-1.008 (4) and 1.287 (4) Å in molecule B, -1.072 (5) and 1.230 (5) Å in molecule C and -1.088 (6) and 1.223 (5) Å in molecule D (Katrusiak, 1989b). Thus, the position of the side chain in (I) appears ideal for lactonization. In the light of the previous studies of Karle & Karle (1972) the 'trimethyl lock' is unlikely to be responsible for this side-chain conformation and further structural studies are needed to explain the influence of over-methylation on the rate of lactonization of these compounds.

References

BORCHARDT, R. T. & COHEN, L. A. (1972a). J. Am. Chem. Soc. **94**, 9166–9174.
BORCHARDT, R. T. & COHEN, L. A. (1972b). J. Am. Chem. Soc. **94**, 9175–9181.
JOHNSON, C. K. (1970). ORTEP. Report ORNL-3794, second version. Oak Ridge National Laboratory, Tennessee, USA.
KARLE, J. M. & KARLE, I. M. (1972). J. Am. Chem. Soc. **94**, 9182–9189.
KATRUSIAK, A. (1989a). Acta Cryst. C45, 275–278.
KATRUSIAK, A. (1989b). Acta Cryst. C45, 1201–1205.
MILSTIEN, S. & COHEN, L. A. (1972). J. Am. Chem. Soc. **94**, 9158–9165.
MOTHERWELL, W. D. S. (1976). PLUTO. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1986). SHELXS86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Structures of Three 1-[(Diphenylphosphinoyl)methyl]cyclohexanols

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Abstract. (2a) 1-[(Diphenylphosphinoyl)methyl]-cyclohex-2-en-1-ol, $C_{19}H_{21}O_2P$, $M_r = 312.4$, monoclinic, Cc, $a = 9.190$ (6), $b = 19.485$ (12), $c = 9.570$ (6) Å, $\beta = 103.66$ (5)°, $V = 1665$ Å³, $Z = 4$, $D_x = 1.25$ Mg m⁻³, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.16$ mm⁻¹, $F(000) = 664$, $T = 155$ K, $R = 0.045$ for 1553 independent observed reflections. (3a) (1SR,2RS,3RS)-1-[(Diphenylphosphinoyl)methyl]-2,3-epoxycyclohexan-1-ol, $C_{19}H_{21}O_3P$, $M_r = 328.4$, monoclinic, Cc, $a = 9.240$ (4), $b = 19.529$ (8), $c = 9.736$ (6) Å, $\beta = 103.88$ (4)°, $V = 1706$ Å³, $Z = 4$, $D_x = 1.28$ Mg m⁻³, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.17$ mm⁻¹, $F(000) = 696$, $T = 175$ K, $R = 0.041$ for 2173 independent observed reflections. (5b) (1SR,2RS,3SR)-1-[(Diphenylphosphinoyl)methyl]-3-methylcyclohexane-1,2,3-triol, $C_{20}H_{25}O_4P$, $M_r = 360.4$, triclinic, $P\bar{1}$, $a = 5.836$ (3), $b = 11.837$ (8), $c = 13.242$ (7) Å, $\alpha = 75.09$ (5), $\beta = 81.25$ (4), $\gamma = 83.86$ (5)°, $V = 871.5$ Å³, $Z = 2$, $D_x = 1.37$ Mg m⁻³, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.17$ mm⁻¹, $F(000) = 384$, $T = 155$ K, $R = 0.049$ for 2822 independent observed reflections. In (2a) and (3a) the six-membered ring exists in a half-chair conformation with the bulky diphenylphosphinoylmethyl substituent in a pseudo-axial position and involved in an intramolecular hydrogen bond to the hydroxyl group. In (5b) the six-membered ring exists in a chair conformation with the diphenylphosphinoylmethyl substituent in an equatorial orientation and involved in an intramolecular hydrogen bond. In addition a network of intermolecular hydrogen bonds exists that involves all three hydroxyl groups of (5b).

Introduction. We have recently developed a new synthetic route for the efficient conversion of cyclohexenones (1) to the volatile vinyl epoxides (4) by way of the stable crystalline intermediates (2) and (3) containing diphenylphosphinoylmethyl substituents (Battiste & Campbell, 1990). A key feature of this procedure is the stereoselective hydroxyl-directed epoxidation of (2) to give a single diastereoisomer of (3). In the presence of traces of water, epoxide (3) undergoes stereoselective ring opening to triol (5). Despite much careful spectroscopic work there still existed some doubt as to the relative stereochemistry of the substituents in (3) and (5). In order to unambiguously resolve this problem and to examine the conformation and possible hydrogen bonding in the precursor alcohol (2) single-crystal X-ray structure determinations were carried out on (2a), (3a) and (5b).

(a) R = H
(b) R = CH$_3$
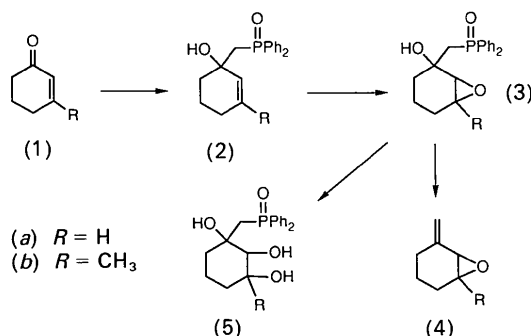
Experimental. Colourless plates of dimensions 0.49 × 0.46 × 0.07 mm (from dichloromethane) for (2a), 0.70 × 0.58 × 0.10 mm (from chloroform) for (3a) and 0.40 × 0.33 × 0.08 mm (from acetone/ethyl acetate) for (5b) were used on a Nicolet R3m diffractometer. Lattice parameters were determined from 25 reflections with $2\theta > 20°$. Data collections [ω scans; $-11 \le h \le 11$, $0 \le k \le 25$, $0 \le l \le 12$ for (2a), $-12 \le h \le 12$, $0 \le k \le 27$, $0 \le l \le 13$ for (3a) and $-7 \le h \le 7$, $0 \le k \le 15$, $0 \le l \le 17$ for (5b)] were made to $2\theta = 55°$ for (2a) and (5b) and to $2\theta = 60°$ for (3a) with standard reflections (and intensity variations used to scale the data) 200, 0,10,0, 022 (4%) for (2a), 800, 080, 008 (4%) for (3a), 202, 050, 005 (3%) for (5b) monitored every 100 measurements. The number of reflections measured, unique reflections, R_{int} and observed reflections [$I > 3\sigma(I)$] are: 2071, 2016, 0.032, 1553 for (2a), 2786, 2492, 0.034, 2173 for (3a), 4157, 3990, 0.065, 2822 for (5b). Corrections were made for Lorentz and polarization effects but not for absorption. The space groups were selected on the basis of systematic absences and data statistics.

The three structures were solved by direct methods and refined on $|F|$ by blocked-cascade least-squares procedures (Sheldrick, 1984). All non-H atoms were given anisotropic displacement parameters, and H

atoms were assigned isotropic displacement parameters equal to the isotropic equivalent of their carrier C atom and included in calculated positions (C—H = 0.96 Å) except for the O—H hydrogens which were located from difference Fourier syntheses and their positions refined. (2a) and (3a) had minor disorder in the positions of C(5) and O(2) respectively; the occupancy factors of the disordered atoms were originally determined by refinement and then fixed; the minor occupancy atoms were refined with isotropic displacement parameters and, in the case of C(5') in (2a), without attached H atoms. Absolute configurations were not determined. The refinements converged at $R = 0.045$, $wR = 0.056$, $g = 0.0011$, $S = 1.19$ for 204 parameters for (2a), $R = 0.041$, $wR = 0.053$, $g = 0.00125$, $S = 1.13$ for 213 parameters for (3a) and $R = 0.049$, $wR = 0.061$, $g = 0.00053$, $S = 1.69$ for 235 parameters for (5b) with $w^{-1} = [\sigma^2(F) + g(F)^2]$. The final refinement had $(\Delta/\sigma)_{max} = 0.085$ for (2a), 0.018 for (3a), 0.037 for (5b) and a difference map had $(\Delta\rho)_{max} = 0.31$, 0.37, 0.37 and $(\Delta\rho)_{min} = -0.35$, -0.30, -0.29 e Å^{-3} for (2a), (3a) and (5b), respectively. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations, including the drawing of diagrams, were performed on a Nova 4X computer using *SHELXTL* (Sheldrick, 1984).

Discussion. Figs. 1–3 show perspective views and atom labelling of the three structures. Tables 1–4 list atomic coordinates and bonding parameters for each of the three structures.* Crystals of (2a) and (3a) are isomorphous. Each of these structures also shows some disorder; in the case of (2a) the location of C(5) is disordered over the two sides with relative occupancies of 0.75 and 0.25, while in (3a) the location of O(2) is disordered over the two sides [C(2)—C(3) and C(5)—C(6)] of the cyclohexane ring (but always cis to the OH) with relative occupancies of 0.9 and 0.1.

In (2a) and (3a), the six-membered ring exists in a half-chair conformation with, surprisingly, the bulky diphenylphosphinoylmethyl substituent in the pseudo-axial position and the hydroxyl group equatorial. In both structures an intramolecular hydrogen bond exists between the OH and the PO groups with O(1)···O(10) = 2.777 (5) and 2.772 (3) Å and H(1)···O(10) = 2.05 (6) and 1.89 (4) Å with O(1)—H(1)···O(10) hydrogen-bond angles of 161 (4) and 155 (3)° for (2a) and (3a) respectively. The existence

of these hydrogen bonds is of interest given that 2-(diphenylphosphinoyl)ethanol has an intermolecular hydrogen bond in the solid state rather than an intramolecular bond despite the fact that the PO and OH groups are separated by the same number of bonds as in (2a) and (3a) (Tkachev, Bondarenko, Matrosov, Cvetkov, Atovmjan & Kabachnik, 1981a). In (3a) the epoxide O atom is *cis* to the hydroxyl group, consistent with a hydroxyl-directed epoxidation. There are no unusually short intermolecular interactions with all contacts between non-H atoms being > 3.15 Å.

In (5b) the six-membered ring exists in a chair conformation but this time with the diphenylphosphinoylmethyl substituent in an equatorial orientation. The intramolecular hydrogen bond still exists
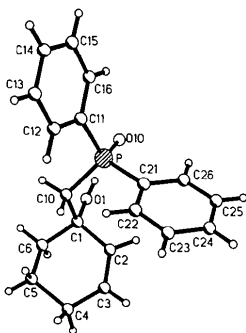

Fig. 1. Perspective view and atom labelling of 1-[(diphenylphosphinoyl)methyl]cyclohex-2-en-1-ol (2a).
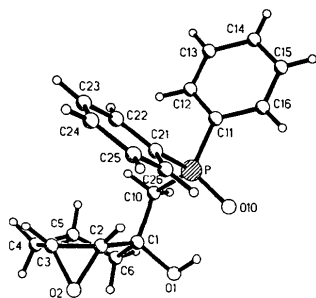

Fig. 2. Perspective view and atom labelling of (1SR,2RS,3RS)-1-[(diphenylphosphinoyl)methyl]-2,3-epoxycyclohexan-1-ol (3a).
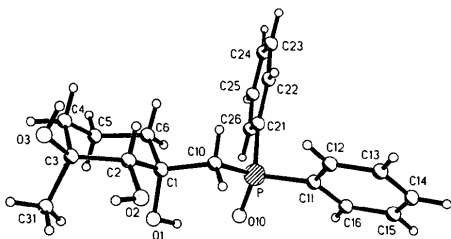

Fig. 3. Perspective view and atom labelling of (1SR,2RS,3SR)-1-[(diphenylphosphinoyl)methyl]-3-methylcyclohexane-1,2,3-triol (5b).

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\mathring{A}^2 \times 10^3$) *for* (2a) *with e.s.d.'s in parentheses*

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	2088 (4)	1491 (2)	4695 (4)	25 (1)
O(1)	630 (3)	1509 (2)	3744 (4)	40 (1)
C(2)	3005 (5)	920 (2)	4288 (5)	33 (1)
C(3)	3859 (7)	510 (3)	5258 (5)	51 (2)
C(4)	3791 (6)	447 (3)	6763 (6)	52 (2)
C(5)*	3133 (7)	1142 (3)	7274 (7)	35 (2)
C(5)†	2756 (23)	785 (11)	7049 (23)	39 (5)‡
C(6)	1795 (5)	1334 (3)	6189 (5)	35 (2)
C(10)	2840 (4)	2199 (2)	4734 (4)	24 (1)
P	3000§	2508 (1)	3000§	21 (1)
O(10)	1567 (3)	2406 (1)	1879 (3)	28 (1)
C(11)	3521 (4)	3403 (2)	3226 (4)	26 (1)
C(12)	4605 (5)	3643 (2)	4391 (5)	33 (1)
C(13)	4966 (6)	4343 (2)	4480 (6)	43 (2)
C(14)	4243 (6)	4790 (2)	3450 (7)	51 (2)
C(15)	3169 (7)	4553 (3)	2280 (7)	52 (2)
C(16)	2793 (6)	3862 (2)	2180 (6)	41 (2)
C(21)	4539 (4)	2075 (2)	2529 (4)	23 (1)
C(22)	5931 (4)	2027 (2)	3493 (5)	30 (1)
C(23)	7105 (5)	1675 (2)	3152 (6)	39 (2)
C(24)	6903 (6)	1368 (2)	1813 (6)	42 (2)
C(25)	5523 (6)	1416 (2)	821 (5)	41 (2)
C(26)	4351 (5)	1767 (2)	1183 (5)	33 (1)

* Occupancy 0.75.
† Occupancy 0.25.
‡ Isotropic.
§ Origin-defining parameter.

Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\mathring{A}^2 \times 10^3$) *for* (3a) *with e.s.d.'s in parentheses*

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	2104 (3)	1474 (1)	4706 (3)	22 (1)
O(1)	709 (2)	1457 (1)	3696 (2)	33 (1)
C(2)	3124 (3)	914 (1)	4403 (3)	26 (1)
O(2)*	2729 (3)	230 (1)	4651 (3)	34 (1)
O(2')†	1171 (22)	730 (10)	6280 (22)	28 (4)‡
C(3)	4068 (4)	515 (2)	5537 (4)	36 (1)
C(4)	4041 (4)	587 (2)	7070 (4)	46 (1)
C(5)	3143 (4)	1221 (2)	7343 (4)	42 (1)
C(6)	1752 (3)	1338 (2)	6158 (3)	30 (1)
C(10)	2848 (3)	2187 (1)	4722 (3)	21 (1)
P	3000§	2496 (1)	3000§	19 (1)
O(10)	1586 (2)	2377 (1)	1885 (2)	25 (1)
C(11)	3487 (3)	3391 (1)	3229 (3)	21 (1)
C(12)	4478 (3)	3640 (2)	4451 (3)	27 (1)
C(13)	4862 (4)	4329 (2)	4535 (4)	33 (1)
C(14)	4272 (4)	4771 (2)	3413 (4)	39 (1)
C(15)	3302 (4)	4521 (2)	2211 (4)	39 (1)
C(16)	2896 (4)	3835 (2)	2100 (3)	31 (1)
C(21)	4577 (3)	2075 (1)	2572 (3)	21 (1)
C(22)	5979 (3)	2082 (2)	3504 (3)	27 (1)
C(23)	7172 (4)	1734 (2)	3184 (4)	33 (1)
C(24)	6952 (4)	1374 (2)	1919 (4)	36 (1)
C(25)	5562 (4)	1370 (2)	975 (4)	35 (1)
C(26)	4372 (4)	1718 (2)	1297 (3)	29 (1)

* Occupancy 0.90.
† Occupancy 0.10.
‡ Isotropic.
§ Origin-defining parameter.

with   O(1)···O(10) = 2.828 (3),   H(1)···O(10) = 2.00 (3) Å and   O(1)—H(1)···O(10) = 159 (2)°. In addition a network of intermolecular hydrogen bonds exists, wherein the O(2) H atom interacts with O(3) of a molecule related by a centre of inversion

Table 3. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *for* (5b) *with e.s.d.'s in parentheses*

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	2803 (4)	7301 (2)	1411 (2)	20 (1)
O(1)	5208 (3)	6964 (2)	1094 (1)	24 (1)
C(2)	1239 (4)	6594 (2)	1009 (2)	22 (1)
O(2)	1795 (3)	5382 (2)	1413 (1)	28 (1)
C(3)	1145 (4)	6930 (2)	− 187 (2)	24 (1)
O(3)	− 789 (3)	6362 (2)	− 373 (2)	31 (1)
C(31)	3242 (4)	6467 (3)	− 823 (2)	28 (1)
C(4)	685 (5)	8257 (2)	− 562 (2)	29 (1)
C(5)	2451 (5)	8918 (2)	− 241 (2)	29 (1)
C(6)	2320 (4)	8615 (2)	957 (2)	25 (1)
C(10)	2315 (4)	6983 (2)	2623 (2)	18 (1)
P	4063 (1)	7666 (1)	3278 (1)	18 (1)
O(10)	6540 (3)	7708 (2)	2772 (1)	24 (1)
C(11)	3752 (4)	6841 (2)	4635 (2)	19 (1)
C(12)	1927 (6)	6181 (4)	5102 (2)	60 (2)
C(13)	1801 (6)	5555 (4)	6144 (2)	59 (1)
C(14)	3496 (5)	5584 (2)	6732 (2)	28 (1)
C(15)	5299 (6)	6250 (3)	6285 (3)	59 (1)
C(16)	5437 (6)	6877 (3)	5244 (3)	56 (1)
C(21)	2782 (4)	9117 (2)	3305 (2)	21 (1)
C(22)	495 (5)	9345 (3)	3675 (3)	60 (2)
C(23)	− 388 (6)	10472 (3)	3697 (3)	55 (1)
C(24)	975 (5)	11382 (3)	3342 (2)	36 (1)
C(25)	3245 (7)	11170 (3)	2964 (3)	64 (2)
C(26)	4157 (6)	10049 (3)	2941 (3)	45 (1)

[O(2)···O(3′) = 2.911 (3),   H(2a)···O(3′) = 2.09 (3) Å, O(2)—H(2a)···O(3′) = 163 (2)°], and the O(3) H atom interacts with O(1) of an adjacent molecule [O(3)···O(1″) = 2.952 (3), H(3a)···O(1″) = 2.11 (3) Å; O(3)—H(3a)···O(1″) = 173 (2)°].

In all three structures the geometry at the P atom is slightly distorted tetrahedral (Table 4), with C—P—C angles less than C—P—O angles, as has been observed in other diphenylphosphinoylmethyl structures (Bernardinelli & Gerdil, 1979; Tkachev, Bondarenko, Matrosov, Cvetkov, Atovmjan & Kabachnik, 1981b; Szlyk, Zhang, Palenik, Palenik & Colgate, 1989). Other bonding geometry is normal. The phenyl rings are all planar to within 0.006 Å

Table 4. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	(2a)	(3a)	(5b)
C(1)—O(1)	1.431 (5)	1.422 (3)	1.447 (3)
C(1)—C(2)	1.501 (6)	1.517 (4)	1.535 (4)
C(1)—C(10)	1.540 (6)	1.551 (4)	1.540 (3)
C(2)—O(2)	*	1.422 (4)	1.417 (4)
C(2)—C(3)	1.331 (6)	1.458 (4)	1.539 (3)
C(3)—O(2/3)		1.439 (4)	1.455 (4)
C(10)—P	1.804 (4)	1.818 (3)	1.804 (3)
P—O(10)	1.503 (3)	1.503 (2)	1.498 (2)
P—C(11)	1.807 (4)	1.805 (3)	1.804 (2)
P—C(21)	1.793 (4)	1.807 (3)	1.806 (3)
O(1)—C(1)—C(2)	110.6 (3)	110.5 (2)	108.9 (2)
O(1)—C(1)—C(10)	109.9 (3)	110.7 (2)	109.2 (2)
C(2)—C(1)—C(10)	113.2 (4)	110.7 (2)	107.5 (2)
C(1)—C(2)—O(2)		116.6 (3)	109.1 (2)
C(1)—C(2)—C(3)	122.6 (5)	121.7 (3)	116.0 (2)
O(2)—C(2)—C(3)		60.0 (2)	113.1 (2)
C(2)—O(2)—C(3)		61.3 (2)	
C(2)—C(3)—O(2/3)		58.8 (2)	107.2 (2)
C(1)—C(10)—P	114.2 (3)	114.9 (2)	115.4 (2)
C(10)—P—O(10)	111.4 (2)	111.6 (1)	112.3 (1)
C(10)—P—C(11)	106.8 (2)	106.2 (1)	105.6 (1)
O(10)—P—C(11)	112.1 (2)	112.7 (1)	113.2 (1)
C(10)—P—C(21)	108.4 (2)	107.9 (1)	109.3 (1)
O(10)—P—C(21)	111.6 (2)	111.9 (1)	111.0 (1)
C(11)—P—C(21)	106.3 (2)	106.1 (1)	105.2 (1)

with their mean planes mutually inclined at angles of 67.2 (4), 70.4 (3) and 78.7 (3)° for (2a), (3a) and (5b) respectively.

References

Battiste, M. A. & Campbell, C. R. (1990). Unpublished results.

Bernardinelli, G. & Gerdil, R. (1979). *Cryst. Struct. Commun.* **8**, 921–925.

Sheldrick, G. M. (1984). *SHELXTL Users Manual*. Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Szlyk, E., Zhang, Z.-Y., Palenik, G. J., Palenik, R. C. & Colgate, S. O. (1989). *Acta Cryst.* C45, 1234–1236.

Tkachev, V. V., Bondarenko, N. A., Matrosov, E. I., Cvetkov, E. N., Atovmjan, L. O. & Kabachnik, M. I. (1981a). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 209–211.

Tkachev, V. V., Bondarenko, N. A., Matrosov, E. I., Cvetkov, E. N., Atovmjan, L. O. & Kabachnik, M. I. (1981b). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 211–212.

Structure of Disodium β-D-Fructopyranose 1-Phosphate Pentahydrate

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Abstract. $2\text{Na}^+.\text{C}_6\text{H}_{11}\text{O}_9\text{P}^{2-}.5\text{H}_2\text{O}$, $M_r = 394.18$, monoclinic, $P2_1$, $a = 8.991$ (9), $b = 6.247$ (7), $c = 13.611$ (15) Å, $\beta = 92.53$ (6)°, $V = 763.7$ (15) Å^3, $Z = 2$, $D_m = 1.72$, $D_x = 1.714$ (4) g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 3.0$ cm^{-1}, $F(000) = 412$, $T = 302$ (3) K, final $R = 0.042$ for 2520 observed data including both hkl and $\overline{hkl}$ reflections. The β-D-fructopyranose ring adopts the $^2C_5$ conformation. The arrangement of the C(1)—O(1) bond with respect to the C(2)—O(6) and C(2)—C(3) ring bonds