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(3a*R*,5*R*,7*S*,7a*S*)-5-[(*tert*-Butyldimethylsilyloxy)-methyl]-7-ethoxy-3-methyl-7,7a-dihydro-3a*H*-pyrano[4,3-*d*]isoxazol-4(5*H*)-one

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The title compound, $C_{16}H_{29}NO_5Si$, is a unique heterocyclic compound where the 3-methyl-4,5-dihydroisoxazole (3-methyl-Δ^2-isoxazoline) ring has a tetrahydropyran-4-one group fused to the five-membered heterocyclic ring. This bicyclic heterocycle has four asymmetric centers with well defined configurations at all stereocenters.

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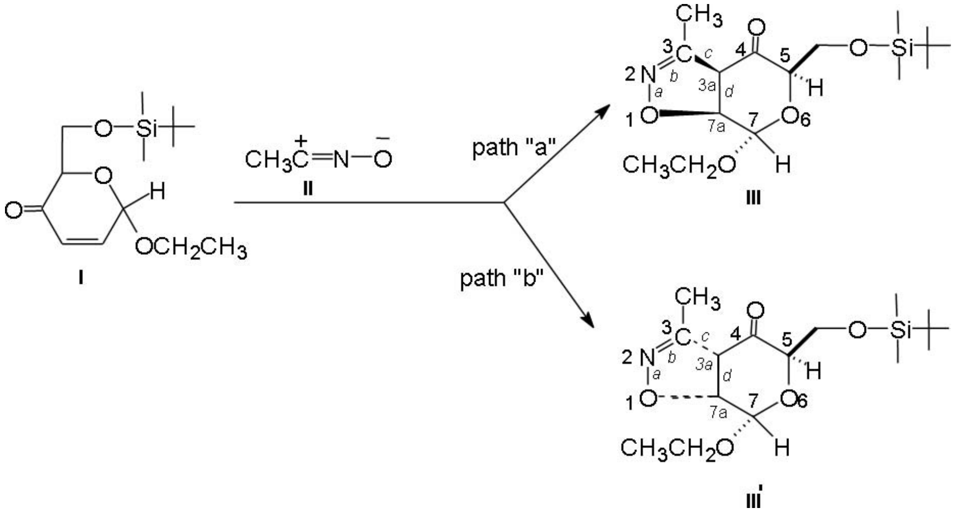
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.006 Å
R factor = 0.046
wR factor = 0.047
Data-to-parameter ratio = 7.9

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

Comment

The title compound, (III), has recently been synthesized by 1,3-dipolar cycloaddition of acetonitrile oxide (II) to an α,β-unsaturated enone, ethyl 6-*O*-*tert*-butyldimethylsilyl-α-D-*glycero*-hex-2-enopyranosid-4-ulose, (I). The *ORTEP* diagram of this compound has been reported without any further details (de Freitas Filho *et al.*, 2003). The absolute configuration of the starting compound (I) was know since it was synthesized from tri-*O*-acetyl-D-glucal. Therefore, the addition of acetonitrile oxide (II) to (I) could have occurred either from the same (path b) or the opposite side (path a) of the aglycone (ethoxy group), as shown in the scheme. If the approach of (II) occurs from the same side, the reactive species would encounter steric hindrance from the ethoxy group. Approach from the opposite side did not face this problem. Therefore, it was highly probable that the reaction would take place as expected to give (III) and not (III′). In order to verify this with certainty, the X-ray structure determination was carried out and the results confirmed our expectations. All distances and angles for (III) are consistent with the expected values. The configuration adopted by the six-membered heterocycle is a distorted boat. The five-membered heterocycle is nearly planar, with a maximum deviation of 0.018 (4) Å from the mean plane.



Experimental

The title compound, (III), was obtained *via* the 1,3-dipolar cycloaddition of acetonitrile oxide (II) to α-D-*glycero*-hex-2-enopyranosid-4-ulose (I) (de Freitas Filho *et al.*, 2003). The crystallized compound (III), obtained after purification on silica gel, was dissolved in a mixture of petroleum ether and ethyl acetate (70:30 *v*/*v*). Slow evaporation gave crystals of good quality for X-ray analysis.

Crystal data

$C_{16}H_{29}NO_5Si$
$M_r = 343.49$
Orthorhombic, $P2_12_12_1$
$a = 7.366\ (5)$ Å
$b = 11.372\ (5)$ Å
$c = 23.020\ (5)$ Å
$V = 1928.3\ (16)$ Å^3
$Z = 4$
$D_x = 1.183$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2082 reflections
$\theta = 1.0$–27.5°
$\mu = 0.14$ mm^{-1}
$T = 173\ (2)$ K
Needle, colorless
0.04 × 0.02 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: part of the refinement model (Δ*F*) (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.78$, $T_{\max} = 1.00$
3739 measured reflections

2388 independent reflections
1647 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.049$
$\theta_{\max} = 27.4°$
$h = -9 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -29 \rightarrow 29$

Refinement

Refinement on *F*
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F) = 0.048$
$S = 1.06$
1647 reflections
208 parameters
H-atom parameters not refined
Weighting scheme: Chebychev polynomial (Watkin, 1994; Prince, 1982): $w = [1 - (F_o - F_c)^2/36\sigma^2(F_o)]^2/[1.31T_0(x) - 0.0224T_1(x) + 0.584T_2(x) + 0.0446T_3(x)]$, where $x = F/F_{\max}$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C11—Si	1.860 (5)	C13—Si	1.879 (4)
C12—Si	1.857 (4)	O21—Si	1.663 (3)
C13—Si—C11	110.5 (2)	C13—Si—O21	109.31 (15)
C13—Si—C12	111.3 (2)	C11—Si—O21	104.85 (17)
C11—Si—C12	111.2 (2)	C12—Si—O21	109.54 (17)

The H atoms were located in a difference Fourier map. They were initially refined using soft restraints on the bond lengths and angles to regularize their geometry [C—H = 0.95 (4) to 0.98 (2) Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$], after which they were fixed during the final cycles. In the absence of signficant anomalous scattering, Friedel pairs were merged; the absolute configuration is known from the synthesis.

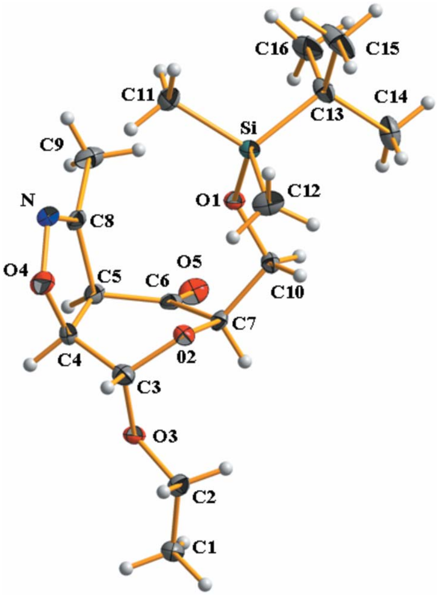


Figure 1
A view of (III) (displacement ellipsoids are plotted at the 30% probability level).

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *DIAMOND* (Brandenburg & Putz, 1996); software used to prepare material for publication: *CRYSTALS*.

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