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The Structure of Methyl (1-Hydroxy-1-phenylethyl)phenylphosphinate, the Product of Sterically Controlled Grignard Addition to the Carbonyl Group of an α-Ketophosphine Oxide

By M. L. Główka and Z. Gałdecki

Institute of General Chemistry, Technical University of Łódź, 36 Żwirki, 90-924 Łódź, Poland

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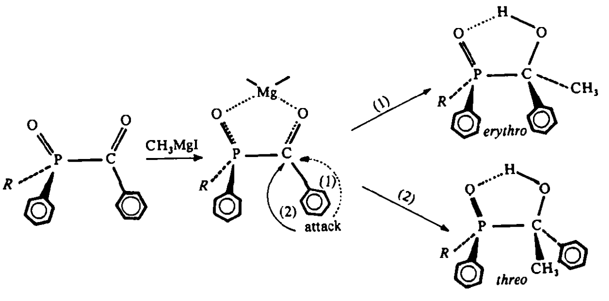
Abstract

$C_{15}H_{17}O_3P$, M_r = 276·3, is triclinic, $P\bar{1}$, with two molecules in the independent part of the unit cell, a = 8·518 (3), b = 11·259 (3), c = 15·345 (4) Å, α = 98·28 (5), β = 96·10 (5), γ = 89·61 (5)°, V = 1448·0 Å^3, D_m = 1·262, D_x = 1·267 Mg m^{-3}, Z = 4, μ(Cu $K\alpha$) = 1·69 mm^{-1}, m.p. 401–402 K. The structure was solved by direct methods and refined by least squares to a final R = 0·043 for 3088 observed reflections. The independent molecules have very similar conformations. They form chains along the [010] direction by means of hydrogen bonding with O···O distances of 2·70 Å. The configuration found is different from that assumed from NMR measurements, and the results of the study throw new light on the earlier proposed mechanism of the addition.

Introduction

Musierowicz & Waszkuć (1977) have shown that Grignard addition to the carbonyl group of α-ketophosphine oxides occurs with steric control of the chiral P group.



These authors proposed coordination of the Mg of the Grignard reagent giving a transition state with a different conformation from that of the ground state. The proportion of each isomer obtained in the reaction was determined by NMR assuming the formation of an intramolecular hydrogen bond. Such an assumption seemed justified in light of the theories hitherto proposed. Concentrations of the isomers formed differed considerably for (1-hydroxy-1-phenylethyl)ethylphenylphosphine oxide (R = Et) and for methyl (1-hydroxy-1-phenylethyl)phenylphosphinate (R = OMe), and for a full explanation of the mechanism of this addition reaction corroborative evidence was needed. Crystalline methyl (1-hydroxy-1-phenylethyl)phenylphosphinate [m.p. 401–402 K, (±)-*erythro* isomer assumed] provided a convenient model compound for X-ray analysis which we decided to use to establish the stereochemistry. Also, we are interested in the conformations and hydrogen bonding in crystals of phosphine oxide derivatives (Gałdecki & Główka, 1977*a*,*b*, 1978; Główka, 1978).

Experimental

Colourless, prismatic crystals of the compound, presumably the *erythro* isomer, were grown from a mixture of methanol and ethyl acetate (1:1). The crystals are triclinic, space group $P\bar{1}$ with Z = 4.

Crystal data

$C_{15}H_{17}O_3P$, M_r = 276·275, $F(000)$ = 584. $P\bar{1}$ with a = 8·518 (3), b = 11·259 (3), c = 15·345 (4) Å, α = 98·28 (5), β = 96·10 (5) and γ = 89·61 (5)°; V = 1448·0 Å^3; D_m = 1·262, D_x = 1·267 Mg m^{-3}, Z = 4; μ(Cu $K\alpha$) = 1·69 mm^{-1}, m.p. 401–402 K.

A Syntex $P2_1$ four-circle automatic diffractometer was used to measure 3626 intensities with the θ–2θ scan method to $2\theta_{\max}$ = 111° (Cu $K\alpha$ radiation) from a spherical crystal of diameter ~0·3 mm.

In the first attempt at structure solution, the reflections that were to have phases assigned to them were allowed to be specified by the program *MULTAN* (Germain, Main & Woolfson, 1971). However, none of the 16 solutions was satisfactory and the Fourier synthesis, phased on the molecular fragments taken from the E maps, did not reveal further atoms. The basic difficulty in determining the structure was that

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Table 1. *Atomic parameters (positional* × 10^4) *for non-hydrogen atoms*

	Molecule (I)				Molecule (II)			
	x	y	z	B_{iso} (Å^2)	x	y	z	B_{iso} (Å^2)
P	7967 (1)	9123 (1)	3257 (1)	2·9 (1)	8373 (1)	4145 (1)	3254 (1)	2·8 (1)
O(1)	8021 (2)	10417 (1)	3601 (1)	4·3 (1)	8428 (2)	5449 (1)	3566 (1)	4·2 (1)
O(2)	7005 (2)	8343 (2)	3796 (1)	4·4 (1)	9545 (2)	3385 (2)	3816 (1)	4·1 (1)
O(3)	9712 (2)	7210 (1)	2841 (1)	3·8 (1)	6467 (2)	2231 (1)	2922 (1)	4·0 (1)
C(01)	7136 (3)	8796 (2)	2129 (2)	3·4 (1)	8770 (3)	3770 (2)	2127 (2)	3·6 (2)
C(02)	6367 (3)	7718 (3)	1812 (2)	5·2 (2)	9444 (3)	2682 (3)	1832 (2)	4·9 (2)
C(03)	5790 (4)	7460 (3)	926 (2)	7·0 (2)	9684 (4)	2388 (3)	954 (2)	7·6 (3)
C(04)	5981 (5)	8285 (4)	370 (2)	7·7 (3)	9249 (5)	3185 (4)	372 (2)	7·5 (3)
C(05)	6725 (4)	9355 (3)	678 (2)	6·9 (2)	8595 (5)	4269 (3)	655 (2)	7·6 (3)
C(06)	7308 (4)	9628 (3)	1561 (2)	5·0 (2)	8359 (4)	4571 (3)	1537 (2)	5·2 (2)
C(07)	9903 (3)	8377 (2)	3332 (2)	3·2 (1)	6476 (3)	3436 (2)	3359 (2)	3·1 (1)
C(11)	11016 (3)	9070 (2)	2879 (2)	3·5 (1)	5178 (3)	4099 (2)	2870 (2)	3·1 (1)
C(12)	11700 (3)	10151 (3)	3297 (2)	5·1 (2)	4659 (3)	5216 (2)	3234 (2)	4·7 (2)
C(13)	12744 (4)	10747 (3)	2855 (3)	6·7 (2)	3450 (3)	5783 (3)	2780 (2)	5·4 (2)
C(14)	13101 (4)	10290 (3)	2030 (3)	6·8 (2)	2764 (3)	5265 (3)	1964 (2)	5·7 (2)
C(15)	12405 (4)	9254 (3)	1616 (2)	6·8 (2)	3305 (4)	4194 (3)	1594 (2)	5·8 (2)
C(16)	11367 (3)	8643 (2)	2038 (2)	5·0 (2)	4506 (3)	3604 (2)	2040 (2)	4·5 (2)
C(17)	10507 (3)	8314 (3)	4299 (2)	4·8 (2)	6237 (3)	3488 (3)	4342 (2)	4·7 (2)
C(20)	5482 (4)	8715 (3)	4021 (3)	7·3 (3)	11179 (3)	3765 (3)	4031 (2)	6·0 (2)

Table 2. *Hydrogen-atom parameters* (× 10^3) *and* H–X (X = O, C) *bond lengths* (Å)

	x	y	z	B_{iso} (Å^2)	Bonded to	Bond length (Å)
H(3)	932 (3)	677 (2)	312 (2)	2·8 (6)	O(3)	0·80 (3)
	704 (3)	180 (3)	323 (2)	5·3 (8)		0·84 (3)
H(02)	629 (3)	712 (3)	225 (2)	5·4 (8)	C(02)	1·03 (3)
	970 (3)	208 (2)	226 (2)	3·3 (6)		1·02 (3)
H(03)	528 (4)	663 (3)	71 (2)	8·1 (10)	C(03)	1·03 (3)
	1021 (4)	155 (3)	77 (2)	6·7 (9)		1·06 (3)
H(04)	557 (4)	801 (3)	−27 (2)	7·7 (10)	C(04)	1·01 (3)
	947 (4)	311 (3)	−24 (2)	7·2 (9)		0·97 (4)
H(05)	688 (4)	1001 (3)	34 (2)	8·8 (11)	C(05)	0·99 (4)
	816 (4)	488 (3)	25 (2)	7·3 (9)		1·03 (3)
H(06)	790 (3)	1043 (2)	179 (2)	4·2 (7)	C(06)	1·04 (3)
	781 (3)	539 (2)	177 (2)	4·7 (7)		1·06 (3)
H(12)	1141 (3)	1044 (2)	395 (2)	3·7 (6)	C(12)	1·06 (3)
	525 (3)	564 (2)	386 (2)	3·2 (6)		1·08 (2)
H(13)	1327 (3)	1142 (3)	318 (2)	5·4 (8)	C(13)	0·93 (3)
	304 (4)	654 (3)	304 (2)	6·8 (9)		0·97 (3)
H(14)	1407 (4)	1078 (3)	177 (2)	7·4 (9)	C(14)	1·14 (4)
	185 (3)	569 (2)	165 (2)	4·3 (7)		1·02 (3)
H(15)	1264 (4)	887 (3)	100 (2)	7·9 (10)	C(15)	1·02 (4)
	276 (3)	377 (3)	102 (2)	6·1 (9)		1·01 (3)
H(16)	1088 (3)	792 (2)	178 (2)	2·4 (5)	C(16)	0·93 (2)
	488 (3)	282 (2)	176 (2)	4·5 (7)		0·99 (3)
H(17,1)	1062 (3)	913 (2)	471 (2)	3·5 (6)	C(17)	1·03 (2)
	637 (3)	437 (2)	467 (2)	3·5 (6)		1·05 (3)
H(17,2)	1165 (3)	802 (2)	434 (2)	4·0 (7)	C(17)	1·02 (3)
	704 (3)	294 (2)	462 (2)	7·3 (7)		1·02 (3)
H(17,3)	978 (3)	781 (2)	454 (2)	3·6 (7)	C(17)	0·98 (3)
	508 (3)	316 (2)	436 (2)	4·6 (7)		1·06 (3)
H(20,1)	576 (5)	946 (4)	441 (3)	11·0 (13)	C(20)	0·97 (4)
	1175 (5)	312 (4)	400 (3)	12·6 (15)		0·87 (4)
H(20,2)	513 (5)	819 (4)	434 (3)	10·5 (13)	C(20)	0·89 (5)
	1124 (4)	458 (3)	403 (2)	8·8 (10)		0·92 (4)
H(20,3)	462 (5)	846 (4)	334 (3)	12·7 (14)	C(20)	1·21 (4)
	1135 (5)	389 (4)	466 (3)	12·7 (14)		0·96 (4)

normalized structure factors with k odd were too small to contribute to the Σ_2 relationships. After increasing all E values with k odd by 0·3, defining the phase of the $6\bar{1}4$ reflection to be 2π (from previous calculations) and specifying the origin $[0,10,\bar{5}(\pi), 3\bar{8}\bar{2}(\pi), 5\bar{7}1(\pi)]$, the third solution given by *MULTAN* was promising (M_{abs} = 1·172, R_{Karle} = 27·60, COMFOM = 2·700). The E map based on the 375 $E \geq 1{\cdot}6$ revealed only seven atoms [P(1), O(11), O(12), O(13), C(101), C(107) and C(108)] of one of the two molecules existing in the independent part of the unit cell. Successive use of Fourier and difference syntheses allowed us to locate the remaining 31 non-hydrogen atoms (R = 25%). That and further calculations were processed with the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). The model was refined by the least-squares method [block-diagonal, $w^{-2} = \sigma(F)$, dumping factor = 0·8]. Four cycles of refinement with isotropic followed by three cycles with anisotropic thermal parameters resulted in R = 0·079 (R_w = 0·090). The positions of all H atoms were found from a difference synthesis and their inclusion in the refinement with isotropic temperature factors resulted, after six cycles, in a final R of 0·043 and R_w = 0·051 for 3088 reflections with $F \geq 3\sigma(F)$. Maximum and mean values of shift/error in the final cycle were 1·39 and 0·262 respectively.

The scattering factors for P, O and C were those of Doyle & Turner (1968) and those in *International Tables for X-ray Crystallography* (1962) for H. The calculations were carried out on IBM 370/145 and ODRA-1305 (*MULTAN* only) computers.

Atomic parameters are given in Tables 1 and 2.*

Discussion

The symmetrically independent molecules of methyl (1-hydroxy-1-phenylethyl)phenylphosphinate are

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35304 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

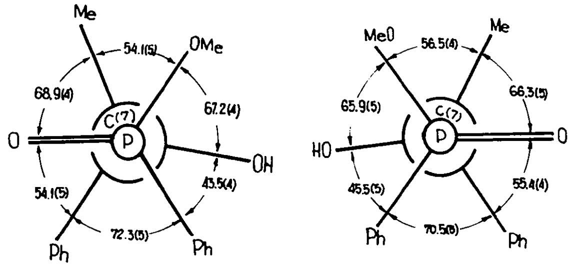
	(I)	(II)		(I)	(II)		(I)	(II)
P–O(1)	1·475 (2)	1·477 (2)	C(02)–C(03)	1·385 (5)	1·376 (5)	C(11)–C(12)	1·391 (4)	1·390 (3)
P–O(2)	1·587 (2)	1·578 (2)	C(03)–C(04)	1·371 (6)	1·377 (6)	C(12)–C(13)	1·404 (5)	1·386 (4)
P–C(01)	1·787 (3)	1·788 (3)	C(04)–C(05)	1·364 (5)	1·371 (5)	C(13)–C(14)	1·361 (5)	1·374 (4)
P–C(07)	1·846 (3)	1·840 (3)	C(05)–C(06)	1·384 (4)	1·383 (4)	C(14)–C(15)	1·353 (5)	1·356 (4)
O(2)–C(20)	1·422 (4)	1·449 (3)	C(06)–C(01)	1·386 (4)	1·385 (4)	C(15)–C(16)	1·390 (5)	1·389 (4)
O(3)–C(07)	1·419 (3)	1·423 (3)	C(07)–C(17)	1·529 (4)	1·536 (4)	C(16)–C(11)	1·373 (4)	1·380 (3)
C(01)–C(02)	1·383 (4)	1·387 (4)	C(07)–C(11)	1·517 (4)	1·522 (3)			

Table 4. *Valence angles* (°) *with e.s.d.'s in parentheses*

	(I)	(II)		(I)	(II)		(I)	(II)
O(1)–P–O(2)	114·2 (1)	114·5 (1)	P–C(07)–C(11)	107·5 (2)	107·8 (2)	C(07)–C(11)–C(12)	121·3 (2)	121·4 (2)
O(1)–P–C(01)	113·5 (1)	113·2 (1)	P–C(07)–C(17)	110·5 (2)	109·9 (2)	C(07)–C(11)–C(16)	120·4 (2)	120·1 (2)
O(1)–P–C(07)	114·4 (1)	113·5 (1)	O(3)–C(07)–C(11)	107·6 (2)	107·3 (2)	C(11)–C(12)–C(13)	119·0 (3)	119·9 (2)
O(2)–P–C(01)	106·1 (1)	106·7 (1)	O(3)–C(07)–C(17)	110·9 (2)	111·5 (2)	C(12)–C(13)–C(14)	121·4 (2)	121·0 (3)
O(2)–P–C(07)	100·8 (1)	100·6 (1)	C(01)–C(02)–C(03)	120·2 (3)	120·2 (3)	C(13)–C(14)–C(15)	119·4 (3)	119·2 (3)
C(01)–P–C(07)	106·7 (1)	107·3 (1)	C(02)–C(03)–C(04)	119·4 (3)	119·5 (3)	C(14)–C(15)–C(16)	120·4 (3)	120·9 (3)
P–O(2)–C(20)	120·0 (2)	119·5 (2)	C(03)–C(04)–C(05)	120·8 (3)	121·0 (3)	C(15)–C(16)–C(11)	121·3 (2)	120·5 (2)
P–C(01)–C(02)	121·1 (2)	121·0 (2)	C(04)–C(05)–C(06)	120·5 (3)	119·8 (3)	C(16)–C(11)–C(12)	118·4 (2)	118·5 (2)
P–C(01)–C(06)	119·1 (2)	119·2 (2)	C(05)–C(06)–C(01)	119·2 (3)	119·7 (3)	C(17)–C(07)–C(11)	112·4 (2)	111·5 (2)
P–C(07)–O(3)	107·8 (2)	108·8 (2)	C(06)–C(01)–C(02)	119·8 (2)	119·8 (3)			

almost identical. Thus, the bond lengths do not differ by more than the sum of their standard deviations (Table 3). The only exception is O(2)–C(20) of 1·422 (4) and 1·449 (3) Å, respectively, for molecules (I) and (II). Corbridge (1974) reported values between 1·40 and 1·45 Å in compounds of the type $(RO)_3PO$, and even 1·32–1·49 Å in other structures. Up to the present, only six structures of esters of *R*-substituted phosphinic acid derivatives have been determined and in general the O–C bond in the POC group seems to be longer than in the present compound; it is 1·47 Å in methyl fluoromethylphosphinate (Zeil, Kratz, Haase & Oberhammer, 1973), 1·48 Å in 1,8-diethoxy-3a,4,7,7a-tetrahydro-4,7-phosphinidenephosphindole 1,8-dioxide (Chiu & Lipscomb, 1969), 1·46 Å in racemic *O*-methyl-α-phenylphosphinylpropionic acid (Gałdecki & Główka, 1977*b*), 1·45 Å in 12-ethoxybenzo[*e*]-naphtho[1,2-*b*][1,4]thiaphosphorin 7,7,12-trioxide (Dhaneshwar, Kulkarni, Tavale & Pant, 1975) and racemic *O*-methylphenylphosphinylacetic acid (Gałdecki & Główka, 1977*a*), whereas only in the enantiomeric acid was the bond shorter (1·412 Å; Gałdecki & Główka, 1978). Also, the bond angles in both molecules are very similar (Table 4) and the differences are only greater than 3σ for O(2)–P–C(01), C(01)–P–C(07), P–C(07)–O(3), P–C(07)–C(17) and C(17)–C(07)–C(11).

The mean bond lengths in all benzene rings are the same (1·38 Å). This length is significantly less than the standard value of 1·396 Å, probably because of thermal motion. The high temperature factors for the atoms in the benzene rings, especially for those in the *para* positions, confirm this supposition. Also, the bond lengths involving the *para* atoms are extremely short. The remaining interatomic distances and bond angles are very close to the published values.



(I) (II)

Fig. 1. Conformations of the independent molecules, showing some torsion angles (°).

The conformations of both independent molecules are shown in Fig. 1. They are very similar and are in agreement with the expected conformations. Repulsive interactions between the two phenyl groups result in variations in the torsion angles, an increase to 65–70° accompanying a decrease to 45–55°. At the same time, characteristic deformations of the tetrahedral valency angles at the P and Cα atoms occur because of steric hindrance. The O(1)–P–O(2), O(1)–P–C(01) and O(1)–P–C(07) angles increase to about 114° whereas O(2)–P–C(01) and C(01)–P–C(07) decrease to 106–107° and O(2)–P–C(07) decreases to 100·7° (Table 2). The other valency angles are very close to 108°.

The similarity of the conformations of the independent molecules is expressed in the crystal

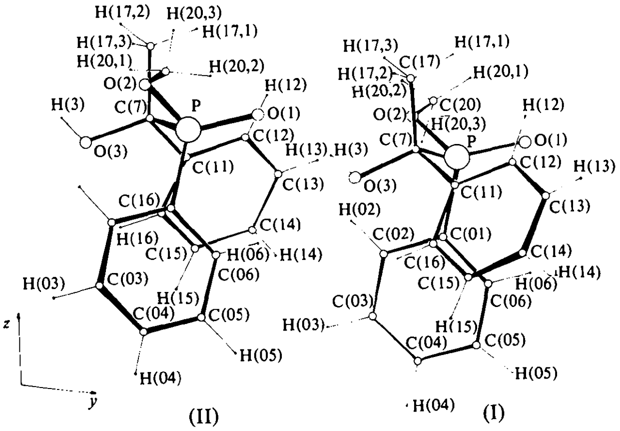


Fig. 2. View of the molecules along [100] showing the atom-numbering system.

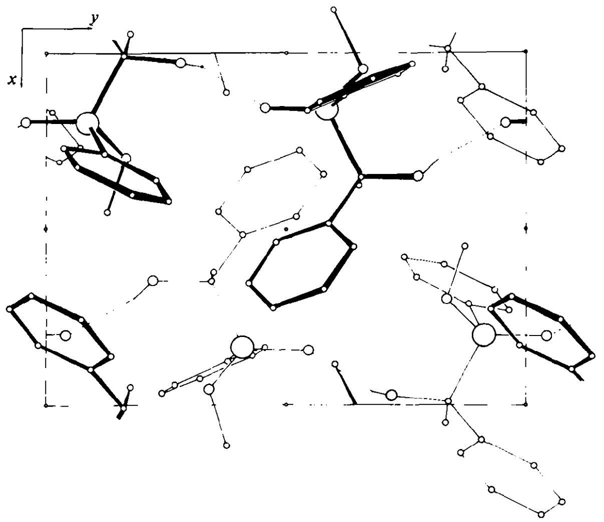


Fig. 3. Packing of molecules in the unit cell and hydrogen bonding.

structure. Namely, careful examination of the coordinates for corresponding atoms in the two molecules reveals the relationship between them: $x_{II} \simeq 1{\cdot}6 - x_I$ [subscripts I and II refer to molecules (I) and (II) as indicated in Table 1], $y_{II} \simeq y_I - 0{\cdot}5$ and $z_{II} \simeq z_I$. These nearly agree with the symmetry relations for the space group $P2_1/b$, with a 2_1 axis in the [100] direction (Fig. 2). Indeed, the observation that the $h00$ reflections with h odd and $0kl$ with k odd are weaker confirms this.

The molecules form chains by means of hydrogen bonding between the phosphoryl O atom (acceptor of H) and the hydroxy group of the other molecule with opposite configuration. The chains are extended in the [010] direction (Fig. 3). O···O distances are 2·698 and 2·702 Å.

The configuration of the molecule appears to be not *erythro* but *threo*. This fact requires the mechanism of Grignard addition to the carbonyl group of α-keto-phosphine oxides to be revised (Bodalski, Waszkuć, Gałdecki & Główka, 1980).

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