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GROUND STATE CONFORMATION OF (-)-*S*-METHYLPHENYLVINYLPHOSPHINE OXIDE: A CRYSTALLOGRAPHIC AND PCMODEL INQUIRY[1]

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Abstract: A single-crystal X-ray diffraction experiment has been performed on (-)-methylphenylvinylphosphine oxide 1. $C_9H_{11}OP$, monoclinic, space group $P2_1$, a=10.689(2)Å, b=16.431(2)Å, c=11.108(1)Å, β=109.46(1)°, Z=8. The structure was solved by direct methods and refined by full matrix least-squares calculations to R=0.0548 and R =0.0656. The measurement discerned four independent molecules of 1 which were found to be selectively paired in the crystal by intermolecular C-H...O interactions involving phosphoryl oxygens and vinyl a hydrogens. All of the four molecules were found to possess the C=C-P=O fragment in an almost co-planar s-cis arrangement. The experiment confirmed also the validity of the previous assignment of the *S* configuration to (-)-1. MMX-type (PCMODEL) analysis of 1 revealed the presence of two closely lying minima corresponding to two s-cis conformations with torsional angles $\theta_{C=C-P=O}$ equal to -54 and 65°, respectively. The single high energy maximum found corresponds to the respective s-trans conformer with $\theta_{C=C-P=O}$=209° .

Recent stereochemical studies related to various asymmetric addition and cycloaddition reactions involving conjugated olefins bearing strongly activating groups revealed that under thermal conditions the reactive conformations of the conjugated systems reflect the conformational preferences seen in the corresponding ground states and that for majority of the studied systems they are s-cis.[2] In our studies on cycloaddition of nitrones and nitrile oxides to P-chiral and P-prochiral phosphinyl ethenes the resulting stereochemistry was similarly best explained by assuming s-cis conformational array of the C=C-P=O fragments in the cycloaddition transition states.[3] No pertinent ground state data in support of this assumption could however be found in the literature[4] and we decided to initiate a study on some simple phosphinyl ethenes in this regard.[5] In this paper we would like to present an X-ray and MMX-type (PCMODEL Version 2.0)[6] analysis of (-)-methylphenylvinylphosphine oxide, 1, a model P-chiral compound of this class as well as a versatile homochiral reagent.[7]

RESULTS AND DISCUSSION

The crystal used for the X-ray measurement was found to contain four crystallographically independent molecules of 1 which differed in some conformational features as well as in the respective bond lengths and, to a lesser extent, bond angles. The ORTEP view of the molecules showing also the absolute configuration is displayed in Fig. 1. The packing of the molecules in a unit cell is shown in Fig. 2. The pertinent positional parameters, bond lengths and bond angles are listed in Table I, II and III, respectively.

The four found values of the P-O bond length are not far apart and range from 1.480(3) to 1.493(3) Å. Much greater differences among the four molecules are however seen in the corresponding lengths of P-C and C=C bonds for which the greatest discrepancy was revealed in the vinyl-P fragments (Table II). For example, in molecules II and III the values of 1.788(5) and 1.740(5) Å, and 1.331(6) and 1.290(11) Å for P-C2 and C2=C3 bonds, respectively, are recorded.

The phosphorus tetrahedron in all the four molecules is deformed in the usual way showing increased O-P-C angles and decreased C-P-C angles with the corresponding values ranging from 112.1(2) to 115.4(2), and 103.9(3) to 107.8(2), respectively (Table III). Other bond angles represent rather typical values and are closely similar in all the four cases.

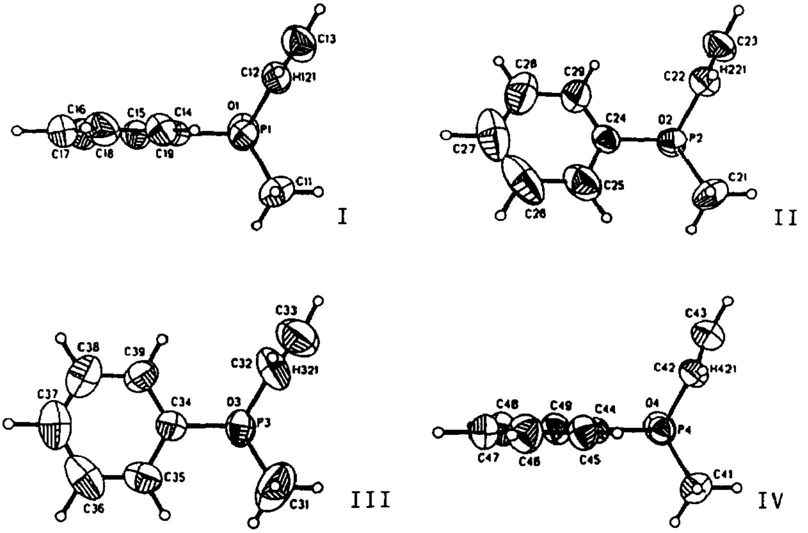

Figure 1. ORTEP view of the four independent molecules of 1 showing 50% probability elipsoids.

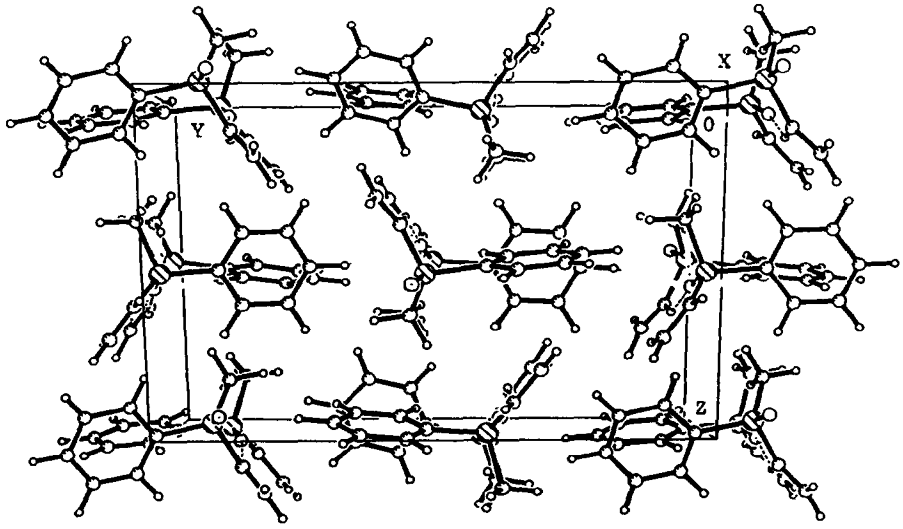

Figure 2. The unit cell packing for 1 showing also intermolecular C-H...O interactions.

Table I. Positional parameters (x 10^4) for the nonhydrogen atoms in 1 with estimated standard deviations in parentheses.

	x	y	z
molecule I			
P(1)	0.1807(1)	-0.0970	0.0093(1)
O(1)	0.3220(3)	-0.1210(2)	0.0463(4)
C(11)	0.0808(6)	-0.1232(3)	-0.1496(4)
C(12)	0.0958(3)	-0.1417(2)	0.1061(4)
C(13)	0.1562(6)	-0.1932(3)	0.1970(5)
C(14)	0.1603(3)	0.0122(2)	0.0225(3)
C(15)	0.2739(4)	0.0605(3)	0.0556(4)
C(16)	0.2635(5)	0.1432(3)	0.0670(5)
C(17)	0.1406(5)	0.1787(3)	0.0469(5)
C(18)	0.0274(5)	0.1308(3)	0.0146(5)
C(19)	0.0376(4)	0.0469(2)	0.0030(4)
molecule II			
P(2)	0.3410(1)	0.4108(1)	0.0313(1)
O(2)	0.2164(2)	0.3910(2)	0.0579(3)
C(21)	0.4910(3)	0.3846(3)	0.1581(4)
C(22)	0.3562(4)	0.3590(2)	-0.1047(4)
C(23)	0.2566(5)	0.3142(3)	-0.1791(5)
C(24)	0.3504(4)	0.5175(2)	-0.0055(3)
C(25)	0.2589(5)	0.5476(3)	-0.1168(5)
C(26)	0.2552(7)	0.6279(4)	-0.1455(7)
C(27)	0.3427(8)	0.6813(4)	-0.0630(8)
C(28)	0.4370(8)	0.6532(4)	0.0442(9)
C(29)	0.4405(6)	0.5698(3)	0.0758(6)
molecule III			
P(3)	0.4155(1)	0.5005(1)	0.4810(1)
O(3)	0.5263(3)	0.5222(2)	0.4347(3)
C(31)	0.4336(9)	0.5409(5)	0.6387(7)
C(32)	0.2623(5)	0.5380(3)	0.3857(7)
C(33)	0.2502(7)	0.5841(5)	0.2885(7)
C(34)	0.3959(3)	0.3921(2)	0.4926(3)
C(35)	0.4710(5)	0.3518(4)	0.6044(4)
C(36)	0.4647(6)	0.2680(4)	0.6087(7)
C(37)	0.3834(6)	0.2243(3)	0.5032(7)
C(38)	0.3131(6)	0.2636(4)	0.3953(7)
C(39)	0.3171(5)	0.3468(3)	0.3882(4)
molecule IV			
P(4)	0.0794(1)	0.0111(1)	0.4790(1)
O(4)	-0.0620(2)	0.0336(2)	0.4489(3)
C(41)	0.1488(4)	0.0392(3)	0.3586(4)
C(42)	0.1885(4)	0.0552(2)	0.6229(4)
C(43)	0.1445(6)	0.0963(3)	0.6998(5)
C(44)	0.1061(3)	-0.0968(2)	0.5023(3)
C(45)	-0.0024(4)	-0.1471(3)	0.4917(5)
C(46)	0.0178(6)	-0.2307(3)	0.5105(6)
C(47)	0.1400(6)	-0.2637(2)	0.5356(5)
C(48)	0.2491(5)	-0.2146(3)	0.5469(5)
C(49)	0.2322(4)	-0.1310(2)	0.5307(4)

Table II. Bond lenghts (Å) in 1 with estimated standard deviations in parentheses

molecule I		molecule II	
P(1) - O(1)	1.480(3)	P(2) - O(2)	1.493(3)
P(1) - C(11)	1.785(4)	P(2) - C(21)	1.799(3)
P(1) - C(12)	1.780(5)	P(2) - C(22)	1.788(5)
P(1) - C(14)	1.819(3)	P(2) - C(24)	1.811(4)
C(12)- C(13)	1.311(6)	C(22)- C(23)	1.331(6)
C(14)- C(15	1.394(5)	C(24)- C(25)	1.387(5)
C(14)- C(19)	1.379(5)	C(24)- C(29)	1.379(6)
C(15)- C(16)	1.373(7)	C(25)- C(26)	1.355(8)
C(16)- C(17)	1.386(7)	C(26)- C(27)	1.383(9)
C(17)- C(18)	1.387(7)	C(27)- C(28)	1.359(10)
C(18)- C(19)	1.392(6)	C(28)- C(29)	1.412(8)
molecule III		molecule IV	
P(3) - O(3)	1.483(4)	P(4) - O(4)	1.482(2)
P(3) - C(31)	1.822(8)	P(4) - C(41)	1.792(5)
P(3) - C(32)	1.740(5)	P(4) - C(42)	1.788(4)
P(3) - C(34)	1.803(4)	P(4) - C(44)	1.801(4)
C(32)- C(33)	1.290(11)	C(42)- C(43)	1.294(8)
C(34)- C(35)	1.400(5)	C(44)- C(45)	1.397(6)
C(34)- C(39)	1.399(5)	C(44)- C(49)	1.396(5)
C(35)- C(36)	1.380(9)	C(45)- C(46)	1.395(7)
C(36)- C(37)	1.402(9)	C(46)- C(47)	1.355(9)
C(37)- C(38)	1.348(9)	C(47)- C(48)	1.389(8)
C(38)- C(39)	1.371(8)	C(48)- C(49)	1.389(6)

The molecules I-IV differ considerably in the relative spatial arrangement of the phosphoryl and phenyl groups. As indicated by the O-P-C4-C5 torsional angles of 4.4 and -0.5° in molecules I and IV, respectively, these two groups assume a nearly co-planar arrangement seen already in some other molecules of similar structure.[5] Interestingly however, this seemingly satisfying conformational arrangement is no longer present in molecules II and III for which the O-P-C4-C5 angles are found to be 65.9 and 86.1°, respectively.

Table III. Bond angles (°) in 1 with estimated standard deviations in parentheses

molecule I				molecule II			
O(1)	- P(1)	- C(11)	115.4(2)	O(2)	- P(2)	- C(21)	114.5(2)
O(1)	- P(1)	- C(12)	113.6(2)	O(2)	- P(2)	- C(22)	113.7(2)
O(1)	- P(1)	- C(14)	112.3(2)	O(2)	- P(2)	- C(24)	112.1(2)
C(11)	- P(1)	- C(12)	103.9(2)	C(21)	- P(2)	- C(22)	103.9(2)
C(11)	- P(1)	- C(14)	105.6(2)	C(21)	- P(2)	- C(24)	107.8(2)
C(12)	- P(1)	- C(14)	105.0(2)	C(22)	- P(2)	- C(24)	104.0(2)
P(1)	- C(12)	- C(13)	120.8(4)	P(2)	- C(22)	- C(23)	120.6(4)
P(1)	- C(14)	- C(15)	117.8(3)	P(2)	- C(24)	- C(25)	118.1(3)
P(1)	- C(14)	- C(19)	121.9(3)	P(2)	- C(24)	- C(29)	122.3(3)
C(15)	- C(14)	- C(19)	120.3(3)	C(25)	- C(24)	- C(29)	119.5(4)
C(14)	- C(15)	- C(16)	120.9(4)	C(24)	- C(25)	- C(26)	120.9(5)
C(15)	- C(16)	- C(17)	120.2(5)	C(25)	- C(26)	- C(27)	120.1(6)
C(16)	- C(17)	- C(18)	120.1(5)	C(26)	- C(27)	- C(28)	120.3(6)
C(17)	- C(18)	- C(19)	119.8(5)	C(27)	- C(28)	- C(29)	119.9(8)
C(14)	- C(19)	- C(18)	119.6(4)	C(24)	- C(29)	- C(28)	119.1(6)
molecule III				molecule IV			
O(3)	- P(3)	- C(31)	113.8(3)	O(4)	- P(4)	- C(41)	114.3(2)
O(3)	- P(3)	- C(32)	113.7(2)	O(4)	- P(4)	- C(42)	114.4(2)
O(3)	- P(3)	- C(34)	112.8(2)	O(4)	- P(4)	- C(44)	112.3(2)
C(31)	- P(3)	- C(32)	103.5(3)	C(41)	- P(4)	- C(42)	104.7(2)
C(31)	- P(3)	- C(34)	105.6(3)	C(41)	- P(4)	- C(44)	106.0(2)
C(32)	- P(3)	- C(34)	106.6(2)	C(42)	- P(4)	- C(44)	104.2(2)
P(3)	- C(32)	- C(33)	121.9(5)	P(4)	- C(42)	- C(43)	122.0(4)
P(3)	- C(34)	- C(35)	119.0(3)	P(4)	- C(44)	- C(45)	118.9(3)
P(3)	- C(34)	- C(39)	121.2(3)	P(4)	- C(44)	- C(49)	121.6(3)
C(35)	- C(34)	- C(39)	119.5(4)	C(45)	- C(44)	- C(49)	119.5(3)
C(34)	- C(35)	- C(36)	118.8(4)	C(44)	- C(45)	- C(46)	119.1(4)
C(35)	- C(36)	- C(37)	120.4(6)	C(45)	- C(46)	- C(47)	121.0(5)
C(36)	- C(37)	- C(38)	120.3(5)	C(46)	- C(47)	- C(48)	120.6(5)
C(37)	- C(38)	- C(39)	120.7(6)	C(47)	- C(48)	- C(49)	119.6(5)
C(34)	- C(39)	- C(38)	120.3(4)	C(44)	- C(49)	- C(48)	120.1(4)

Contrasting with the apparently low rotational preference of the phenyl ring, the similar rotation in the vinyl C=C-P=O fragment seems to be much more biased and fixed at an almost co-planar s-cis alignment observed in all the four independent molecules of **1**. The found values of O-P-C2-C3 torsional angle are -2.6(5), 6.3(5), -3.7(7) and 6.7(5) for I, II, III and IV, respectively.

The conformational preference for the s-cis arrangement of C=C-P=O in **1** has also been indicated by PCMODEL calculations which revealed two closely lying minima corresponding to the two s-cis conformations **A** and **B** , being however in both cases considerably more distorted from planarity than those found in the crystal.

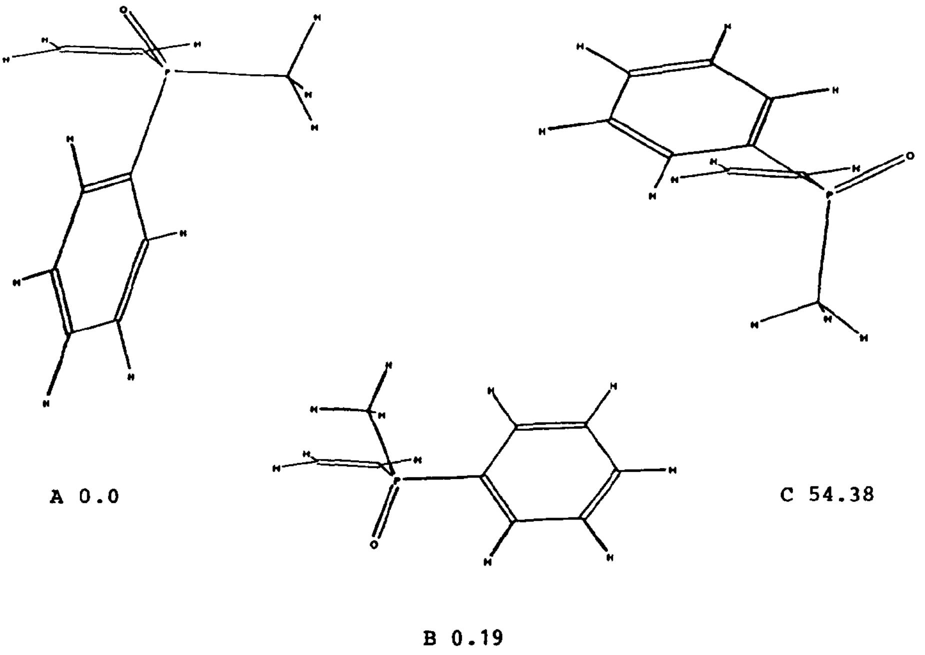

Figure 3. PCMODEL conformations of 1 with relative energies (kcal/mol)

The corresponding O-P-C2-C3 torsional angles for the two minima are -54 and 65°, respectively. The single high-energy maximum was found for the s-trans conformation C characterized by the O-P-C2-C3 torsional angle of 209°. The three conformations together with their relative energies are displayed in Fig. 3.

An additional interesting feature of the crystal structure of 1 is the occurrence of intermolecular C-H...O interactions.[8] These were found to involve vinyl α hydrogens and phosphoryl oxygens and to result in selective pairing of the molecules in the crystal. As indicated by the short contacts detailed in Table IV molecules I are associated in this way only with molecules II while molecules III are analogously associated only with molecules IV. Similar intermolecular C-H...O short contacts involving vinyl α hydrogens and phosphoryl oxygens have been recorded recently for one of the P-epimeric menthyl phenylvinylphosphinylacetates,[5,9] however, in that particular case one hydrogen interacted simultaneously with the two oxygens of the P(O)-CH_2-C(O) unit acting as a bidentate acceptor.

Table IV. Details of short contacts in 1 involving molecules I and II and molecules III and IV.

	Distance (Å)			Angle (°)
D-H...A	D-H	D...A	H...A	D-H...A
C12-H121...O2^{a}	1.06	3.270(4)	2.33	147.0(4)
C22-H221...O1^{b}	1.06	3.298(5)	2.36	146.7(4)
C32-H321...O4^{c}	1.06	3.254(8)	2.34	142.9(6)
C42-H421...O3^{d}	1.06	3.361(6)	2.43	146.4(4)

Symmetry code: ^{a} -x, y-0.5, -z; ^{b} -x+1, y+0.5, -z; ^{c} -x, y+0.5, -z+1; ^{d} -x+1, y-0.5, -z+1

It is also important to note that the presented crystallographic experiment confirms unambiguously the *S* configuration of (-)-1 assigned previously via chemical correlation.[10]

EXPERIMENTAL

(-)-Methylphenylvinylphosphine oxide (1) was prepared as described previously.[10] Its ^1H and ^{13}C NMR spectra obtained with 300 MHz Bruker MSL-300 instrument are listed below to complement the data of the original report. ^1H NMR ($CDCl_3$) δ 1.79 (d, $^2J_{PH}$ =13.2 Hz, 3H), 6.17 (ddd, $^3J_{PH}$=12.3, 1.9 Hz, $^3J_{PH}$=40.6 Hz, 1H), 6.21 (ddd, J_{HH}=18.6, 1.9 Hz, $^3J_{HH}$=22 Hz, 1H), 6.44 (ddd, J_{HH}=18.6, 12.3 Hz, $^2J_{PH}$=25.1 Hz, 1H), 7.45-7.56 (m, 3H), 7.69-7.76 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 17.04 ($^1J_{PC}$=74.4 Hz, 129.34 ($^3J_{PC}$=11.7 Hz), 130.78 ($^2J_{PC}$=9.4 Hz), 132.41, 133.36 ($^1J_{PC}$ =95.3 Hz), 133.46, 134.06 ($^1J_{PC}$=104 Hz).

A crystal of 1 suitable for the X-ray measurement was obtained by slow crystallization from hexane and was handled with complete exclusion of the air moisture. $C_9H_{11}OP$, M=166.16. Monoclinic, space group $P2_1$, a=10.689(2) Å, b=16.431(2) Å, c=11.108(1) Å, β=109.46(1)°, Vc=1839.5(5)$Å^3$, Z=8, Dx=1.200(3) Mgm^{-3}, Dm=1.19(2) Mgm^{-3}, μ(CuKα)=2.19 cm^{-1}, F(000)=704. The measurement was made at room temperature using Enraf Nonius CAD-4 diffractometer operating in the ω-2θ scan mode using graphite monochromated Cu-Kα radiation. The intensity data of 3877 independent reflections were collected within the θ range of 1-75°

and 3784 of them with $I > 2\sigma(I)$ were used for the structure and absolute configuration determination. Accurate cell parameters and the orientation matrix were determined from the least-squares of the angular settings of 25 high-order reflections. The intensities were corrected for Lorentz, polarization, extinction and absorption effects. The structure was solved by direct methods, using the SHELX S-86 program[11] and refined by full-matrix least-squares method, using the SHELX-76 program.[12] Hydrogen atoms were placed in geometrically calculated positions and were refined in the riding mode. The function $\Sigma w(F_o-F_c)^2$ was minimized and in the final cycles of calculation a weighting scheme was used; $w=[\sigma^2(F_o)+0.006(F_o)^2]^{-1}$. An empirical isotropic extinction correction was introduced, and the parameter κ was refined to the value of 0.004(1). Refinement was terminated when the maximum shift in any parameter was $<0.1\sigma$. The values of $R=0.0548$ and $R_w=0.0656$ were obtained using expressions $R=\Sigma([F_o]-[F_c])/\Sigma F_o$ and $R_w=\Sigma 1/2([F_o]-[F_c])/\Sigma_w 1/2[F_o]$. The final difference Fourier map did not show any peaks higher than 0.3 $eÅ^{-3}$. The absolute configuration was determined by Hamilton's method.[13] The model of the structure was refined as described above with the reversed signs of all the f'' values. The resulting R^- and R_w values of 0.0554 and 0.0659, respectively, showed that the model with inverse configuration had to be rejected with very high probability. The $R(\text{ratio})= R^-(R_w)/R(R_w)=1.011(1.005)$ for $N=3337$. According to the Pearson and Hartley[14] tables of R(ratio) values as the function of the significance level α and the number of independent parameters N, for a one-dimensional hypothesis the significance level was $\alpha < 10^{-6}$. All calculations were performed on AMSTRAD 1512 minicomputer.

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REFERENCES AND NOTES

1. Part 12 in a series on Optically Active Phosphine Oxides. For Part 11 see ref. 3b.
2. A.R.Chamberlin and S.H.Reich, *J.Am.Chem.Soc.*, 1985, 107, 1440. R.J.Loncharich, T.R.Schwartz and K.N.Houk, *J.Am.Chem.Soc.*, 1987,

109, 14. G.Montaudo, V.Librando, S.Caccanese and P.Maravigna, *J.Am.Chem.Soc.*, 1973, 95, 6365. W.Oppolzer, G.Poli, C.Starkemann and G.Bernardinelli, *Tetrahedron Lett.*, 1988, 29, 3559. T.Koizumi, Y.Arai, H.Takayama, K.Kuriyama and M.Shiro, *Tetrahedron Lett.*, 1987, 28, 3689. S.D.Kahn and W.J.Hehre, *Tetrahedron Lett.*, 1986, 27, 6041. S.G.Pyne, R.Griffith and M.Edwards, *Tetrahedron Lett.*, 1988, 29, 2089. D.P.Curran, B.H.Kim, H.P.Piyasena, R.J.Loncharich and K.N.Houk, *J.Org.Chem.*, 1987, 52, 2137.

3. a) A.Brandi, P.Cannavo', K.M.Pietrusiewicz, M.Zabłocka and M.Wieczorek, *J.Org.Chem.*, 1989, 54, 3073. b) A.Brandi, S.Cicchi, A.Goti, K.M.Pietrusiewicz, M.Zabłocka and W.Wiśniewski, *J.Org.Chem.*, in press.
4. Instead, an assumption favoring s-trans conformation of the unsaturated phosphinyl system in the Diels-Alder cycloaddition transition state is on record: R.Bodalski, J.Koszuk, H.Krawczyk and K.M.Pietrusiewicz, *J.Org.Chem.*, 1982, 47, 2219.
5. K.M.Pietrusiewicz, M.Zabłocka, M.Kuźnikowski, W.Wieczorek, W.Maniukiewicz and M.Rospenk, *Heteroatom Chem.*, 1991, 2, 111.
6. MMX-calculations were carried out using the PCMODEL (Version 2.0) program of K.E.Gilbert and J.J.Gajewski available from Serena Software, Bloomington, Indiana, USA.
7. K.M.Pietrusiewicz, M.Zabłocka and W.Wiśniewski, *Phosphorus, Sulfur and Silicon*, 1990, 49/50b, 263.
8. R.Taylor and O.Kennard, *J.Am.Chem.Soc.*, 1982, 104, 5063.
9. In these molecules intermolecular C-H...O interactions of α-methylene and aromatic (para) hydrogens with phosphoryl oxygens were also revealed.
10. K.M.Pietrusiewicz, M.Zabłocka and J.Monkiewicz, *J.Org.Chem.*, 1984, 49,1522.
11. SHELX S-86: G.M.Sheldrick, C.Krüger and R.Goddard, "Crystallographic Computing 3", Oxford University Press, 1985, pp. 175/189.
12. G.M.Sheldrick, "SHELX-76. Program for Structure Determination", University of Cambridge, England 1876.
13. W.C.Hamilton, *Acta Cryst.*, 1965, 18, 502.
14. E.S.Pearson and H.O.Hartley, "Biometrica Tables for Statisticians", 3rd ed., Cambridge University Press, 1966, vol. 1, Table 18.