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A Dinitrobenzoate Derivative of an α -Methoxy- γ -hydroxysilane

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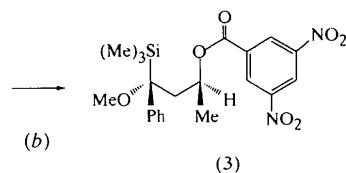
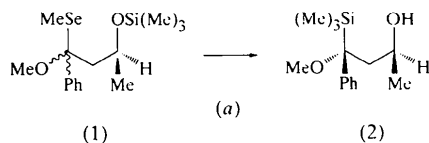
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Abstract

The structure of (2*S**, 4*S**)-4-methoxy-4-phenyl-4-(trimethylsilyl)-2-butyl 3,5-dinitrobenzoate, C₂₁H₂₆N₂O₇Si, is presented and discussed. The compound was synthesized by a stereoselective [1–4] retro-Brook reaction, followed by acylation using 3,5-dinitrobenzoyl chloride. The Si–O_{carboxy} chain adopts a sterically hindered conformation resembling a five-membered ring.

Comment

We have recently studied the configurational stability of benzylolithiums using, as probes, γ -silyloxybenzyl-lithiums produced by cleavage of γ -silyloxybenzyl-selenides (Bousbaa *et al.*, 1997). The stereoisomers of compound (1) bearing a methyl and a phenyl group



(a) (i) *tert*-BuLi, THF, 195 K, 2 h; (ii) MeOH, 195 K.
(b) Cl(CO)Ph(NO₂)₂, DMAP, pyridine, 293 K, 0.25 h.

in 'syn' or 'anti' positions have been reacted, as 1/1 mixtures, with *tert*-butyllithium, and the product, (2), arising from the [1–4] retro-Brook rearrangement (Simchen & Pflutschinger, 1976) was obtained as almost a single stereoisomer (72–76% diastereomeric excess

in the crude reaction mixture and 94% diastereomeric excess after a first purification). The structure of the 3,5-dinitrobenzoate, (3), was established by single-crystal X-ray diffraction analysis and shows unambiguously the *syn* relationship between the methyl and phenyl groups.

Compound (3) (Fig. 1) has the relative stereochemistry 2*S**, 4*S**. A striking feature of this structure is the conformation of the chain O1—C1—C2—C3—Si, which resembles a five-membered ring. The values of the torsion angles defined by these five atoms (Table 1) correspond fairly well with the ideal sequence of the 'envelope' conformation ($\omega_1, -\omega_1, \omega_2, 0, -\omega_2$; Dunitz, 1979) and the distance between the two non-bonded atoms, O1 and Si, is 3.443 (1) Å. So the molecule, despite its supposed flexibility (due to possible free rotation around the O1—C1, C1—C2 and C2—C3 bonds), adopts a quite sterically hindered conformation. Examination of the crystal packing shows no clear intermolecular interactions to explain this state.

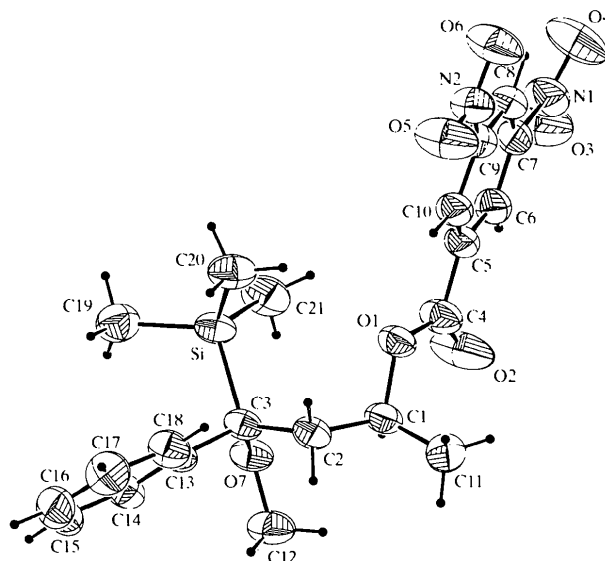


Fig. 1. The molecular structure of compound (3). Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Compound (2) was synthesized as follows: in a two-necked flask under argon, compound (1) (346 mg, 1.00 mmol; *M*_r 346), as a 1/1 mixture of 'syn' and 'anti' stereoisomers, was dissolved in dry THF (4 ml). The temperature was lowered to 195 K and then *tert*-butyllithium (0.70 ml of a 1.7 *M* solution in pentane) was added. The reaction mixture turned red. After 2 h, this colour had disappeared. Methanol (1 ml) was added and the reaction mixture extracted with diethyl ether. The organic phases were washed three times with a saturated solution of aqueous Na₂CO₃, dried over MgSO₄ and evaporated under reduced pressure to obtain 250 mg of crude reaction product. This product was purified on chromatographic plates [silica gel, diethyl ether/pentane

eluent (4:6 *v/v*) to obtain 180 mg (71% yield) of compound (2) (R_f 0.47, M_r 236.43), which is a 97/3 mixture of the 'syn' and 'anti' stereoisomers. Compound (2) is relatively unstable in acid medium. Compound (2) was then used to prepare compound (3). Compound (2) (176 mg, 0.75 mmol; M_r 236), as the 97/3 mixture of 'syn' and 'anti' stereoisomers, and 4-dimethylaminopyridine (8 mg, 0.067 mmol; M_r 122) were dissolved in 2 ml of pyridine in a round-bottomed flask. 3,5-Dinitrobenzoyl chloride (DMAP) (170 mg, 0.74 mmol; M_r 230) was added under agitation in one shot and the reaction mixture left under agitation for 15 min, after which time it was extracted with diethyl ether and the organic phases washed three times with water, dried over Mg_2SO_4 and the solvent evaporated under reduced pressure to give the crude product (350 mg). This mixture, purified on chromatographic plates [silica gel, diethyl ether/pentane eluent (2:8 *v/v*)], led to a solid product (250 mg; R_f 0.46; m.p. 378–380 K). This product, recrystallized from a hot diethyl ether/pentane mixture, led to 200 mg (59.7% yield) of pure 'syn' compound (3) ($C_{21}H_{26}N_2O_7Si$; M_r 446.54; m.p. 393–394 K; analysis found: C 56.32, H 5.81, N 6.24%; calculated: C 56.49, H 5.87, N 6.27%).

Crystal data

$C_{21}H_{26}N_2O_7Si$
 $M_r = 446.53$
 Monoclinic
 $C2/c$
 $a = 32.421(3) \text{ \AA}$
 $b = 6.235(1) \text{ \AA}$
 $c = 22.646(1) \text{ \AA}$
 $\beta = 91.333(7)^\circ$
 $V = 4576.5(9) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.296 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (NRCVAX; Gabe *et al.*, 1989)
 $T_{\min} = 0.774$, $T_{\max} = 0.879$
 5404 measured reflections
 4450 independent reflections

Refinement

Refinement on F^2
 $R(F) = 0.040$
 $wR(F^2) = 0.122$
 $S = 1.110$
 4450 reflections
 281 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 1.6345P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Cu $K\alpha$ radiation
 $\lambda = 1.54178 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 40\text{--}50^\circ$
 $\mu = 1.285 \text{ mm}^{-1}$
 $T = 292(2) \text{ K}$
 Parallelepiped
 $0.30 \times 0.20 \times 0.10 \text{ mm}$
 Transparent, colourless

3734 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$
 $\theta_{\text{max}} = 71.81^\circ$
 $h = -39 \rightarrow 39$
 $k = 0 \rightarrow 7$
 $l = 0 \rightarrow 27$
 3 standard reflections
 frequency: 60 min
 intensity decay: 4.0%

$(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.249 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.246 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick, 1997a)
 Extinction coefficient: 0.00080 (7)
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Si—O1	3.443 (1)		
O1—C1—C2—C3	83.9 (2)	C3—Si—O1—C1	9.78 (9)
C1—C2—C3—Si	−72.8 (2)	Si—O1—C1—C2	−38.8 (1)
C2—C3—Si—O1	24.6 (1)		

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1992). Cell refinement: CAD-4 EXPRESS. Data reduction: NRCVAX (Gabe *et al.*, 1989). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997b). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a). Molecular graphics: PLATON (Spek, 1990). Software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1185). Services for accessing these data are described at the back of the journal.

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1,4-Dihydro-1-methyl-4-nitriminopyridine Dihydrate

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Abstract

Molecules of the title compound, $C_6H_7N_3O_2 \cdot 2H_2O$, are almost planar with the NNO_2 nitrimino group twisted $8(1)^\circ$ out of the plane of the pyridine ring.