

are in Table 1, bond lengths and angles in Table 2 and a view of the molecule is in Fig. 1.*

Related literature. The structure has been determined as part of a study of the photochemistry of cyclohexenones (Zimmerman, Rieke & Scheffer, 1967; Schuster, 1980; Chen, Hwang, Scheffer & Trotter, 1991). An orthorhombic form is obtained from hexane solvent (Zimmerman & Zuraw, 1989).

* Lists of positional parameters, bond lengths and angles, a stereoview of the molecule (Mo data), anisotropic thermal parameters, H-atom positions, torsion angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54502 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0362]

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Structure of [(1*S*)-1-[(1'*S*)-3'-Oxocyclohexyl]-3,3-dimethoxy-1-propyl] [(1*S*,2*S*,3*R*)-1,3,7,7-Tetramethyl-2-hydroxy-3-bicyclo[2.2.1]heptyl] Sulfone

BY J. FENEAU-DUPONT AND J.-P. DECLERCQ

Laboratoire de chimie physique et de cristallographie, Université Catholique de Louvain, 1 place Louis Pasteur, 1348 Louvain la Neuve, Belgium

AND C. HUART

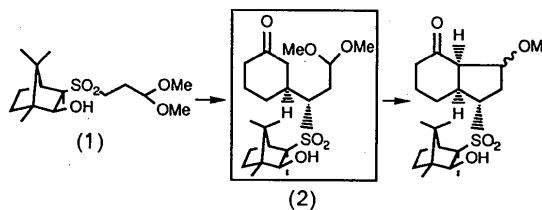
Laboratoire de chimie organique de synthèse, Université Catholique de Louvain, 1 place Louis Pasteur, 1348 Louvain la Neuve, Belgium

(Received 10 April 1991; accepted 2 August 1991)

Abstract. $C_{22}H_{38}O_6S$, $M_r = 430.60$, monoclinic, $P2_1$, $a = 6.922(2)$, $b = 16.733(2)$, $c = 10.070(3)$ Å, $\beta = 96.88(2)^\circ$, $V = 1158.0(4)$ Å³, $Z = 2$, $D_x = 1.24$ g cm⁻³, $Cu K\alpha$, $\lambda = 1.54178$ Å, $\mu = 14.9$ cm⁻¹, $F(000) = 468$, $T = 291$ K, $R = 0.050$ for 3558 observed reflections. The development of methods for the construction of five-membered carbocycles is a topic of current interest as a result of the ubiquitous occurrence of such rings in many biologically active products. We have recently developed [De Lombaert, Nemery, Roekens, Carretero, Kimmel & Ghosez (1986). *Tetrahedron Lett.* **27**, 5099–5102] a novel two-step (3 + 2) annulation yielding highly functionalized fused cyclopentanones. We are now developing an enantioselective version of this sequence. In this context we have studied the asymmetric Michael addition of a chiral homoenolate to cyclohexenone from which the title compound was obtained in an optically pure crystalline form. The

present X-ray crystallographic study establishes unambiguously the absolute stereochemistry of the title compound and the precursor homoenolate.

Experimental. Title compound prepared as shown below.



D_m not measured. Parallelepiped crystal with dimensions $0.35 \times 0.4 \times 0.2$ mm. Lattice parameters refined using 18 reflections in the range $10 \leq 2\theta \leq 49^\circ$. Huber four-circle diffractometer and Rigaku rotating

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U_{eq}
C1	10522 (5)	6275 (2)	2975 (4)	61 (1)
C2	10034 (4)	7014 (2)	2068 (4)	56 (1)
C3	8562 (5)	6665 (2)	899 (4)	57 (1)
C4	8145 (5)	5810 (2)	1452 (4)	61 (1)
C5	9870 (5)	5293 (2)	1166 (4)	69 (1)
C6	11551 (5)	5665 (2)	2119 (4)	66 (1)
C7	8527 (5)	5876 (2)	2998 (4)	65 (1)
C8	8642 (7)	5045 (3)	3686 (5)	86 (2)
C9	7094 (6)	6345 (3)	3757 (4)	78 (1)
C10	11726 (6)	6493 (3)	4275 (5)	84 (2)
C11	9499 (6)	6686 (2)	-396 (4)	72 (1)
O12	9291 (4)	7680 (2)	2734 (3)	69 (1)
S13	6213 (1)	7179	452 (1)	60 (0)
O14	4986 (3)	7129 (2)	1484 (3)	75 (1)
O15	5430 (4)	6833 (2)	-817 (3)	79 (1)
C1'	6733 (5)	8247 (2)	166 (3)	56 (1)
C2'	5905 (6)	8516 (2)	-1244 (4)	70 (1)
C3'	6866 (7)	8216 (2)	-2400 (4)	75 (1)
C4'	3743 (5)	8874 (2)	1065 (4)	64 (1)
C5'	5949 (4)	8752 (2)	1268 (4)	55 (1)
C6'	6972 (5)	9564 (2)	1429 (4)	66 (1)
C7'	6336 (6)	9994 (2)	2648 (4)	78 (1)
C8'	4152 (6)	10078 (2)	2608 (4)	79 (1)
C9'	3076 (5)	9310 (2)	2237 (4)	66 (1)
O10'	1776 (4)	9073 (2)	2811 (3)	84 (1)
O11'	8849 (5)	8370 (2)	-2187 (3)	81 (1)
C12'	9962 (9)	8011 (3)	-3121 (6)	102 (2)
O13'	6031 (6)	8640 (2)	-3546 (3)	109 (1)
C14'	5125 (11)	8221 (5)	-4599 (6)	131 (3)

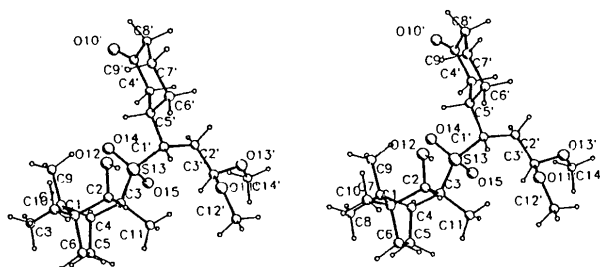


Fig. 1. Stereoscopic view of the molecule with atom numbering.

anode, graphite-monochromatized Cu $K\alpha$ radiation, θ - θ scan technique, 4172 independent reflections with $\sin\theta/\lambda \leq 0.60 \text{ \AA}^{-1}$; $-7 \leq h \leq 7$, $-20 \leq k \leq 20$, $0 \leq l \leq 11$; 3558 with $I \geq 2.5\sigma(I)$. A standard reflection (042) was checked every 50 reflections, no significant deviation. Structure solved by direct methods using *SHELXS86* (Sheldrick, 1985). H atoms in computed positions, except the hydroxyl group H atom, from Fourier difference synthesis. Anisotropic least-squares refinement (*SHELXL76*; Sheldrick, 1976) using F ; H isotropic with common refined temperature factor ($U = 0.103 \text{ \AA}^2$). $w = 1/(\sigma^2 + 0.00050F^2)$, $R = 0.050$, $wR = 0.052$, $S = 1.83$ for 3558 observed reflections. Final maximum shift/e.s.d. = 0.028. Maximum and minimum heights in final difference Fourier synthesis = 0.62 and $-0.64 e \text{ \AA}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography*

Table 2. Bond distances (\AA) and bond angles ($^\circ$)

C2—C1	1.550 (5)	C6—C1	1.562 (5)
C7—C1	1.537 (5)	C10—C1	1.510 (5)
C3—C2	1.574 (5)	O12—C2	1.428 (4)
C4—C3	1.573 (4)	C11—C3	1.525 (5)
S13—C3	1.847 (3)	C5—C4	1.530 (5)
C7—C4	1.552 (5)	C6—C5	1.547 (5)
C8—C7	1.551 (5)	C9—C7	1.537 (5)
O14—S13	1.422 (3)	O15—S13	1.447 (3)
C1'—S13	1.852 (3)	C2'—C1'	1.534 (5)
C5'—C1'	1.544 (4)	C3'—C2'	1.495 (6)
O11'—C3'	1.388 (5)	O13'—C3'	1.417 (5)
C5'—C4'	1.530 (4)	C9'—C4'	1.506 (5)
C6'—C5'	1.532 (4)	C7'—C6'	1.532 (5)
C8'—C7'	1.514 (6)	C9'—C8'	1.510 (5)
O10'—C9'	1.194 (5)	C12'—O11'	1.419 (5)
C14'—O13'	1.360 (7)		
C6—C1—C2	106.1 (3)	C7—C1—C2	102.9 (2)
C7—C1—C6	101.2 (3)	C10—C1—C2	112.2 (3)
C10—C1—C6	113.3 (3)	C10—C1—C7	119.7 (3)
C3—C2—C1	102.7 (2)	O12—C2—C1	114.3 (3)
O12—C2—C3	113.8 (2)	C4—C3—C2	101.7 (3)
C11—C3—C2	109.1 (3)	C11—C3—C4	116.0 (3)
S13—C3—C2	118.8 (2)	S13—C3—C4	108.4 (2)
S13—C3—C11	103.5 (2)	C5—C4—C3	105.5 (3)
C7—C4—C3	105.9 (3)	C7—C4—C5	100.7 (3)
C6—C5—C4	101.6 (3)	C5—C6—C1	104.3 (3)
C4—C7—C1	93.5 (3)	C5—C7—C1	113.5 (3)
C8—C7—C4	112.2 (3)	C9—C7—C1	114.9 (3)
C9—C7—C4	119.5 (3)	C9—C7—C8	103.7 (3)
O14—S13—C3	112.3 (2)	O15—S13—C3	104.7 (2)
O15—S13—O14	115.4 (2)	C1'—S13—C3	107.8 (1)
C1'—S13—O14	108.3 (2)	C1'—S13—O15	108.0 (2)
C2'—C1'—S13	111.6 (2)	C5'—C1'—S13	109.0 (2)
C5'—C1'—C2'	112.3 (3)	C3'—C2'—C1'	118.1 (3)
O11'—C3'—C2'	110.0 (3)	O13'—C3'—C2'	106.9 (3)
O13'—C3'—O11'	109.4 (3)	C9'—C4'—C5'	110.8 (3)
C4'—C5'—C1'	114.1 (3)	C6'—C5'—C1'	111.3 (3)
C6'—C5'—C4'	109.7 (3)	C7'—C6'—C5'	109.2 (3)
C8'—C7'—C6'	113.8 (3)	C9'—C8'—C7'	112.9 (3)
C8'—C9'—C4'	114.7 (3)	O10'—C9'—C4'	122.5 (3)
O10'—C9'—C8'	122.8 (4)	C12'—O11'—C3'	115.1 (4)
C14'—O13'—C3'	118.8 (4)		

(1974, Vol. IV). At the end of the refinement, the 1652 Friedel pairs of reflections present in the data set were sorted according to $w^{1/2}||F_c(hkl)| - |F_c(\bar{h}\bar{k}\bar{l})||$, by decreasing magnitude. Among the first 200 pairs of reflections, the signs of 193 observed differences were consistent with the signs of the corresponding calculated differences, establishing that the molecule is described with the correct absolute configuration. The atomic parameters are given in Table 1.* Fig. 1 is a stereoscopic view of the molecule, showing the numbering of the atoms (*PLUTO*; Motherwell & Clegg, 1978). Bond distances and angles are given in Table 2.

Related literature. The structures of (2*S*,3*R*)-*exo*-3-propylsulfonyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54488 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0072]

ol and (2*S*,3*R*)-*exo*-3-propylsulfonyl-1,3,7,7-tetramethylbicyclo[2.2.1]heptan-2-ol (Declercq, Feneau-Dupont, Huart & Nemery, 1991, and references cited therein) are closely related to the title compound.

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***N*-{2-[(1-Cyanocyclohexyl)(*tert*-butyldimethylsilyloxy)aminolpropionyl]-2,5-bis(methoxymethyl)pyrrolidine and *N*-(2-Anilinopropionyl)-2,5-bis(methoxymethyl)pyrrolidine**

BY B. TINANT AND J.-P. DECLERCQ

Laboratoire de chimie physique et de cristallographie, Université Catholique de Louvain, 1 place Louis Pasteur, 1348 Louvain la Neuve, Belgium

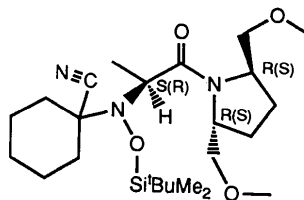
AND P. HENDERSON

Laboratoire de chimie organique de synthèse, Université Catholique de Louvain, 1 place Louis Pasteur, 1348 Louvain la Neuve, Belgium

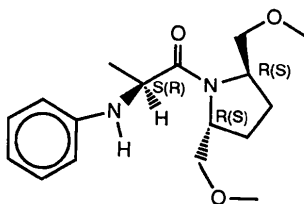
(Received 4 July 1991; accepted 2 August 1991)

Abstract. (1): C₂₄H₄₅N₃O₄Si, *M_r* = 467.73, monoclinic, *P*2₁/*c*, *a* = 12.947 (3), *b* = 13.814 (4), *c* = 16.186 (5) Å, β = 108.61 (3)°, *V* = 2744 (1) Å³, *Z* = 4, *D_x* = 1.13 g cm⁻³, Cu *K*α, λ = 1.5418 Å, μ = 9.90 cm⁻¹, *F*(000) = 1024, *T* = 291 K, *R* = 0.058 for 4276 observed reflections. (2): C₁₇H₂₆N₂O₃, *M_r* = 306.41, monoclinic, *P*2₁/*c*, *a* = 9.579 (2), *b* = 9.601 (1), *c* = 18.826 (2) Å, β = 103.25 (2)°, *V* = 1685.3 (4) Å³, *Z* = 4, *D_x* = 1.21 g cm⁻³, Mo *K*α, λ = 0.71069 Å, μ = 0.89 cm⁻¹, *F*(000) = 664, *T* = 291 K, *R* = 0.042 for 2361 observed reflections. The relative configuration of the propionyl asymmetric carbon is inverse with respect to that of the pyrrolidine ring carbon atoms (*i.e.* one is *R* and the other *S*). The conformation of the pyrrolidine is different in the two compounds: in (1), it is an envelope with torsion angles of 23.0 (6), -36.0 (6), 36.5 (6), -22.2 (6) and 0.0 (6)°; in (2), it adopts a half-chair conformation with the twofold axis through N, the endocyclic torsion angles being 8.8 (5), -27.7 (5), 36.5 (5), -30.3 (5) and 13.4 (5)°. In (2), an intermolecular hydrogen bond between the N—H and the carbonyl O is observed: N—H⋯O, N⋯O = 3.098 (3), H⋯O = 2.24 (2) Å, N—H⋯O = 175 (1)° (O: 1 - *x*, -*y*, 1 - *z*).

Experimental. Crystals were obtained by evaporation from pentane–methanol, 1:1, for (1) and from hexane for (2). *D_m* not measured. Lattice parameters refined using 20 reflections in the range 5 ≤ 2θ ≤ 50° for (1) and 30 reflections in the range 5 ≤ 2θ ≤ 25° for (2). Huber four-circle diffractometer, monochromatized Cu *K*α for (1), Mo *K*α radiation for (2).



(1)



(2)