Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N13—H13$\cdots$O35	0.860	1.977	2.834 (4)	174.3
O35—H1W$\cdots$O34	0.948	1.743	2.688 (3)	174.3
N15—H15A$\cdots$O33^i	0.860	2.181	3.023 (4)	166.2
O35—H2W$\cdots$O32^{ii}	0.833	2.352	3.099 (4)	149.4
O35—H2W$\cdots$O33^{ii}	0.833	2.525	3.232 (4)	143.3
N15—H15B$\cdots$O32^{iii}	0.860	2.227	3.035 (4)	156.4
N15—H15B$\cdots$O34^{iii}	0.860	2.499	3.232 (5)	143.6

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-1-x, 1-y, 1-z$; (iii) $1+x, y, z$.

The data were collected using a fixed scan speed of 1.2° min^{-1} and a scan width of 1.2°. The structure was solved by a combination of Patterson and direct methods on the difference structure. Refinement was performed with full-matrix least-squares on F^2 for all reflections. The sum of the occupation factors of the disordered *m*-tolyl moiety was constrained to 1.0. The ring distances of these moieties were tied to a free variable and restrained to vary within 0.03 Å. Adjacent non-H atoms were restrained to have the same U_{ij} components within 0.01 Å^2. H atoms were calculated at geometrical positions and allowed to ride on their parent atoms.

Data collection: Hilger & Watts Y290 software. Cell refinement: *XRAY76 PARAM* (Stewart *et al.*, 1976). Data reduction: *REDU4* (Stoe & Cie, 1992). Program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1981). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEX2.1b* (McArdle, 1994). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1140). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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tert-Butyl 2-[(Hydroxy)(5-hydroxy-1,3-benzodioxol-6-yl)methyl]pyrrolidine-1-carboxylate

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Abstract

The title compound, $C_{17}H_{23}NO_6$, was prepared from a phenoxymagnesium bromide derivative and *N*-*tert*-butoxycarbonyl-L-prolinal in a chemical reaction which is an example of controlled α-chelation. The structure of the compound elucidates the chemical pathway of the synthesis process.

Comment

Ephedrine-like compounds have been obtained with good to excellent diastereoselection (Bigi, Casnati, Sartori, Araldi & Bocelli, 1989; Bigi, Casnati, Sartori & Araldi, 1990) *via* coordinated Friedel–Crafts alkylation of phenols. In particular, the reaction at room temperature of phenoxymagnesium bromide derivatives (1) with *N*-*tert*-butoxycarbonyl-L-prolinal, (2) (Boc = *tert*-butoxycarbonyl), gives the 2-hydroxy-α-[1-(*tert*-butoxycarbonylamino)-2-pyrrolidinyl]benzenemethanol derivatives (3) and (4) in good yields and with excellent diastereoselectivity (d.e. > 94%).
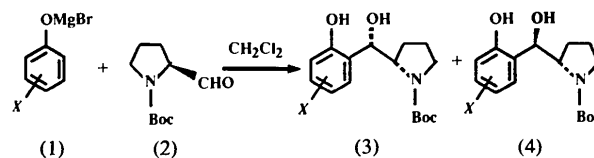
This general approach to the synthesis of chiral β-amino-*ortho*-hydroxybenzyl alcohols *via* direct *ortho*-hydroxyalkylation of phenol rings at room temperature with good yields and good diastereoselectivity has already been used with different *N*-(Boc)-α-

aminoaldehydes (Bigi *et al.*, 1989, 1990; Bocelli & Cantoni, 1990). The present paper constitutes a further step in this field of research and reports the structure of (3) with X = 4,5-OCH$_2$O:
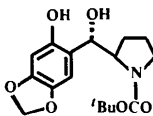
The pyrrole ring is not planar; in terms of Cremer & Pople (1975) notation [Q = 0.36 (1) Å, φ = 88.9 (9)°] it assumes a twist conformation. The dioxole ring [Q = 0.18 (10) Å, φ = 33.7 (19)°] has an envelope conformation; atom C5 deviates by 0.29 (1) Å from the plane through the other four atoms. This ring forms a dihedral angle of 0.8 (2)° with the planar benzene ring.

The shortest intramolecular contact is H1O4$\cdots$O5 = 2.04 (9) Å and the shortest intermolecular contacts are O1$\cdots$H12B^i = 2.74 (7) and O3$\cdots$H17B^{ii} = 2.74 (13) Å [symmetry codes: (i) $\frac{1}{2}$ − x, $\frac{1}{2}$ + y, $\frac{1}{2}$ − z; (ii) −$\frac{1}{2}$ − x, y − $\frac{1}{2}$, $\frac{1}{2}$ − z].

The relative configuration of the chiral centres (C8 and C9) corresponds to a *syn* relative stereo-disposition of the carbon chain, as expected for an α-chelation controlled reaction (Reetz, 1985).
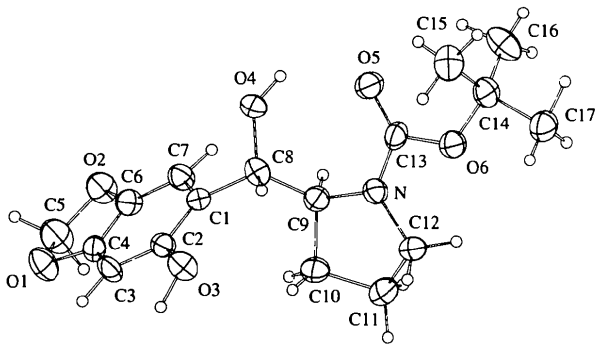
Fig. 1. Perspective view of the molecule showing the atom-labelling scheme. Displacement ellipsoids are plotted at the 30% probability level.
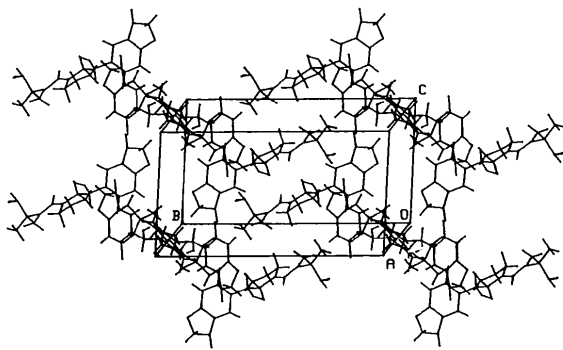
Fig. 2. Crystal packing.

Experimental

The diastereoisomer (3) with X = 4,5-OCH$_2$O was obtained as a major isomer from the reaction of (1) [X = 4,5-OCH$_2$O] and (2) (d.e. 94%). Crystals were isolated from pentane/dichloromethane solution (10:4). The space group indicates that the crystal is a racemate rather than a conglomerate in which both the enantiomers are present. Indeed the enantiomeric excess was measured to be 93% by HPLC analysis of MPTA derivatives (Bigi *et al.*, 1990) and the racemate crystallizes preferentially.

Crystal data

$C_{17}H_{23}NO_6$	Cu $K\alpha$ radiation
M_r = 337.4	λ = 1.5418 Å
Monoclinic	Cell parameters from 29
$P2_1/n$	reflections
a = 9.791 (2) Å	θ = 11.1–37.6°
b = 18.974 (3) Å	μ = 0.790 mm^{-1}
c = 10.358 (2) Å	Room temperature
β = 117.51 (2)°	Prism
V = 1706.7 (6) Å^3	0.9 × 0.13 × 0.15 mm
Z = 4	Colourless
D_x = 1.313 Mg m^{-3}	

Data collection

Siemens AED diffractometer	R_{int} = 0.019
ω–2θ scans	θ_{max} = 70°
Absorption correction:	h = −11 → 10
refined from ΔF	k = 0 → 23
(*DIFABS*; Walker &	l = 0 → 11
Stuart, 1983)	1 standard reflection
3209 measured reflections	monitored every 50
3174 independent reflections	reflections
1202 observed reflections	intensity decay: 9%
[I > 3$\sigma(I)$]	

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.43
R = 0.059	$\Delta\rho_{max}$ = 0.22 e Å^{-3}
wR = 0.066	$\Delta\rho_{min}$ = −0.24 e Å^{-3}
S = 1.36	Extinction correction: none
1202 reflections	Atomic scattering factors
309 parameters	from *International Tables*
All H-atom parameters	*for X-ray Crystallography*
refined	(1974, Vol. IV, Tables
w = 3.4864/[$\sigma^2(F_o)$	2.2A and 2.3.1 for O, N,
+ 0.01159F^2]	C and Table 2.2C for H)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

U_{eq} = $(1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ (Hamilton, 1959).

	x	y	z	U_{eq}
O1	0.1553 (6)	0.6154 (2)	−0.0713 (5)	0.075 (3)
O2	0.0343 (6)	0.7020 (2)	−0.2407 (4)	0.073 (3)
O3	0.0706 (5)	0.7380 (2)	0.2988 (5)	0.060 (2)
O4	−0.2317 (5)	0.8573 (2)	−0.0124 (6)	0.065 (3)
O5	−0.2648 (5)	0.9829 (2)	0.0648 (6)	0.078 (3)
O6	−0.1237 (5)	1.0570 (2)	0.2521 (5)	0.067 (3)
N1	−0.0038 (6)	0.9709 (2)	0.2030 (5)	0.050 (2)
C1	−0.0143 (7)	0.7826 (3)	0.0621 (7)	0.047 (3)
C2	0.0589 (7)	0.7302 (3)	0.1614 (7)	0.049 (3)
C3	0.1169 (8)	0.6716 (4)	0.1266 (8)	0.058 (4)

C4	0.1081 (7)	0.6680 (3)	−0.0086 (7)	0.053 (3)
C5	0.1386 (15)	0.6444 (6)	−0.2036 (11)	0.090 (6)
C6	0.0344 (7)	0.7196 (3)	−0.1098 (7)	0.054 (3)
C7	−0.0265 (8)	0.7775 (3)	−0.0793 (7)	0.055 (3)
C8	−0.0815 (8)	0.8473 (3)	0.1000 (8)	0.056 (4)
C9	0.0216 (7)	0.9113 (3)	0.1257 (7)	0.053 (3)
C10	0.1917 (8)	0.8966 (4)	0.2212 (9)	0.060 (4)
C11	0.2643 (11)	0.9672 (5)	0.2892 (12)	0.083 (5)
C12	0.1389 (8)	0.9998 (4)	0.3168 (8)	0.070 (4)
C13	−0.1425 (9)	1.0014 (3)	0.1635 (8)	0.055 (3)
C14	−0.2565 (8)	1.0996 (3)	0.2370 (7)	0.061 (3)
C15	−0.3733 (13)	1.0563 (5)	0.2552 (12)	0.079 (5)
C16	−0.3260 (11)	1.1365 (5)	0.0905 (10)	0.084 (5)
C17	−0.1801 (11)	1.1508 (4)	0.3641 (10)	0.078 (4)

Table 2. *Selected geometric parameters* (Å, °)

O1—C4	1.382 (9)	C1—C7	1.417 (11)
O1—C5	1.414 (13)	C1—C8	1.527 (10)
O2—C5	1.422 (13)	C2—C3	1.370 (11)
O2—C6	1.396 (9)	C3—C4	1.365 (12)
O3—C2	1.382 (10)	C4—C6	1.371 (8)
O4—C8	1.404 (7)	C6—C7	1.355 (10)
O5—C13	1.213 (8)	C8—C9	1.522 (9)
O6—C13	1.354 (8)	C9—C10	1.519 (9)
O6—C14	1.477 (9)	C10—C11	1.528 (12)
N1—C9	1.472 (9)	C11—C12	1.515 (15)
N1—C12	1.456 (8)	C14—C15	1.489 (15)
N1—C13	1.354 (10)	C14—C16	1.517 (11)
C1—C2	1.371 (8)	C14—C17	1.525 (10)
C4—O1—C5	105.1 (5)	C1—C7—C6	117.4 (5)
C5—O2—C6	104.1 (5)	O4—C8—C1	107.8 (5)
C13—O6—C14	121.2 (5)	C1—C8—C9	110.9 (6)
C12—N1—C13	122.5 (5)	O4—C8—C9	113.2 (5)
C9—N1—C13	124.2 (5)	N1—C9—C8	116.3 (5)
C9—N1—C12	112.9 (5)	C8—C9—C10	114.0 (5)
C7—C1—C8	118.7 (5)	N1—C9—C10	101.3 (5)
C2—C1—C8	121.9 (5)	C9—C10—C11	106.0 (6)
C2—C1—C7	119.4 (5)	C10—C11—C12	101.5 (7)
O3—C2—C1	117.4 (5)	N1—C12—C11	104.6 (6)
C1—C2—C3	121.8 (6)	O6—C13—N1	109.0 (5)
O3—C2—C3	120.7 (5)	O5—C13—N1	126.4 (5)
C2—C3—C4	118.2 (6)	O5—C13—O6	124.7 (7)
O1—C4—C3	130.0 (5)	O6—C14—C17	101.6 (6)
C3—C4—C6	120.7 (6)	O6—C14—C16	108.9 (6)
O1—C4—C6	109.2 (5)	O6—C14—C15	112.0 (5)
O1—C5—O2	107.9 (7)	C16—C14—C17	112.6 (5)
O2—C6—C4	109.6 (5)	C15—C14—C17	109.9 (7)
C4—C6—C7	122.3 (6)	C15—C14—C16	111.4 (7)
O2—C6—C7	128.1 (5)		
C14—O6—C13—O5	1.8 (11)	C2—C1—C8—O4	−132.2 (7)
C13—O6—C14—C15	58.9 (9)	C7—C1—C8—C9	−75.6 (8)
C13—O6—C14—C16	−64.8 (8)	C2—C1—C8—C9	103.4 (8)
C13—O6—C14—C17	176.2 (6)	C7—C1—C2—O3	178.8 (6)
C14—O6—C13—N1	−178.5 (5)	C8—C1—C2—O3	−0.2 (10)
C12—N1—C13—O5	175.6 (7)	O3—C2—C3—C4	−177.2 (6)
C9—N1—C13—O5	3.3 (11)	O4—C8—C9—N1	75.8 (7)
C12—N1—C13—O6	−4.1 (9)	C1—C8—C9—N1	−162.9 (6)
C9—N1—C13—O6	−176.4 (5)	C1—C8—C9—C10	−45.5 (8)
C13—N1—C9—C8	−52.4 (9)	O4—C8—C9—C10	−166.8 (6)
C7—C1—C8—O4	48.8 (8)		

The relatively low number of reflections is probably due to both the small dimensions and the quality of the crystal. H atoms were located in a difference Fourier map and refined isotropically. The model with the opposite configuration and the same data set produced an unchanged R factor making it unnecessary to apply the Hamilton (1965) test. The atomic coordinates and Fig. 1 correspond to the configuration of the title compound, which is known from the starting material.

All calculations were performed on an IBM PS2/80 personal computer using the *CRYSRULER* (Rizzoli, Sangermano, Calestani & Andreetti, 1987) package.

Data collection: Belletti, Cantoni & Pasquinelli (1988). Cell refinement: Belletti *et al.* (1988). Data reduction: *DI-*

FAU (Belletti *et al.*, 1988). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Software used to prepare material for publication: *CRYSRULER* (Rizzoli *et al.*, 1987).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1057). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Intramolecular Diels–Alder Adduct in the Hydroxy-β-ionone Series

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Abstract

The title compound, (2aβ,8aβ,8bβ)-4-acetyl-3,6,6,8b-tetramethyl-2a,6,7,8,8a,8b-hexahydro-2*H*-naphtho-[8,8a,1-*bc*]furan-2-one, $C_{17}H_{22}O_3$, was synthesized by the intramolecular reaction of a butynoate ester of hydroxy-β-ionone. Ring *A* adopts the most stable chair

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