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The Structure of the Precursor of Phosphafuranoses: 2-Hydroxy-5-hydroxymethyl-1-phenylphospholane 1-Oxide*

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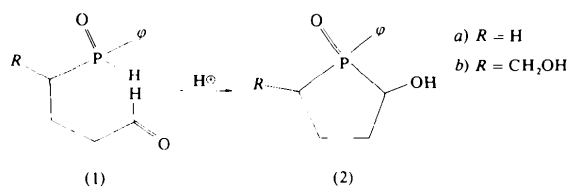
Abstract. C₁₁H₁₅O₃P, *M_r* = 226.2, triclinic, *P*1̄, *a* = 8.711 (3), *b* = 8.014 (3), *c* = 8.782 (3) Å, *α* = 94.74 (4), *β* = 115.11 (5), *γ* = 99.97 (4)°, *V* = 538.3 Å³, *D_m* = 1.383 (floatation), *D_x* = 1.395 Mg m⁻³, *Z* = 2, *μ*(Cu Kα) = 2.12 mm⁻¹, *F*(000) = 240. The crystal structure of one of the two isomeric products formed in the intramolecular cyclization of the respec-

tive secondary δ-oxoalkylphosphine oxide has been determined from 1354 intensities collected on a four-circle diffractometer with copper radiation. The structure was solved by direct methods and refined by least squares to a final *R* of 0.042. The molecules are linked into chains along [010] by hydrogen bonds with O...O distances of 2.74 Å.

* The atom-numbering scheme adopted in the paper does not correspond to the numbering in the title which is in agreement with the IUPAC convention.

Introduction. It has been shown that intramolecular cyclization of secondary phosphine oxides containing a

δ -oxoalkyl group leads to formation of 2-hydroxyphospholane 1-oxide systems (Musierowicz, Waszkuc & Krawczyk, 1980).



The compounds are very interesting not only from the point of view of their chemistry but also because of their potential biological activity (Takayanagi, Seo, Yamashita, Yoshida, Ogata & Inokawa, 1978). The two isomeric 2-hydroxy-5-hydroxymethyl-1-phenylphospholane 1-oxides obtained in the cyclization can be considered precursors of the corresponding phosphafuranoses. The same compound has been synthesized in a different way by Yamashita, Nakatsukasa, Yoshikane, Yoshida, Ogata & Inokawa (1977). In both the cases there were insufficient data for the determination of the relative configurations of the isomers.

The predominant isomer of 2-hydroxy-5-hydroxymethyl-1-phenylphospholane 1-oxide (I) was separated in a crystalline form and the determination of its crystal structure was attempted. Colourless, prismatic crystals suitable for X-ray studies were kindly provided by Dr H. W. Krawczyk of the Institute of Organic Chemistry. An irregular crystal was used for the data collection. Intensities were recorded on a Syntex P_2 diffractometer using copper radiation. The total number of independent reflections measured was 1354; 1304 of them had $F_o \geq 3\sigma(F_o)$. Intensities were not corrected for absorption.

The structure of the compound has been solved by direct methods (*MULTAN*; Germain, Main & Woolfson, 1971). The E map based on $400E \approx 1.1$ revealed the positions of all the heavy atoms but one. Full-matrix least-squares refinement resulted in an R of

Table 1. Atomic parameters (positional $\times 10^4$) for the non-hydrogen atoms

	x	y	z	$B_{\text{iso}} (\text{\AA}^2)$
P	2978 (1)	7617 (1)	2994 (1)	2.5 (1)
O(1)	4677 (3)	7888 (3)	4546 (3)	3.2 (1)
O(2)	3188 (3)	3691 (3)	3015 (3)	4.3 (1)
O(5)	2250 (3)	9911 (3)	4817 (3)	3.7 (1)
C(1)	2218 (4)	4359 (4)	3754 (4)	3.3 (1)
C(2)	1386 (4)	5659 (4)	2722 (4)	3.0 (1)
C(3)	57 (4)	6313 (4)	3183 (5)	3.9 (1)
C(4)	-172 (4)	8000 (4)	2482 (5)	4.2 (1)
C(5)	1635 (4)	9150 (4)	3101 (4)	3.1 (1)
C(11)	3270 (4)	7686 (4)	1095 (4)	2.8 (1)
C(12)	2146 (4)	8275 (4)	-304 (4)	3.8 (1)
C(13)	2464 (5)	8360 (5)	-1715 (4)	4.2 (1)
C(14)	3894 (5)	7883 (4)	1728 (4)	4.0 (1)
C(15)	4990 (5)	7256 (5)	-374 (5)	4.4 (2)
C(16)	4694 (4)	7186 (5)	1054 (4)	4.0 (1)

Table 2. Atomic parameters ($\times 10^3$) and bond lengths (\AA) for the hydrogen atoms

	x	y	z	$B_{\text{iso}} (\text{\AA}^2)$	Bonded to	Bond length
H(O2)	398 (5)	324 (6)	380 (5)	5.0 (1.2)	O(2)	0.90 (4)
H(O5)	335 (4)	1079 (5)	527 (4)	2.9 (0.8)	O(5)	0.98 (4)
H(10)	306 (3)	498 (4)	510 (3)	0.7 (0.6)	C(1)	1.10 (3)
H(11)	128 (4)	340 (4)	373 (4)	1.3 (0.7)	C(1)	1.01 (3)
H(12)	102 (4)	852 (4)	-33 (4)	1.4 (0.7)	C(12)	1.02 (4)
H(13)	171 (4)	886 (4)	-268 (4)	2.7 (0.8)	C(13)	1.00 (4)
H(14)	403 (4)	795 (4)	-266 (4)	2.3 (0.8)	C(14)	0.88 (4)
H(15)	611 (4)	691 (4)	-33 (4)	2.5 (0.8)	C(15)	1.05 (4)
H(16)	548 (4)	676 (4)	197 (4)	2.1 (0.7)	C(16)	0.95 (3)
H(21)	78 (4)	513 (4)	144 (4)	0.9 (0.6)	C(2)	1.03 (3)
H(31)	45 (4)	650 (4)	435 (4)	2.1 (0.8)	C(3)	0.92 (3)
H(32)	116 (5)	547 (5)	271 (5)	4.0 (0.9)	C(3)	1.04 (4)
H(41)	89 (4)	853 (4)	291 (4)	2.0 (0.7)	C(4)	0.99 (4)
H(42)	81 (4)	785 (4)	113 (4)	2.0 (0.8)	C(4)	1.06 (3)
H(51)	165 (4)	1008 (4)	233 (4)	0.7 (0.6)	C(5)	1.05 (3)

0.078 after five cycles of calculations with isotropic and two successive cycles with anisotropic temperature factors. At this stage of refinement the H atoms were found from the difference Fourier map and included in the block-diagonal refinement of all atoms. The final R factor after six cycles of calculations was 0.042 ($R_w = 0.051$). The weights were $w^{-2} = \sigma(F)$. Neutral-atom scattering factors for P, O and C were those given by Doyle & Turner (1968) and those from *International Tables for X-ray Crystallography* (1962) for H. All calculations were performed using the XRAY 70 system of Stewart, Kundell & Baldwin (1970) on a RIAD 32 computer except for *MULTAN*, for which an ODRA 1305 computer was used.

Final atomic parameters together with their standard deviations as obtained from the refinement are given in Tables 1 and 2.*

Discussion. Bond lengths and valency angles found in the structure are close to those reported earlier [Galdecki & Głowka (hereinafter GG), 1980a] in 2-hydroxy-2-methyl-1-phenylphospholane 1-oxide (II), if differences in chemical formulae are taken into

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35453 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

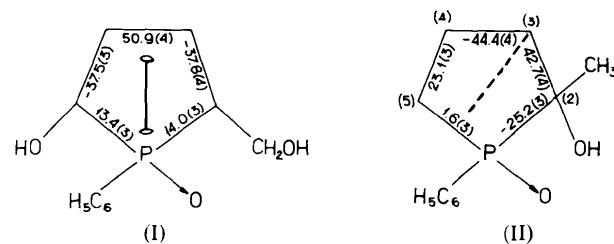


Fig. 1. (I) and (II) showing torsion angles ($^\circ$) and the numbering of atoms.

Table 3. Comparison of bond lengths (Å) and valency angles (°) in phospholane rings

Although the only difference between the substituents in (I) and (II) is the presence of the hydroxymethyl group in (I) instead of the methyl group in (II), because of the different substitution positions the numbering used here does not correspond exactly with that shown in Fig. 1.

	(II) (Galdecki & Glówka, 1980a)	(I) (present work)
P-C(2)	1.812 (4)	1.829 (3)
P-C(5)	1.851 (4)	1.859 (4)
C(1)-C(2)	1.509 (5)	1.515 (5)
C(2)-C(3)	1.523 (7)	1.534 (6)
C(3)-C(4)	1.530 (5)	1.540 (5)
C(4)-C(5)	1.542 (8)	1.520 (5)
C(5)-O(5)	1.429 (4)	1.407 (4)
P-C(2)-C(1)	116.1 (4)	112.6 (2)
P-C(2)-C(3)	106.3 (3)	104.1 (2)
P-C(5)-O(5)	108.1 (3)	108.8 (2)
P-C(5)-C(4)	101.9 (3)	103.5 (2)
C(1)-C(2)-C(3)	113.4 (4)	114.9 (3)
C(2)-P-C(5)	96.4 (2)	96.4 (2)
C(2)-C(3)-C(4)	108.4 (4)	107.0 (4)
C(3)-C(4)-C(5)	108.5 (4)	107.5 (3)
C(4)-C(5)-O(5)	110.4 (4)	109.1 (3)

account (Table 3). However, surprisingly high differences in the phospholane ring conformation are visible (Fig. 1). In (I) the ring adopts a nearly ideal half-chair conformation with a twofold axis through the P atom and asymmetry parameters (Duax & Norton, 1975) $\Delta C_2^1 = 0.5$ (3), $\Delta C_5^3 = 19.0$ (3) and $\bar{\varphi} = 30.7$ (3)°, whereas in (II) the phospholane ring has a C(3) sofa conformation with $\Delta C_5^3 = 1.9$ (4), $\Delta C_2^5 = 20.4$ (3) and $\bar{\varphi} = 27.4$ (4)°. The differences in conformations probably result from the different positions of the substituents, especially those participating in hydrogen bonding.

Molecules of (I) are linked into 'bands' along [010] by hydrogen bonds. Each molecule is connected to two others having opposite configurations (Fig. 2). The

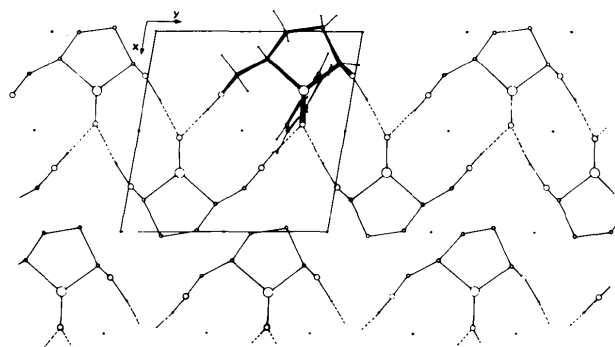


Fig. 2. Projection of the structure along [001], showing the packing of molecules and the hydrogen-bonding system.

Table 4. Bond lengths (Å), valency angles (°) and hydrogen bonding

P-O(1)	1.491 (2)	C(4)-C(5)	1.520 (5)
P-C(2)	1.829 (3)	C(5)-O(5)	1.407 (4)
P-C(5)	1.859 (4)	C(11)-C(12)	1.388 (5)
P-C(11)	1.794 (4)	C(12)-C(13)	1.383 (6)
C(1)-O(2)	1.409 (5)	C(13)-C(14)	1.369 (7)
C(1)-C(2)	1.515 (5)	C(14)-C(15)	1.371 (5)
C(2)-C(3)	1.534 (6)	C(15)-C(16)	1.387 (6)
C(3)-C(4)	1.540 (5)	C(16)-C(11)	1.381 (6)
O(1)-P-C(2)	114.5 (1)	O(2)-C(1)-C(2)	108.0 (3)
O(1)-P-C(5)	114.0 (1)	C(1)-C(2)-C(3)	114.9 (3)
O(1)-P-C(11)	111.6 (1)	C(2)-C(3)-C(4)	107.0 (3)
C(2)-P-C(5)	96.4 (2)	C(3)-C(4)-C(5)	107.5 (3)
C(2)-P-C(11)	110.1 (1)	C(4)-C(5)-O(5)	109.1 (3)
C(5)-P-C(11)	109.2 (2)	C(11)-C(12)-C(13)	119.9 (4)
P-C(2)-C(1)	112.6 (2)	C(12)-C(13)-C(14)	120.3 (3)
P-C(2)-C(3)	104.1 (2)	C(13)-C(14)-C(15)	120.5 (4)
P-C(5)-O(5)	108.8 (2)	C(14)-C(15)-C(16)	119.6 (4)
P-C(5)-C(4)	103.5 (2)	C(15)-C(16)-C(11)	120.4 (3)
P-C(11)-C(12)	122.2 (3)	C(16)-C(11)-C(12)	119.2 (4)
P-C(11)-C(16)	118.6 (2)		
O(1)...H(O2)	1.85 (4)	H(O2)-O(2)-C(1)	108 (4)
O(1)...H(O5)	1.79 (4)	H(O5)-O(5)-C(5)	114 (2)
O(1)...O(2)	2.74 (1)	P-O(1)...H(O2)	142 (1)
O(1)...O(5)	2.74 (1)	P-O(1)...H(O5)	123 (1)
		H(O2)...O(1)...H(O5)	89 (2)

band width is equal to a_n , while the length of a recurrent fragment is b_n . The O...O hydrogen-bond distances are both 2.74 (1) Å. This value is slightly higher than those observed in other phosphine oxides containing a hydroxy group. The distances are: 2.70 Å in (II) (GG, 1980a) and in both independent molecules of methyl (1-hydroxy-1-phenylethyl)phenylphosphinate (Glówka & Galdecki, 1980), and 2.72 Å in 4-hydroxy-1-phenyl-2-phospholene 1-oxide (GG, 1980c). In structures containing a carboxyl group as well as a phosphoryl group, O...O hydrogen-bond distances should be, and indeed are, shorter. Their mean value is 2.57 Å (Glówka, 1977). Such a shortening is also observed if the hydroxyl group is bonded to an sp^2 C atom, as in

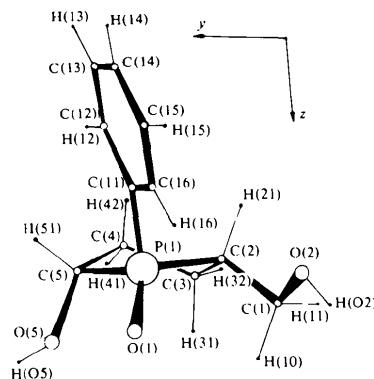


Fig. 3. Configuration of the molecule and numbering system.

3-hydroxy-2-phospholenes. The distances 2.59 and 2.61 Å have been found respectively by Washecheck, Helm, Purdum & Berlin (1974) and GG (1980b). It appears that the acidity of the hydroxyl H atom is the most important factor affecting both the hydrogen-bond distance and its strength. Table 4 shows the hydrogen-bonding geometry for (I).

The same configurations at P and C(2) and the opposite configuration at C(5) have been suggested (Musierowicz, Waszkuć & Krawczyk, 1979) and confirmed in this study (Fig. 3).

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Structure of 2-(4'-Chloro-2'-hydroxybenzoyl)benzoic Acid

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Abstract. $C_{14}H_9ClO_4$, $M_r = 276.7$, monoclinic, $P2_1/c$, $a = 10.838$ (3), $b = 15.205$ (3), $c = 7.347$ (1) Å, $\beta = 91.18$ (1)°, $V = 1210.46$ Å³, $D_x = 1.52$, $D_m = 1.50$ Mg m⁻³, $Z = 4$, $F(000) = 568$. The structure was solved by the heavy-atom method and refined by least-squares calculations to $R = 0.064$ for 622 visually estimated reflexions. The crystal structure consists of centrosymmetric dimers linked by hydrogen bonds [2.627 (13) Å] between the carboxyl groups.

Introduction. This work forms part of the studies on the structures of substituted 2-aryloxybenzoic acids. Crystals of the title compound were synthesized and kindly supplied by Professor J. Gronowska of the Organic Chemistry Department of N. Copernicus University.

Cell dimensions were obtained from rotation and Weissenberg photographs and were confirmed by measurements on a Syntex 2₁ diffractometer. From

systematic absences the space group was determined as $P2_1/c$. Intensities of 623 reflexions were collected photographically with the equi-inclination Weissenberg technique about the c axis (zones $hk0-hk5$), and about the a axis (zones $0kl-1kl$), using Ni-filtered Cu $K\alpha$ radiation. Intensities were corrected for Lorentz and polarization factors and for spot shape, but not for absorption.

The structure was solved by the heavy-atom method. The phases for the first Fourier synthesis were based on the structure factor calculation ($R = 0.568$) from the position of the Cl atom. All non-hydrogen atoms were then located in two successive Fourier syntheses ($R = 0.252$). Full-matrix least-squares refinements with isotropic and then anisotropic thermal parameters reduced R from 0.252 to 0.073. At this stage, seven of the nine H atoms were located from a difference Fourier map. The H atoms were given the isotropic