

References

- GUTSCHE, C. D. (1989). *Calixarenes*. Cambridge: Royal Society of Chemistry.
- IWAMOTO, K., ARAKI, K. & SHINKAI, S. (1991). *Tetrahedron*, **47**, 4325–4342.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England and Louvain, Belgium.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- VICENS, J. & BOHMER, V. (1991). *Calixarenes: a Versatile Class of Macrocyclic Compounds*. Dordrecht: Kluwer Academic Publishers.

Acta Cryst. (1993). **C49**, 75–77

Structure of Dimethyl (2*R*,3*R*)-2-[(*S*)-Bromo(cyclohexyl)methyl]oxy}-3-[(diphenylboryl)oxy]-1,4-butanedioate

BY MARC DROUIN AND ANDRÉ G. MICHEL*

Laboratoire de Chimie Structurale et Modélisation Moléculaire, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

YVAN GUINDON

Department of Chemistry, Université de Montréal, Montréal, Québec, Canada H3C 3J7 and Bio-Méga Inc., 2100 rue Cunard, Laval, Québec, Canada H7S 2G5

AND WILLIAM OGILVIE

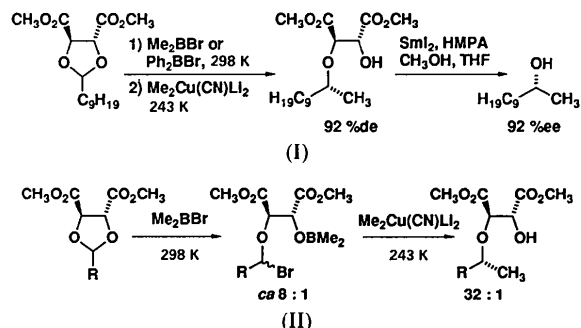
Bio-Méga Inc., 2100 rue Cunard, Laval, Québec, Canada H7S 2G5

(Received 24 February 1992; accepted 2 June 1992)

Abstract. C₂₅H₃₀BBrO₆, *M_r* = 517.23, monoclinic, *P*2₁, *a* = 9.1584 (14), *b* = 6.910 (3), *c* = 20.224 (4) Å, β = 96.241 (14)°, *V* = 1272.3 (6) Å³, *Z* = 2, *D_x* = 1.350 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 16.3 cm⁻¹, *F*(000) = 535.62, *T* = 230 (1) K, final *R* = 0.041 for 1531 observed reflections. A reactive intermediate in the dialkylboron bromide promoted opening of tartrate acetals by higher-order cuprates has been isolated and characterized by X-ray crystallography.

Introduction. The Lewis-acid-mediated reaction of acetals with nucleophiles such as allylsilanes has proven to be an extremely effective and often highly stereoselective method for the formation of carbon-carbon bonds (Alexakis & Mangeney, 1990). Recently, we described a novel reaction in which acetals of dimethyl tartrate are treated with dimethyl- or diphenylboron bromides and higher-order cuprates to produce, after auxiliary removal, secondary alcohols in high enantiomeric excess (I)

(Guindon, Simoneau, Yoakim, Gorys, Lemieux & Ogilvie, 1991). Our studies of the mechanism of this reaction have revealed that the process involves two steps with several unusual features (II). In order to better understand the reaction, it became necessary to determine the structure of the reactive bromoether intermediates. The structure of one of these highly reactive intermediates was elucidated by single-crystal X-ray diffraction (Fig. 1). We are continuing to investigate the mechanism of this process and will disclose our results in due course.



* Author to whom correspondence should be addressed.

Experimental. Crystals were obtained by the addition of Ph₂BBr (1.0 equiv.) to a solution of dimethyl (2*R*,3*R*)-2-cyclohexyl-1,3-dioxolane-4,5-dicarboxylate (ca 10 mg) in CH₂Cl₂ (ca 300 μl) at 195 K. After warming to room temperature, the solvent was removed *in vacuo* and the residue dissolved in hexane (ca 300 μl) before being sealed in a 5 mm glass tube. Crystal deposition occurred after several hours at 273 K. A small sample crystal was placed in an NMR tube and carefully dissolved in CD₂Cl₂ at 195 K. An NMR spectrum was then taken at 193 K and showed a 12:1 ratio of isomers. Observations were made on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator using Mo Kα radiation. The ω/2θ scan mode was used for data collection at a constant speed of 2.7° min⁻¹. Two standard reflections were monitored every 30 min without significant deviation. Cell parameters were obtained by least-squares procedure on 22 reflections with 2θ in the range 20–32°. Crystal: 0.15 × 0.25 × 0.30 mm; *hkl* range: -9 ≤ *h* ≤ 9, 0 ≤ *k* ≤ 6, 0 ≤ *l* ≤ 21; 1787 unique reflections were measured, 1531 were considered observed with $I_{\text{net}} \geq 2.5\sigma I_{\text{net}}$; $2\theta_{\text{max}} = 45.0^\circ$. The *NRCVAX* system was used for all calculations (Gabe, Lee & Le Page, 1985). The structure was solved by the application of direct methods and refined by full-matrix least squares on *F*. Anisotropic thermal parameters were refined for all non-H atoms. Function minimized: $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$. All H-atom positional parameters were calculated but not refined. The final residuals obtained at convergence were $R = 0.041$, $wR = 0.038$ and $\text{GOF} = 2.28$ for 298 parameters; the maximum (Δ/σ) ratio was 0.001. In the last difference map the deepest hole was $-0.48 \text{ e } \text{\AA}^{-3}$ and the highest peak $0.43 \text{ e } \text{\AA}^{-3}$. The secondary-extinction coefficient was 0.48 (7) (Larson, 1967; Zachariasen, 1963). Atomic scattering factors as stored in the *NRCVAX* program are taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on an IBM RISC/6000/320.

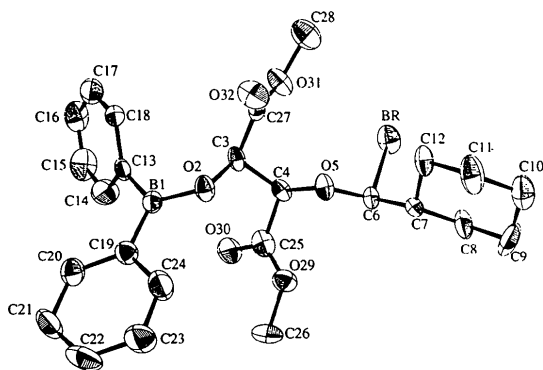


Fig. 1. ORTEP (Johnson, 1976) perspective view of the title compound with crystallographic numbering.

Table 1. Final coordinates and equivalent isotropic displacement parameters (\AA^2) for non-H atoms with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	B_{eq}
Br	0.27227 (9)	0.81821	0.93936 (4)	3.81 (5)
B(1)	0.4595 (10)	1.1403 (17)	0.6496 (4)	2.4 (5)
O(2)	0.3683 (5)	1.1320 (9)	0.6987 (2)	2.6 (3)
C(3)	0.4209 (8)	1.0829 (14)	0.7654 (4)	2.3 (4)
C(4)	0.3508 (8)	0.8959 (13)	0.7850 (4)	2.3 (4)
O(5)	0.2111 (5)	0.9389 (9)	0.8068 (2)	2.6 (3)
C(6)	0.1585 (8)	0.7985 (19)	0.8473 (3)	2.4 (4)
C(7)	-0.0039 (7)	0.8329 (23)	0.8523 (3)	2.8 (5)
C(8)	-0.0682 (12)	0.6697 (17)	0.8910 (5)	3.5 (5)
C(9)	-0.2371 (13)	0.7011 (23)	0.8893 (6)	5.0 (7)
C(10)	-0.2710 (12)	0.8997 (21)	0.9171 (5)	4.4 (6)
C(11)	-0.2049 (11)	1.0560 (19)	0.8788 (5)	4.5 (6)
C(12)	-0.0372 (11)	1.0318 (17)	0.8783 (5)	3.0 (5)
C(13)	0.6330 (8)	1.1636 (14)	0.6682 (4)	2.3 (4)
C(14)	0.7306 (10)	1.0319 (16)	0.6490 (4)	4.2 (5)
C(15)	0.8809 (11)	1.0525 (18)	0.6679 (5)	4.5 (6)
C(16)	0.9344 (10)	1.2031 (21)	0.7033 (5)	4.2 (6)
C(17)	0.8402 (10)	1.3365 (25)	0.7222 (4)	4.2 (6)
C(18)	0.6888 (8)	1.3241 (21)	0.7051 (3)	3.0 (5)
C(19)	0.3829 (8)	1.1222 (14)	0.5771 (4)	2.7 (4)
C(20)	0.4584 (8)	1.1303 (14)	0.5214 (4)	3.0 (4)
C(21)	0.3899 (11)	1.0994 (16)	0.4578 (4)	4.0 (6)
C(22)	0.2406 (11)	1.0583 (17)	0.4508 (4)	4.8 (6)
C(23)	0.1604 (9)	1.0528 (18)	0.5043 (4)	4.7 (6)
C(24)	0.2310 (10)	1.0834 (16)	0.5670 (4)	3.9 (5)
C(25)	0.3407 (11)	0.7605 (13)	0.7262 (5)	3.3 (5)
C(26)	0.1965 (9)	0.5835 (15)	0.6440 (4)	3.9 (5)
C(27)	0.3854 (9)	1.2431 (17)	0.8118 (5)	2.4 (5)
C(28)	0.4177 (8)	1.3289 (24)	0.9257 (4)	4.5 (6)
O(29)	0.2073 (6)	0.7148 (9)	0.6999 (2)	3.0 (3)
O(30)	0.4525 (6)	0.7068 (10)	0.7038 (3)	3.9 (3)
O(31)	0.4480 (5)	1.2032 (10)	0.8721 (3)	3.4 (3)
O(32)	0.3116 (7)	1.3835 (11)	0.7973 (3)	3.9 (4)

Table 2. Bond lengths (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

Br—C(6)	2.037 (7)	C(13)—C(18)	1.401 (15)
B(1)—O(2)	1.367 (10)	C(14)—C(15)	1.395 (14)
B(1)—C(13)	1.600 (12)	C(15)—C(16)	1.328 (19)
B(1)—C(19)	1.560 (12)	C(16)—C(17)	1.345 (19)
O(2)—C(3)	1.423 (9)	C(17)—C(18)	1.395 (11)
C(3)—C(4)	1.514 (13)	C(19)—C(20)	1.387 (11)
C(3)—C(27)	1.509 (14)	C(19)—C(24)	1.410 (12)
C(4)—O(5)	1.430 (9)	C(20)—C(21)	1.384 (11)
C(4)—C(25)	1.508 (13)	C(21)—C(22)	1.389 (14)
O(5)—C(6)	1.389 (12)	C(22)—C(23)	1.374 (13)
C(6)—C(7)	1.520 (10)	C(23)—C(24)	1.374 (12)
C(7)—C(8)	1.527 (17)	C(25)—O(29)	1.317 (11)
C(7)—C(12)	1.514 (19)	C(25)—O(30)	1.221 (11)
C(8)—C(9)	1.558 (16)	C(26)—O(29)	1.445 (11)
C(9)—C(10)	1.527 (21)	C(27)—O(31)	1.321 (10)
C(10)—C(11)	1.494 (16)	C(27)—O(32)	1.201 (14)
C(11)—C(12)	1.547 (14)	C(28)—O(31)	1.439 (13)
C(13)—C(14)	1.361 (13)		
O(2)—B(1)—C(13)	120.2 (7)	B(1)—C(13)—C(18)	120.0 (8)
O(2)—B(1)—C(19)	115.5 (7)	C(14)—C(13)—C(18)	117.9 (8)
C(13)—B(1)—C(19)	124.2 (7)	C(13)—C(14)—C(15)	120.9 (9)
B(1)—O(2)—C(3)	121.8 (6)	C(14)—C(15)—C(16)	121.5 (10)
O(2)—C(3)—C(4)	110.0 (7)	C(15)—C(16)—C(17)	118.7 (9)
O(2)—C(3)—C(27)	109.9 (7)	C(16)—C(17)—C(18)	122.6 (12)
C(4)—C(3)—C(27)	109.7 (7)	C(13)—C(18)—C(17)	118.4 (11)
C(3)—C(4)—O(5)	108.8 (7)	B(1)—C(19)—C(20)	123.3 (7)
C(3)—C(4)—C(25)	108.3 (7)	B(1)—C(19)—C(24)	119.2 (7)
O(5)—C(4)—C(25)	113.1 (7)	C(20)—C(19)—C(24)	117.4 (7)
C(4)—O(5)—C(6)	114.6 (6)	C(19)—C(20)—C(21)	122.3 (8)
Br—C(6)—O(5)	108.4 (6)	C(20)—C(21)—C(22)	117.9 (7)
Br—C(6)—C(7)	109.6 (5)	C(21)—C(22)—C(23)	122.0 (8)
O(5)—C(6)—C(7)	109.5 (9)	C(22)—C(23)—C(24)	119.0 (8)
C(6)—C(7)—C(8)	110.7 (10)	C(19)—C(24)—C(23)	121.4 (8)
C(6)—C(7)—C(12)	113.6 (9)	C(4)—C(25)—O(29)	116.2 (8)
C(8)—C(7)—C(12)	112.8 (7)	C(4)—C(25)—O(30)	119.9 (8)
C(7)—C(8)—C(9)	108.9 (9)	O(29)—C(25)—O(30)	123.7 (8)
C(8)—C(9)—C(10)	111.0 (10)	C(3)—C(27)—O(31)	108.7 (8)
C(9)—C(10)—C(11)	110.5 (9)	C(3)—C(27)—O(32)	126.5 (8)
C(10)—C(11)—C(12)	112.5 (9)	O(31)—C(27)—O(32)	124.8 (9)
C(7)—C(12)—C(11)	109.7 (9)	C(25)—O(29)—C(26)	116.6 (7)
B(1)—C(13)—C(14)	122.1 (8)	C(27)—O(31)—C(28)	118.1 (8)

Discussion. Table 1* gives the final atomic parameters with their respective B values. Fig. 1 shows an *ORTEP* (Johnson, 1976) perspective view with crystallographic numbering. Bond lengths and angles are given in Table 2.

According to the known configuration of the chiral centers C(3) and C(4) (*R, R* in dimethyl tartrate), the center C(6) was assigned the *S* configuration. As viewed in Fig. 1, O(2) and O(5) are *syn*. The two esters are almost *anti* to one another [$C(27)-C(3)-C(4)-C(25) = 160.1(10)^\circ$]. The boron has a trigonal-planar conformation with a B—O bond distance of 1.367(10) Å. This value is comparable to the mean of 1.371(6) Å observed for $PhB(OH)_2$ (Rettig & Trotter, 1977) and is slightly longer than the distance of 1.354(3) Å observed for Ph_2BOH (Rettig & Trotter, 1983). The B(1)—C(13) and B(1)—C(19) bond lengths are 1.600(12) and

1.560(12) Å, respectively, and are well within the range of B—C bond lengths of 1.571(3) and 1.589(5) Å observed in Ph_3B (Zettler, Hausen & Hess, 1974), of 1.566(3) Å observed in $PhB(OH)_2$ (Rettig & Trotter, 1977) and of 1.572(3) Å observed in Ph_2BOH (Rettig & Trotter, 1983). The torsion angles defining the orientation of the two phenyl rings, O(2)—B(1)—C(13)—C(18) and O(2)—B(1)—C(19)—C(24), are $-58.7(7)$ and $-5.1(4)^\circ$, respectively. The latter group is close to being oriented in the boron coordination plane while the first phenyl group is twisted out of the boron coordination plane because of steric hindrance with C(3). The C—C bond distances in both phenyl rings range from 1.328(19) to 1.410(12) Å. The longer bonds are those located nearest the B atom, as noted by Rettig, Trotter, Kliegel & Becker (1976). In the crystal packing the biphenylborate groups on neighboring molecules are facing each other around the 2_1 screw axis along **b**, as viewed in Fig. 2, with C(20) and C(21) located near the axis. No abnormally short distances were observed.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55475 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1003]

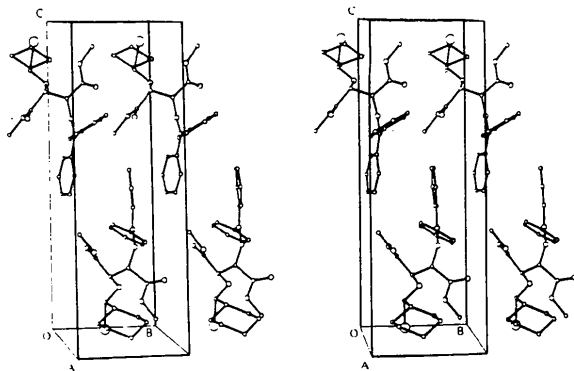


Fig. 2. A stereodiagram of the molecular packing along **a** (*PLUTO*; Motherwell & Clegg, 1978). H atoms are omitted for clarity.

References

- ALEXAKIS, A. & MANGENEY, P. (1990). *Tetrahedron Asymmetry*, **1**, 477–511.
- GABE, E. J., LEE, F. L. & LE PAGE, Y. (1985). *NRCVAX Crystal Structure System*. In *Crystallographic Computing 3*, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 167–174. Oxford: Clarendon Press.
- GUINDON, Y., SIMONEAU, B., YOAKIM, C., GORYS, V., LEMIEUX, R. & OGILVIE, W. (1991). *Tetrahedron Lett.* **32**, 5453–5456.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- RETTIG, S. J. & TROTTER, J. (1977). *Can. J. Chem.* **55**, 3071–3075.
- RETTIG, S. J. & TROTTER, J. (1983). *Can. J. Chem.* **61**, 2334–2340.
- RETTIG, S. J., TROTTER, J., KLIEGEL, W. & BECKER, H. (1976). *Can. J. Chem.* **54**, 3142–3151.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
- ZETTLER, F., HAUSEN, H. D. & HESS, H. (1974). *J. Organomet. Chem.* **72**, 157–162.