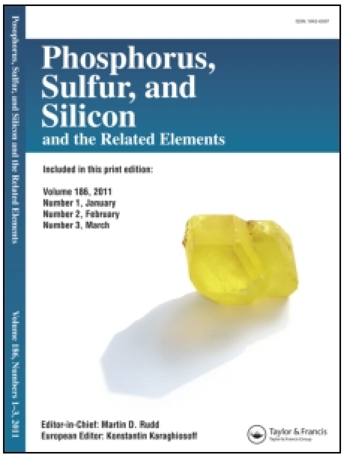

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STEREOCHEMISTRY OF THE PERKOW REACTION. CRYSTAL AND MOLECULAR STRUCTURE OF *O*-[1-(2,4-DICHLOROPHENYL)-2-BROMOVINYL] *O,O*-DIMETHYL PHOSPHATE

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To cite this Article Galdecki, Zdzislaw , Glòwka, Marek L. and Zwierzak, Andrzej(1979) 'STEREOCHEMISTRY OF THE PERKOW REACTION. CRYSTAL AND MOLECULAR STRUCTURE OF *O*-[1-(2,4-DICHLOROPHENYL)-2-BROMOVINYL] *O,O*-DIMETHYL PHOSPHATE', Phosphorus, Sulfur, and Silicon and the Related Elements, 5: 3, 299 — 303

To link to this Article: DOI: 10.1080/03086647908077729
URL: http://dx.doi.org/10.1080/03086647908077729

Phosphorus and Sulfur
1979, Vol. 5, pp. 299–303

STEREOCHEMISTRY OF THE PERKOW REACTION. CRYSTAL AND MOLECULAR STRUCTURE OF *O*-[1-(2,4-DICHLOROPHENYL)-2-BROMOVINYL] *O,O*-DIMETHYL PHOSPHATE

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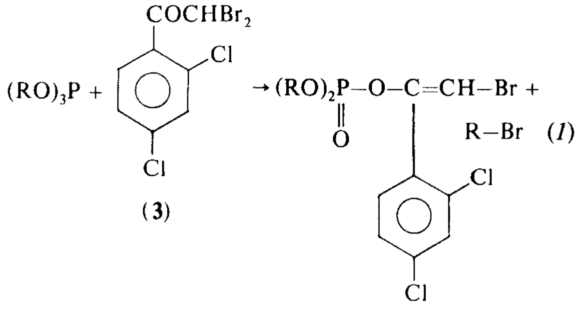
(Received May 29, 1978)

The crystal and molecular structure of the title compound has been determined by x-ray analysis from diffractometer data. Crystals are monoclinic, space group $P2_1/a$ with $a = 12.094(2)$, $b = 15.441(3)$, $c = 7.545(1)$ Å, $\beta = 95.04(1)°$, and $Z = 4$. The structure was solved by the heavy-atom method, and refined by full-matrix least-squares to $R = 0.073$ for 3254 reflections. The examined compound is a highly effective insecticide of relatively low mammalian toxicity. X-ray and nmr studies show the H atom to be in trans position in relation to the phosphoryl group. Although least-squares planes of the benzene ring and the ethylene system are considerably twisted (65°), C(2)–C(5) bond length (1.476Å) indicates the conjugation of both unsaturated systems. The molecules are well separated, there is only one contact Br(1) ··· Cl(1) (3.56 Å) less than the sum of the van der Waals radii (3.75 Å).

INTRODUCTION

In the course of our studies on insecticidally active enolphosphates we have found that *O*-[1-(2,4-dichlorophenyl)-2-bromovinyl] *O,O*-diethyl phosphate (bromfenvinphos) **1** and its *O,O*-dimethyl analogue (proposed common name: methylbromfenvinphos) (**2**) are highly effective insecticides of relatively low mammalian toxicity.[1] Enolphosphates (**1**) and (**2**) can be prepared by the Perkow reaction (*I*) between 2,4-dichlorophenacylidene bromide (**3**) and triethyl or trimethyl phosphite respectively.[2]

The formation of both stereoisomers (Z : E = 95 : 5) was observed for (**1**), the geometry being inferred from the literature statement[3] that the proton *cis* to the phosphoryl group (E-isomer) resonates to low field of the corresponding *trans*-proton (Z-isomer). In the case of compound (**2**) only one single crystalline stereoisomer was obtained to which the Z-configuration has been tentatively ascribed. This assignment was based on the chemical shift of the vinylic proton (6.03 ppm to low field of TMS) close to that of Z-(**1**) (6.10 ppm) and related structures for which the Z-configuration has been claimed.[3] Corroborative evidence was, however, needed, especially because the reliability of nmr assignments was the subject of real controversy in the chemical literature [3–6].



(**1**) (R = Et)
(**2**) (R = Me)

FIGURE 1 Scheme of the Perkow reaction.

Crystalline enolphosphate (**2**) provided a convenient model compound for x-ray analysis which we decided to use for definite stereochemical establishments.

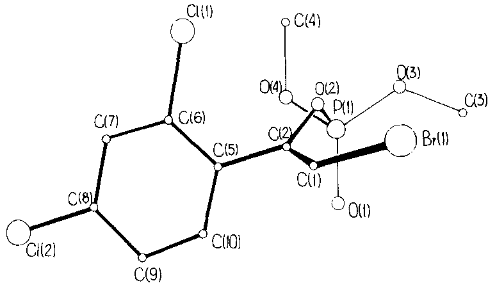


FIGURE 2 Numbering system and projection of the molecule along [001] direction.

RESULTS AND DISCUSSION

Conclusive configurational assignment for the enol-phosphate (**2**) deduced from x-ray analysis strongly confirms the validity of previous statements based on proton nuclear magnetic reasonance chemical shifts and proves the reliability of the relevant spectral-structure correlations. Atom H(1) is in *trans* position to the phosphate substituent. The angle between the plane of the phenyl ring and the ethylene system is 65.24° (Figure 3). Steric hindrance due to *ortho*-substituted chlorine atom appears to be the reason for this nonplanarity. The molecules of the conformationally related unsubstituted *trans*-stilbenes[10] and *trans*-azobenzenes[11] are almost planar. On the other hand, *o*-substituted *trans*-azobenzenes[12] and *trans*-stilbenes,[13] their unsubstituted *cis*-isomers[14] and *p*-substituted isomers[13,15] deviate significantly from planarity. The angle mentioned above is, for example 54.3° in *cis*- and 75.1° in *trans*-1,2-bis (*p*-chlorophenyl)-1,2-dichloroethylene.[15] Both the chlorine atoms deviate from the least-squares benzene plane by 10σ (*o*-Cl) and 6σ (*p*-Cl) respectively.

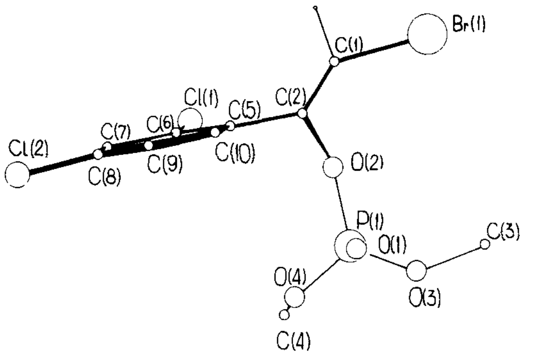


FIGURE 3 A relative position of both the planar (2,4-dichlorophenyl and vinyl) systems in the molecule.

TABLE I

Final atom positional parameters ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Br(1)	3913(1)	4168(1)	10814(1)
Cl(1)	2242(1)	1246(1)	8483(2)
Cl(2)	5489(1)	−930(1)	7005(2)
P(1)	3760(1)	3317(1)	5620(1)
O(1)	4945(3)	3366(2)	5612(5)
O(2)	3345(2)	3067(2)	7511(3)
O(3)	3064(3)	4153(2)	5133(4)
O(4)	3247(3)	2636(2)	4295(4)
C(1)	4315(4)	3023(3)	10327(5)
C(2)	4036(3)	2646(2)	8809(5)
C(3)	3460(4)	4979(3)	5827(7)
C(4)	2063(5)	2524(4)	3899(8)
C(5)	4377(3)	1754(2)	8408(5)
C(6)	3633(3)	1071(2)	8179(5)
C(7)	3950(3)	238(2)	7748(5)
C(8)	5061(3)	101(3)	7584(5)
C(9)	5839(3)	748(3)	7844(6)
C(10)	5487(3)	1576(3)	8250(5)

TABLE III

Fractional co-ordinates ($\times 10^3$) for hydrogen atoms derived from difference Fourier synthesis and C—H distances in Å

Atom	*x*	*y*	*z*	Bonded to	Bond length
H(1)	479	275	1138	C(1)	1.06
H(3,1)	398	480	636	C(3)	0.79
H(3,2)	370	542	511	C(3)	0.92
H(3,3)	281	547	565	C(3)	1.10
H(4,1)	141	298	389	C(4)	1.06
H(4,2)	189	198	502	C(4)	1.20
H(4,3)	188	215	300	C(4)	0.91
H(7)	348	−26	760	C(7)	0.97
H(9)	665	60	784	C(9)	1.01
H(10)	604	201	842	C(10)	0.95

TABLE V

Deviations of the non-hydrogen atoms from the least-squares plantes (in Å). The atoms indicated by an asterisk were omitted from the calculations of the planes

	Deviation from plane I		Deviation from plane II
C(5)	−0.0105	Br(1)	0.0169
C(6)	0.0106	O(2)	−0.0104
C(7)	−0.0008	C(1)	0.0111
C(8)	−0.0088	C(2)	0.0114
C(9)	0.0083	C(5)	−0.0290
C(10)	0.0012	*Cl(2)	0.1706
*C(2)	−0.0420		
*Cl(1)	0.0894		
*Cl(2)	−0.0530		

The equation of the plane is expressed in the form $PX + QY + RZ = S$ (in direct space) where P, Q, R and S equal 0.5989, −3.4040, 7.2886, 5.8040(I) and 10.2574, 5.4936, −3.5124, 2.4881(II).

The average C–C bond length in the phenyl group is 1.384 Å. This value is slightly lower than the "standard" one of 1.394(5) Å, possibly because of the electronegativity of the Cl substituents.[16] The C–C–C bond angles within phenyl ring are visibly differentiated. The ring angle at C(5) is by 2.5° smaller than 120° and the angles at the chlorine-substituted *para* and *ortho* C atoms are by 2.5 and 2.9° greater than 120°. By now similar distortions have been observed in many other substituted phenyl rings.[17]

The distortion of the tetrahedron PO_4 is such that

TABLE IV

Bond lengths (Å) and valency angles (°) for non-hydrogen atoms, with estimated standard deviations in parentheses

(a) Bond lengths			
Br(1)–C(1)	1.878(1)	C(2)–C(5)	1.476(1)
Cl(1)–C(6)	1.739(1)	C(3)–O(3)	1.444(4)
Cl(2)–C(8)	1.741(2)	C(4)–O(4)	1.447(2)
P(1)–O(1)	1.436(1)	C(5)–C(6)	1.387(1)
P(1)–O(2)	1.601(3)	C(6)–C(7)	1.390(4)
P(1)–O(3)	1.567(1)	C(7)–C(8)	1.377(5)
P(1)–O(4)	1.543(4)	C(8)–C(9)	1.374(4)
O(2)–C(2)	1.392(5)	C(9)–C(10)	1.390(5)
C(1)–C(2)	1.302(3)	C(10)–C(5)	1.387(4)
(b) Valency angles			
Br(1)–C(1)–C(2)	122.77(18)	O(2)–P(1)–O(4)	105.89(29)
Cl(1)–C(6)–C(5)	119.35(10)	O(2)–C(2)–C(1)	120.16(32)
Cl(1)–C(6)–C(7)	117.70(26)	O(2)–C(2)–C(5)	116.94(32)
Cl(2)–C(8)–C(7)	118.43(23)	O(3)–P(1)–O(4)	103.39(14)
Cl(2)–C(8)–C(9)	119.07(19)	C(1)–C(2)–C(5)	122.83(6)
P(1)–O(2)–C(2)	121.56(26)	C(2)–C(5)–C(6)	123.03(2)
P(1)–O(3)–C(3)	119.16(11)	C(2)–C(5)–C(10)	119.52(23)
P(1)–O(4)–C(4)	123.37(22)	C(5)–C(6)–C(7)	122.93(26)
O(1)–P(1)–O(2)	114.09(11)	C(6)–C(7)–C(8)	117.05(25)
O(1)–P(1)–O(3)	118.18(8)	C(7)–C(8)–C(9)	122.50(20)
O(1)–P(1)–O(4)	112.17(8)	C(8)–C(9)–C(10)	118.72(16)
O(2)–P(1)–O(3)	101.72(28)	C(9)–C(10)–C(5)	121.31(19)
		C(10)–C(5)–C(6)	117.45(11)

TABLE II

Anisotropic thermal parameters for non-hydrogen atoms (× 10^4). The form of the temperature factors expression is

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^*)]$$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	993(4)	399(2)	489(3)	−15(2)	95(2)	−61(2)
Cl(1)	373(6)	428(6)	1272(12)	−18(5)	133(6)	−27(7)
Cl(2)	754(8)	381(6)	580(7)	145(5)	157(6)	13(5)
P(1)	340(5)	369(5)	392(5)	46(4)	77(4)	61(4)
O(1)	562(21)	841(25)	878(24)	94(18)	238(17)	343(20)
O(2)	369(14)	416(14)	351(14)	68(11)	76(11)	67(11)
O(3)	612(19)	463(17)	617(19)	51(15)	38(15)	107(15)
O(4)	731(22)	590(20)	570(19)	52(18)	83(16)	−57(16)
C(1)	708(29)	331(20)	440(24)	−40(20)	73(21)	50(18)
C(2)	391(21)	329(19)	367(21)	−32(16)	59(17)	58(16)
C(3)	719(33)	344(23)	939(39)	26(23)	202(28)	54(24)
C(4)	609(34)	832(40)	1022(43)	−164(28)	−128(30)	−208(34)
C(5)	344(21)	373(20)	316(19)	−10(16)	40(15)	45(16)
C(6)	355(21)	355(20)	454(23)	7(16)	29(18)	35(17)
C(7)	502(26)	375(22)	395(22)	30(19)	−19(18)	7(17)
C(8)	548(26)	372(21)	311(20)	97(19)	61(17)	41(16)
C(9)	446(24)	441(24)	592(26)	16(20)	159(20)	66(20)
C(10)	431(24)	415(23)	511(24)	−23(18)	44(19)	12(19)

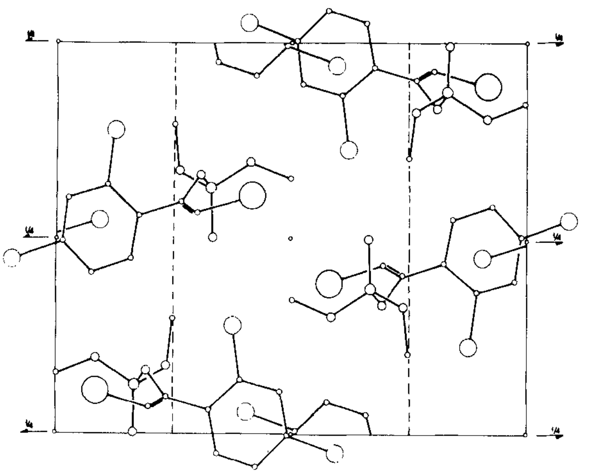


FIGURE 4 Projection of the unit cell contents on the xy plane. Hydrogen atoms are omitted for clarity.

O(1)=P—O angles increase by simultaneous decrease of O—P—O angles to the mean value of 114.8 and 103.7° respectively. The mean length of the simple P—O bond in the tetrahedron PO_4 is 1.57 Å, which is in a good agreement with the values observed in organic phosphates[18] and dioxaphosphorinanes.[19]

The molecular packing in the crystal is illustrated in Figure 4. The molecules are well separated. There is only one contact shorter than the sum of the van der Waals radii. The distance between Br(1) at x, y, z and Cl(1) at $\frac{1}{2} - x, \frac{1}{2} + y, 2 - z$ is 3.557(1) Å, whereas the sum of their van der Waals radii[20] is equal to 3.75 Å. The distance O(4) (x, y, z) ... Cl(2) $(1 - x, -y, 1 - z)$ equal to 3.241(5) is slightly longer than the sum of vdW radii—3.20 Å. The other intermolecular distances are at least by 0.2 Å greater than the sum of their vdW radii.

EXPERIMENTAL

^{1}H nmr spectra were measured with a Tesla BS 487 C spectrometer with tetrachloromethane as solvent and tetramethylsilane as internal standard. Ir spectra were recorded for KBr discs using an UR-10 spectrometer (C. Zeiss, Jena). All solvents were dried and purified according to standard procedures.

2,4-Dichlorophenacylidene bromide **3.**

Bromine (32.0 g, 0.2 mol) was added dropwise with stirring to molten 2,4-dichloroacetophenone (mp 33–34°. 18.9 g, 0.1 mol) at 30–35°. After the addition of bromine had been completed, the reaction mixture was evacuated in order to remove an excess of hydrogen bromide. The product was dissolved in tetrachloromethane (200 ml), the solution washed with 5% sodium bicarbonate and water, dried, and evaporated *in vacuo* to give crude 2,4-dichlorophenacylidene bromide (34.0 g, 98%), which was 94% pure (glc) and contained about 3% of 2,4-dichlorophenacyl bromide and 2,4-dichlorophenacylidine bromide. Distallation *in vacuo*, affording pale-yellow oil, bp 100–103° (0.1 mmHg), $n_D^{20} = 1.6258$, did not improve the purity of the product. Chromatographically pure 2,4-dichlorophenacylidene bromide was obtained by crystallization of the distillate from n-hexane at $-5 \div 0°$. Mp 28.5–29.5°. (Found: C, 27.9; H, 1.3. $C_8H_4Br_2Cl_2O$ requires C, 27.7; H, 1.2%); $\nu_{C=O} = 1719\ cm^{-1}$; δ_H 6.75 (1H, s, $-CHBr_2$), 7.33–7.78 (3H, m, $H_{arom.}$).

O-[1-(2,4-Dichlorophenyl)-2-bromovinyl] O,O-dimethyl phosphate **2.**

Trimethyl phosphite (13.64 g, 0.11 mol) was added dropwise with stirring and occasional cooling to 2,4-dichlorophenacylidene bromide (34.7 g, 0.1 mol) at 40–50°. The mixture was then kept at 80–100° for 1.5 h. Crystalline mass (35.7 g, 95%) was obtained on cooling. It was filtered off, washed with n-hexane (2 × 75 ml), and crystallized from n-hexane–tetrachloromethane (7:3) or from cyclohexane. Mp 67–67.5°. (Found: C, 31.8; H, 2.7; P, 8.1. $C_{10}H_{10}BrCl_2O_4P$ requires C, 31.9; H, 2.7; P, 8.2%); $\nu_{C=C}$ (nujol) 1640 cm^{-1}; $\nu_{P=O}$ 1290 cm^{-1}; ν_{P-O-C} 1030, 1010 cm^{-1}; δ_H 3.65 (6H, d, $^3J_{PH} = 12.0$ Hz, CH_3O), 6.03 (1H, d, $^4J_{PH} = 1.0$ Hz, $=CH$), 7.27–7.55 (3H, m, $H_{arom.}$).

X-Ray Structure Analysis of O-[1-(2,4-Dichlorophenyl)-2-bromovinyl] O,O-dimethyl phosphate **2.**

Crystals of **2** were grown from n-hexane–tetrachloromethane in the form of prisms. Space group and preliminary cell parameters were calculated from oscillation and KFOR-retigraph photographs. Accurate unit-cell dimensions were determined by a least-squares fit of 2θ values, measured for 15 strong reflections on a four-circle diffractometer with Mo Kα radiation.

Crystal data. $C_{10}H_{10}BrCl_2O_4P$, $M = 375.98$. Monoclinic $a = 12.094(2)$, $b = 15.441(3)$, $c = 7.545(1)$ Å, $\beta = 95.04(1)°$, $V = 1403.5$ Å^3. $D_m = 1.76$ (by flotation), $D_x = 1.778\ g \cdot cm^{-3}$, $Z = 4$, $F(000) = 744$. Space group $P2_1/a \cdot$Mo K α radiation, $\lambda = 0.7107$ Å, $\mu \cdot r$(Mo Kα) $= 0.515\ cm^{-1}$.

Three-dimensional intensity data were recorded on a CAD 4 diffractometer, with graphite-monochromatized Mo Kα radiation. Intensities were recorded by the ω–2θ scan technique. Two reference reflections monitored after every 25, showed no significant variation in intensity during data collection. Of the 3254 nonequivalent terms measured to $2\theta_{max} = 56°$, 2132 for which $|F_o| \geqslant 3\sigma(F_o)$ were considered as observed. Intensities were corrected for Lorentz and polarization factors, and for absorption. Scattering factors used in the paper were those given in Ref. 7 for bromine, chlorine, phosphorus, oxygen, and carbon and in Ref. 8 for hydrogen.

The structure was solved by the heavy-atom method. The bromine-atom site was easily derived from a three-dimensional Patterson map. A Fourier synthesis phased on the bromine contributions to the structure factors revealed the sites of the non-hydrogen atoms apart from the two methyl carbons; they were located on a subsequent difference-Fourier map (R = 35%). Least-squares full-matrix refinement of all non-hydrogen atoms with individual isotropic temperature factors yielded R 0.156 after 5 cycles. Further 5 cycles of refinement with anisotropic temperature factors reduced R to 0.054. A difference electron-density synthesis revealed all the hydrogen atom positions. The hydrogen atom parameters (isotropic temperature factors) were refined in two cycles causing considerable increase of agreement factor to the value of 0.073. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(F_o)$.

All calculations were carried out on an IBM-370 computer using the X RAY 70 system.[9]

A listing of structure factors can be obtained from the authors (Z.G. or M.L.G.) upon request.

ACKNOWLEDGEMENT

This research was supported by the project MR.I-9 from the Polish Academy of Sciences.

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