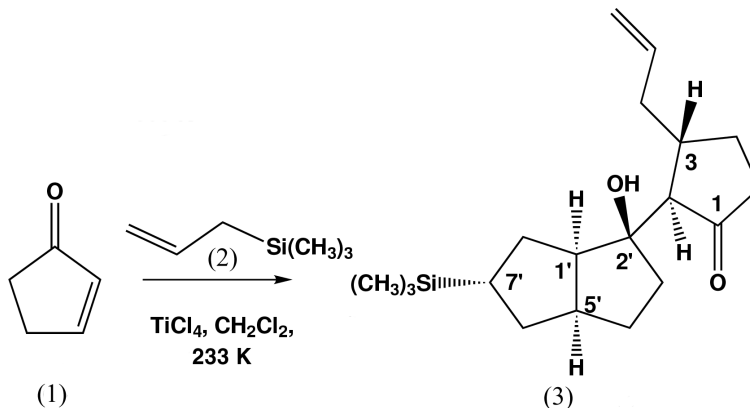
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Comment

In the context of a project described elsewhere (Helbling *et al.*, 1999), we investigated the allylation of cyclopentanone (1) with allyltrimethylsilane (2) (Hosomi & Sakurai, 1977). Careful chromatography of the product mixture gave the aldol product *rel*-(2*R*,3*S*,1'*R*,2'*S*,5'*S*,7'*S*)-3-allyl-2-(2'-hydroxy-7'-trimethylsilylbicyclo[3.3.0]octan-2'-yl)cyclopentanone, (3). In order to determine the stereochemistry of the trimethylsilyl group in (3) and other structural features, its structure was determined by X-ray diffraction.



The distance between the bridgehead atoms 1' and 5' is 1.553 (2) Å and thus in the normal range for C—C bonds. The bond angles $\text{C}8'-\text{C}1'-\text{C}2' = 116.47$ (13)° and $\text{C}4'-\text{C}5'-\text{C}6' = 116.04$ (15)°, at the bridgeheads of the bicyclic structure, are rather large. The torsion angles $\text{C}2'-\text{C}1'-\text{C}5'-\text{C}4'$ and $\text{C}8'-\text{C}1'-\text{C}5'-\text{C}6'$ are 5.76 (17) and 4.65 (17)°, respectively. The two five-membered rings of the bicyclo[3.3.0]octane subunit adopt an *exo* envelope conformation (with the TMS group in the *exo*-envelope ring), while the cyclopentanone ring adopts a twist conformation. The trimethylsilyl substituent is located *exo* to the bridgehead H atoms and thus shows the normal stereoselectivity of the Sakurai reaction (Helbling *et al.*, 1999). In the crystal, molecules related by a center of symmetry are linked by hydrogen bonds, involving hydroxyl O2' and carbonyl O1, to form dimers.

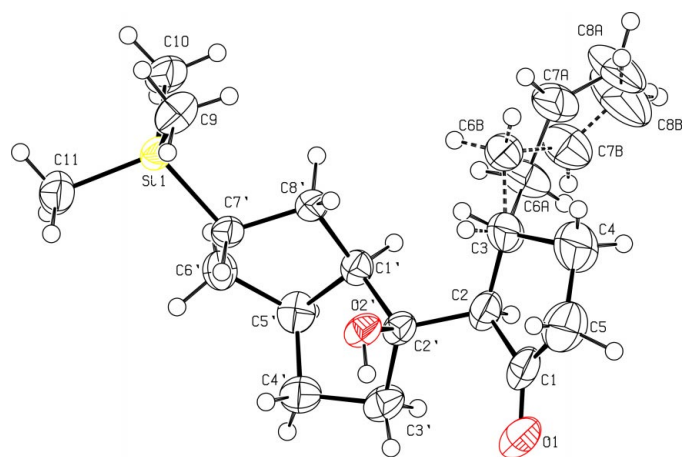


Figure 1
The structure of (3) showing the numbering scheme and displacement ellipsoids at the 50% probability level.

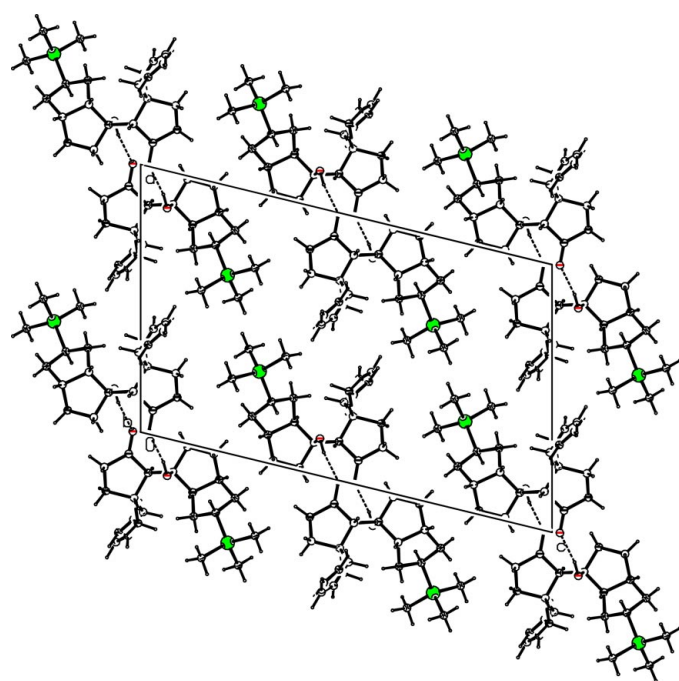


Figure 2
The crystal packing of (3); hydrogen bonding is shown as dotted lines.

Experimental

A solution of (1) (4.1 g, 50 mmol) and allyltrimethylsilane (2) (11.4 g, 100 mmol) in methylene chloride under argon was cooled to 195 K. TiCl_4 (9.5 g, 5.5 ml, 100 mmol) was then added dropwise and the mixture was stirred at 253 K overnight. After warming to 273 K and work up, column chromatography of the crude material (6.4 g) with hexane–ethyl acetate (19:1) gave 630 mg (8%) (3) and some other products (Helbling *et al.*, 1999). Crystallization from hexane gave pure (3). M.p.: 377 K. ^1H NMR: 5.7–5.9 (*m*, 1H), 5.02–5.13 (*m*, 2H), 3.1–3.2 (broad, 1H), 2.0–2.6 (*m*, 8H), 1.4–1.85 (*m*, 7H), 0.95–1.38 (*m*, 4H), -0.05 (*s*, 9H). ^{13}C NMR (CDCl_3): 135.72 (*d*), 117.07 (*t*), 83.76, 60.65 (*d*), 50.03 (*d*), 46.71 (*d*), 40.82 (*t*), 40.76 (*t*), 39.26 (*t*), 37.89 (*d*), 33.94 (*t*), 30.33 (*t*), 29.61 (*t*), 26.77 (*t*), 26.01 (*d*), -2.81 (*q*). MS: 320 (M^+ , 2), 302 (38), 261 (12), 189 (80), 155 (100), 147 (32), 83 (38),

73 (56); HR–MS: calculated for $\text{C}_{19}\text{H}_{30}\text{OSi}$ [$\text{M} - \text{H}_2\text{O}$]: 302.205510; found: 302.206594. Suitable crystals of (3) were grown from ether–hexane as colourless blocks.

Crystal data

$\text{C}_{19}\text{H}_{32}\text{O}_2\text{Si}$
 $M_r = 320.54$
Monoclinic, $P2_1/c$
 $a = 14.1445$ (14) Å
 $b = 6.2718$ (4) Å
 $c = 22.340$ (2) Å
 $\beta = 103.694$ (11)°
 $V = 1925.4$ (3) Å³
 $Z = 4$

$D_x = 1.106$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 5000 reflections
 $\theta = 2.1$ – 25.9°
 $\mu = 0.13$ mm⁻¹
 $T = 223$ (2) K
Block, colourless
 $0.45 \times 0.40 \times 0.30$ mm

Data collection

Stoe IPDS diffractometer
 φ oscillation scans
13 376 measured reflections
3691 independent reflections
2809 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$
 $\theta_{\text{max}} = 25.9^\circ$
 $h = -17 \rightarrow 17$
 $k = -7 \rightarrow 6$
 $l = -27 \rightarrow 27$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.115$
 $S = 1.05$
3691 reflections
231 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0736P)^2 + 0.0262P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.29$ e Å⁻³

Table 1

Hydrogen-bonding geometry (Å, °).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$\text{O2}'\text{---}H2'\cdots\text{O1}^i$	0.83	2.04	2.8605 (16)	168

Symmetry code: (i) $2 - x, 1 - y, -z$.

The H atoms were included in calculated positions and treated as riding atoms using *SHELXL* default parameters. The allyl side chain is disordered. The occupancies of the two positions for atoms C6, C7 and C8 were refined to be $A:B = 0.564:0.436$ (4).

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 2000); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON99* (Spek, 1990); software used to prepare material for publication: *SHELXL97*.

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References

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