Crystal and Molecular Structure of o-Hydroxyphenyl-o-phenylene Phosphate, $(o\text{-HOC}_6\text{H}_4)(\text{C}_6\text{H}_4)\text{PO}_4$. Equilibrium between Pentavalent and Tetravalent Phosphorus in Solutions[1]

Raghupathy Sarma,[2a] Fausto Ramirez,*[2b] Brian McKeever,[2a] Mark Nowakowski,[2b] and James F. Marecek[2b]

Contribution from the Biochemistry and Chemistry Departments, State University of New York at Stony Brook, Stony Brook, New York 11794. Received February 21, 1978

Abstract: The structure of o-hydroxyphenyl-o-phenylene phosphate, $(o\text{-HOC}_6\text{H}_4)(\text{C}_6\text{H}_4)\text{PO}_4$, has been determined by x-ray crystallographic techniques. The compound crystallizes from acetonitrile in space group *Pbca* of the orthorhombic system, with eight molecules in a unit cell of dimensions $a = 7.191$ (3), $b = 14.040$ (2), $c = 23.384$ (9) Å (one molecule per asymmetric unit); $d_{calcd} = 1.480$, $d_{obsd} = 1.475$ g cm^{-3}. Intensity data were collected on a computer-controlled CAD 4 automatic diffractometer; 2400 independent reflections were collected up to a maximum θ of 65° using θ scan, with a scan width of 1.0°. The structure was solved by direct methods (MULTAN program), and refined by full-matrix least-squares techniques to a final R value of 7.0% on F based on 1662 independent reflections with $F \geqslant 2\sigma(F)$. The phosphorus atom is four-coordinate with three 1.59 Å (ester) and one 1.45 Å (phosphoryl) P–O bond distances. The P atom is 3.04 Å from the phenolic oxygen, while the expected P–O distance for five coordination as in hydroxybis-o-phenylenedioxyphosphorane is 1.67 Å. In solutions, the compound exists as a mixture of phosphate and hydroxyphosphorane in dynamic equilibrium according to variable temperature ^{31}P NMR spectrometry. It is suggested that strong *intermolecular* hydrogen bonding, $-\text{O}-\text{H}\cdots\text{O}=\text{P}<$ (2.68 Å O$\cdots$O distance), is mainly responsible for preventing the transformation of the phosphate into the phosphorane in the crystal; the corresponding intramolecular O$\cdots$O distance is 4.41 Å.

A previous publication[3] described the synthesis of trimethylsilyloxybis-o-phenylenedioxyphosphorane (1). The reaction of this spirodicatecholphosphorane with anhydrous hydrogen chloride produced a crystalline substance with the molecular formula of hydroxybis-o-phenylenedioxyphosphorane (2) or o-hydroxyphenyl-o-phenylene phosphate (3), as shown in Scheme I.[4]

The substance, 2 or 3, had sufficient solubility in acetone-d_6 for ^{31}P NMR measurements, and spectra were recorded in the temperature range -48 to 60 °C at 1.0 M concentration.[4] At the lower temperatures distinct signals were observed at -27[5] and $+7$ ppm, and were attributed to the phosphorane and the phosphate, 2 and 3, respectively. Both signals broadened at the higher temperatures and coalesced at about 55 ± 5 °C. A wider temperature range for the NMR measurements was provided by acetonitrile-d_3, and in this solvent spectra were recorded in the range -48 to -23 °C, at 0.25 M concentration, and in the range -23 to 75 °C, at 0.5 M concentration; now the signals coalesced at about 10 ± 5 °C, and there was an opportunity to observe the reappearance of one signal at about $+3$ ppm at higher temperatures.

These spectral data disclose the existence of a mixture of the phosphorane and the phosphate structures in dynamic equilibrium, $2 \rightleftharpoons 3$, in solutions of the crystalline substance. In the two solvents investigated, the phosphorane 2 predominates over the phosphate 3. However, the equilibrium is displaced toward the phosphate as the polarity and the basicity of the solvent are increased: phosphorane:phosphate as 3:1 vs. 1.5:1 in 1.0 M acetone-d_6 (ϵ 21) vs. 0.25 M acetonitrile-d_3 (ϵ 38), both at -48

°C. These solvent effects suggest that the hydroxyl group bonded to pentavalent phosphorus is a relatively weak acid,[6] even weaker than the phenolic hydroxyl group, which has $pK_a \sim 8.5$ (in water). The contrast with the acidity of the hydroxyl group bonded to tetravalent phosphorus is notable, since the phosphodiesters, $(\text{RO})_2\text{P(O)OH}$, have $pK_a \sim 1.2$ (in water).[7]

Stable, isolable oxyphosphoranes have been known for several years.[8] The postulation of transient but relatively long-lived oxyphosphorane intermediates has clarified fundamental questions concerning displacement reactions at four-coordinate phosphorus in general, and biological phosphoryl transfers in particular.[9–11] The direct observation of the hydroxyphosphorane 2 in equilibrium with the phosphate 3 provides support for the earlier[12] and the more recent[13–17] mechanistic interpretations based on transient oxyphosphorane intermediates. It seemed, therefore, desirable to elucidate the molecular structure of the crystalline substance obtained by the acid-promoted desilylation of the stable oxyphosphorane 1. This paper describes the result of such a study by x-ray crystallographic methods.

Experimental Section

The sample of o-hydroxyphenyl-o-phenylene phosphate (3) used for the x-ray analysis was obtained by the procedure described.[4] A solution containing 0.043 g of compound 3 in 0.30 mL of warm, anhydrous acetonitrile (under Ar) was kept for several hours at 20 °C. The resulting crystals were decanted, washed with 0.1 mL of acetonitrile, and stored at -30 °C under Ar until data collection.

Crystal Data. Compound 3: $\text{C}_{12}\text{H}_9\text{O}_5\text{P}$; orthorhombic, *Pbca*; $a = 7.191$ (3), $b = 14.040$ (2), $c = 23.384$ (9) Å; $V = 2360.96$ Å^3 (as determined on the diffractometer); $Z = 8$ (one molecule per asymmetric unit); $d_{calcd} = 1.480$, $d_{obsd} = 1.475$ g cm^{-3}, by flotation in carbon tetrachloride–hexane at 20 °C.

Data Collection and Structure Determination. The diffraction data were collected using a computer-controlled CAD4 automatic diffractometer with Ni-filtered Cu Kα radiation (1.5418 Å). The crystals were sensitive to atmospheric moisture and to prevent decomposition during data collection they were sealed in capillary tubes. Approximately 2400 independent reflections up to a maximum θ of 65° were measured using a single crystal. A θ scan was used with a scan width
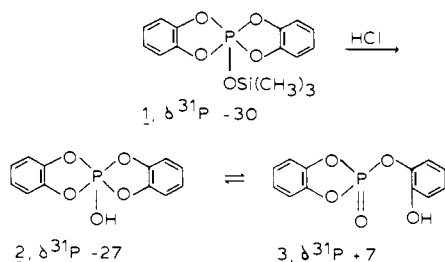
Scheme I

Table I. Bond Distances (Å) and Angles (deg) and Their Standard Deviations[a] for Compound **3**

Bond Distances

P–O(2)	1.566 (3)	O(1)–C(11)	1.355 (5)
P–O(3)	1.448 (3)	O(1)–H(1)	1.042 (34)
P–O(4)	1.600 (3)	O(2)–C(21)	1.424 (4)
P–O(5)	1.601 (3)	O(4)–C(41)	1.406 (4)
		O(5)–C(51)	1.409 (4)
C(11)–C(21)	1.363 (5)	C(41)–C(51)	1.375 (5)
C(11)–C(12)	1.396 (6)	C(41)–C(42)	1.375 (5)
C(12)–C(13)	1.382 (6)	C(42)–C(43)	1.387 (6)
C(12)–H(12)	0.964 (29)	C(42)–H(42)	1.034 (30)
C(13)–C(23)	1.370 (7)	C(43)–C(53)	1.376 (6)
C(13)–H(13)	1.083 (31)	C(43)–H(43)	1.071 (32)
C(21)–C(22)	1.381 (6)	C(51)–C(52)	1.369 (5)
C(22)–C(23)	1.373 (6)	C(52)–C(53)	1.401 (6)
C(22)–H(22)	0.952 (25)	C(52)–H(52)	0.899 (26)
C(23)–H(23)	0.945 (32)	C(53)–H(53)	0.953 (23)

Bond Angles

O(2)–P–O(3)	115.78 (0.12)	C(11)–O(1)–H(1)	110.06 (0.99)
O(2)–P–O(4)	107.85 (0.12)	P–O(2)–C(21)	121.92 (0.18)
O(2)–P–O(5)	101.69 (0.12)	P–O(4)–C(41)	109.00 (0.17)
O(3)–P–O(4)	115.23 (0.12)	P–O(5)–C(51)	108.90 (0.16)
O(3)–P–O(5)	115.74 (0.12)		
O(4)–P–O(5)	98.41 (0.12)		

[a] The standard deviations in bond distances refer to the least significant digits, and the standard deviations in bond angles are in degrees.

Table II. Significant Nonbonded Distances <4.0 Å in Compound **3**

Intramolecular

P···O(1)	3.043 (4)

Intermolecular[a]

P(I)···O(1)(VIII)	3.907 (5)	O(1)(I)···H(13)(IV)	2.884 (34)
O(1)(I)···O(3)(VIII)	2.684[b] (4)	O(1)(I)···H(23)(IV)	3.728 (32)
O(1)(I)···O(1)(VIII)	3.818 (5)	O(1)(I)···H(13)(V)	3.507 (34)
		O(1)(I)···H(1)(VIII)	3.272 (34)
		O(3)(I)···H(12)(VIII)	2.782 (32)

[a] Roman numerals in parentheses refer to the molecules in the unit cells depicted in Figure 2. The following distances are also of interest: P(I)···O(3)(IV) = 6.482 (7) Å; P(IV)···O(3)(I) = 7.707 (7) Å. [b] Intermolecular hydrogen bond.

Table III. Least-Squares Planes and Deviation of Certain Atoms (Å) (Standard Deviations × 10³)

1. P–O(1)–O(4)
   $-0.7278x + 0.0945y + 0.6793z = 0.2963$
   O(5), -0.585 (2)
2. P–O(4)–O(5)
   $0.8897x + (-0.2537)y + (-0.3795)z = 0.8033$
   O(1), 1.088 (3)
3. O(2)–O(3)–O(4)
   $0.4536x + (-0.1654)y + (0.8757)z = 3.9713$
   P, -0.414 (1)
4. O(1)–O(2)–C(11)–C(12)–C(13)–C(21)–C(22)–C(23)
   $0.9445x + 0.0636y + (-0.3222)z = 2.6833$
   deviation of fitted atoms from plane, 0.022 (4)
   P, -1.151 (1)
5. O(4)–O(5)–C(41)–C(42)–C(43)–C(51)–C(52)–C(53)
   $0.8910x + (-0.2398)y + (-0.3854)z = 0.8260$
   deviation of fitted atoms from plane, 0.004 (4)
   P, -0.019 (1)
6. P–O(4)–O(5)–C(41)–C(42)–C(43)–C(51)–C(52)–C(53)
   $0.8910x + (-0.2417)y + (-0.3844)z = 0.8189$
   deviation of fitted atoms from plane, 0.006 (4)

of 1.0° and a scan speed of 1.5°/min; 96 separate measurements were made in each scan. The first and the last 16 measurements were used to determine the background and the remaining measurements were used to determine the integrated intensity of each reflection. The intensities were corrected with the standard Lorentz polarization factor. Since the crystal was sealed inside a capillary tube, an empirical absorption correction was applied; this correction was determined by performing an azimuth scan for a reflection occurring at a χ value of

approximately 90°. The variation in intensity of such a reflection for the different azimuth angles is dependent on the thickness of the crystal traversed by the incident and reflected beams and this variation is used to calculate the transmission factor for the crystal for all the other reflections. The transmission factor varied from a value of 1.00 to approximately 1.80 for the crystal used in current data collection. Of the total number collected, 1662 reflections with $|F| \geq 2\sigma$ (σ measured from counting statistics) were used in the final structure determination; 311 reflections with $E > 1.2$ were used to solve for the phase angles using MULTAN.[18] The phase set with the highest combined figure of merit was used in calculating a Fourier which showed 15 of the 18 nonhydrogen atoms. The remaining three atoms were located using a 15-atom partial-structure-phased Fourier. The positional and thermal parameters of all the atoms were refined by full-matrix least-squares refinement procedure using a program provided by Dr. L. W. Finger (NBS Technical Note No. 854) on the UNIVAC-1110. The function minimized was $\Sigma w(\Delta F)^2$ with weights derived from $\sigma(I)$ through $w = 1/\sigma^2(F)$. All the hydrogen atoms were located from a subsequent difference Fourier. The 18 nonhydrogen atoms were given anisotropic thermal parameters while fixed isotropic thermal parameters were used for all the hydrogen atoms in the final cycles of the least-squares refinement. The final reliability index for 1662 reflections $(\Sigma||F_o| - F_c||/\Sigma|F_o|)$ was 7.0%. The final coordinates are given in Table VI and the anisotropic temperature factors in Table VII. The observed and calculated structure factors are listed in Table VIII; see paragraph at end of paper regarding supplementary material.

Discussion of Results

The main bond distances and angles are listed in Table I. Some significant distances between nonbonded atoms are presented in Table II. Equations of least-squares planes and

Table IV. Dihedral Angles for Least-Squares Planes[a] (deg)

plane 1–plane 2	21.67	plane 3–plane 4	82.20
plane 1–plane 3	75.57	plane 3–plane 5	83.90
plane 1–plane 4	25.81	plane 3–plane 6	83.83
plane 1–plane 5	21.10	plane 4–plane 5	18.09
plane 1–plane 6	21.19	plane 4–plane 6	18.19
plane 2–plane 3	83.50	plane 5–plane 6	0.12
plane 2–plane 4	18.82		
plane 2–plane 5	0.87		
plane 2–plane 6	0.75		

[a] The planes are defined in Table III. The dihedral angles, θ, are expressed as $\leqslant 90°$.

Table V. Torsion Angles (deg) and Their Standard Deviations

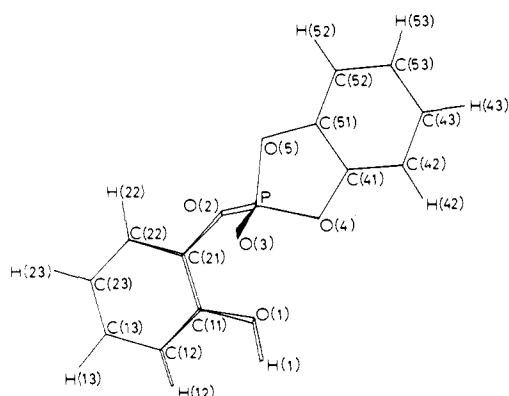| C(21)–O(2)–P–O(3)	−17.04 (0.29)	C(21)–O(2)–P–O(5)	−143.33 (0.25)
C(21)–O(2)–P–O(4)	113.67 (0.25)	C(11)–C(21)–O(2)–P	−67.44 (0.40)

Figure 1. Computer-generated drawing of a molecule of *o*-hydroxy-phenyl-*o*-phenylene phosphate.

deviations of certain atoms from these planes are given in Table III. The dihedral angles formed by pairs of these planes are shown in Table IV. Several torsion angles are listed in Table V. A drawing of the molecule is reproduced in Figure 1, and the packing of the molecules is illustrated in Figure 2.

The P–O bond distances are significantly shorter than the 1.76 Å expected for a pure P–O single bond,[19] as would result from p–d π bonding[20] of lone electron pairs on oxygen and phosphorus d orbitals. In line with this hypothesis, the ester O–C bond distances are longer than the phenolic O(1)–C(11) distance; i.e., the ester-oxygen lone pairs appear to be less available than the phenolic-oxygen lone pairs for interactions with the aromatic rings.

The endocyclic ∠O–P–O bond angle is quite small and comparable to that found by Kaiser, Lee, and Boer[21] in *o*-phenylene phosphate, and by others in analogous cyclic phosphates.[22–25]

The intramolecular nonbonded distance P···O(1) = 3.043 Å clearly shows that there is no covalent bonding between the phosphorus atom and the phenolic oxygen atom in compound **3** in the crystalline state. For reasons given below, a covalent bond between these two atoms would be reflected in a value of approximately 1.67 Å for their interatomic distance.

In principle, the phenolic hydroxyl group in compound **3** could have approached the phosphoryl group, PO(3), of the same molecule with the appropriate orientation to give rise to a relatively strong *intramolecular* hydrogen bond. In fact, the observed 4.410 Å separation between atoms O(1) and O(3) of the same molecule shows the absence of such a bonding in crystalline **3**. Instead, pairs of molecules stack themselves in such a way that the phosphoryl oxygen of one molecule approaches the phosphorus atom of a second molecule. The phenolic hydroxyl groups of a second pair of molecules engage
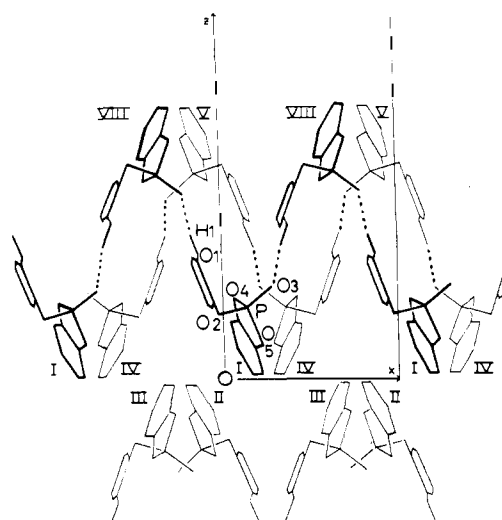

Figure 2. Environment around a molecule, viewed down the *y* axis. Hydrogen bonding denoted by dotted lines. (Equivalent molecules are assigned identical numbers.)
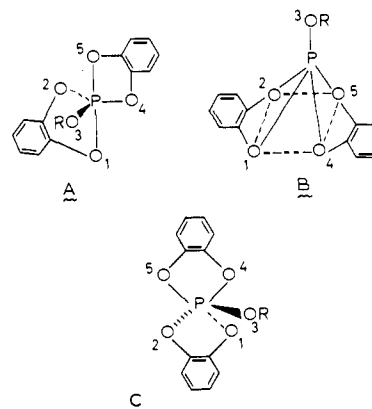

Figure 3. A and B: ligands to the phosphorus in oxybis-o-phenylenedioxyphosphorane placed on hypothetical trigonal bipyramidal and square pyramidal skeletons. C: drawing of the actual skeletal geometry of phenoxy-*o*-phenylenedioxyphosphorane (R = C_6H_5) in the crystal (from ref 27). O(1), O(2), O(4), and O(5) are not in a plane in formula C as they would be in formula B.

in *intermolecular* hydrogen bondings with the phosphoryl oxygens of the former pair, in a criss-cross pattern. Apparently, the observed packing among intermolecularly hydrogen bonded molecules represents a more favorable situation in the crystal than the alternative arrangement involving packing of intramolecularly hydrogen bonded molecules.

Table VI. Fractional Coordinates (Standard Deviations × 10⁴)

name	x	y	z
P	0.3550 (2)	0.0937 (1)	0.1278 (0)
O(1)	0.6309 (4)	0.0478 (2)	0.2225 (1)
O(2)	0.5230 (3)	0.0267 (2)	0.1137 (1)
O(3)	0.2156 (4)	0.0546 (2)	0.1658 (1)
O(4)	0.4372 (4)	0.1950 (2)	0.1464 (1)
O(5)	0.2840 (3)	0.1221 (2)	0.0652 (1)
C(1)	0.6251 (6)	−0.0425 (3)	0.2021 (1)
C(12)	0.6741 (6)	−0.1234 (3)	0.2334 (2)
C(13)	0.6565 (6)	−0.2126 (3)	0.2092 (2)
C(21)	0.5645 (5)	−0.0549 (3)	0.1474 (1)
C(22)	0.5464 (6)	−0.1437 (3)	0 1227 (2)
C(23)	0.5940 (6)	−0.2226 (3)	0.1542 (2)
C(41)	0.4098 (5)	0.2603 (3)	0.1017 (1)
C(42)	0.4588 (6)	0.3550 (3)	0.1022 (2)
C(43)	0.4166 (6)	0.4065 (3)	0.0532 (2)
C(51)	0.3227 (5)	0.2191 (2)	0.0555 (1)
C(52)	0.2799 (6)	0.2689 (3)	0.0070 (2)
C(53)	0.3309 (6)	0.3652 (3)	0.0068 (2)
H(1)	0.6779 (48)	0.0478 (23)	0.2647 (14)
H(12)	0.7080 (43)	−0.1152 (20)	0.2730 (12)
H(13)	0.6815 (48)	−0.2724 (21)	0.2374 (14)
H(22)	0.5169 (39)	−0.1430 (19)	0.0830 (10)
H(23)	0.5816 (47)	−0.2833 (22)	0.1370 (14)
H(42)	0.5163 (46)	0.3839 (21)	0.1388 (12)
H(43)	0.4474 (46)	0.4811 (22)	0.0521 (12)
H(52)	0.2254 (40)	0.2418 (19)	−0.0235 (11)
H(53)	0.3055 (34)	0.3998 (16)	−0.0274 (10)

These considerations could account for the preservation of the tetracoordinate phosphate structure of compound **3** in the crystal. The spectral evidence discussed in the Introduction shows that the hydroxyphenylphosphate **3** is in equilibrium with the hydroxyphosphorane **2** in solutions. Moreover, the data show that the phosphorane structure **2** is favored over the phosphate structure **3**. Therefore, it is not a priori obvious why the compound should exist as the phosphate form in the crystalline state.

Figures 1 and 3 depict the changes required to transform the phosphate **3** into the oxyphosphorane **2**, with the latter in three significantly different skeletal geometries about the phosphorus atom. Formulas A, B, and C depict the hydroxyphosphorane **2** as a trigonal bipyramid, a square pyramid, and a static $x°$-TR configuration,[26-30] respectively. It is known[27] from x-ray crystallographic data that phenoxybis-*o*-phenylenedi-

Scheme II
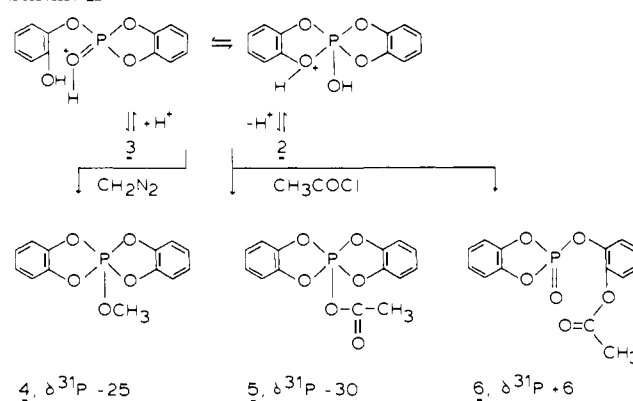
oxyphosphorane has structure C (R = C_6H_5), with a P–O(1) bond distance of 1.666 (10) Å, i.e., a covalent bond to penta-coordinate phosphorus. In solutions this phenoxyphosphorane has a ^{31}P NMR shift of −30 ppm, which is quite close to the value observed for the hydroxyphosphorane **2** in solutions. This analogy suggests that formula C (R = H) is also a reasonable representation of compound **2**.

The equilibrium established between the hydroxyphenyl-phosphate **3** and the hydroxyphosphorane **2**[31] when the crystalline substance is dissolved in aprotic solvents is acid catalyzed (cf. Scheme II).

The addition of 1 molar equiv of diazomethane in ether to a suspension of the crystalline phosphate **3** in dichloromethane at 0 °C gives the methoxyphosphorane **4** as the only detectable product.[4] On the other hand, treatment of the crystalline phosphate with an excess of acetyl chloride at 25 °C produces mostly (~80%) *o*-acetoxyphenyl-*o*-phenylene phosphate (**6**) and some (~20%) acetoxybis-*o*-phenylenedioxyphosphorane (**5**). These figures do not represent the kinetically controlled product ratio of the acetyl chloride reaction, since the ace-toxyphosphorane, **5**, is known to rearrange to the acetoxy-phosphate **6** under the influence of hydrogen chloride, which is a by-product of the reaction. These results again suggest the existence of a dynamic equilibrium between the structures with penta- and tetravalent phosphorus, **2** and **3**, in a variety of liquid media, and reinforce the conclusions derived from ^{31}P NMR spectrometry. It thus appears that, as the crystal lattice is disrupted, the phenolic hydroxyl group approaches the phosphorus atom to effect the changes in the phosphorus valence and coordination number, as well as in overall molecular

Table VII. Anisotropic Temperature Factors (Standard Deviations × 10⁴)[a]

name	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	0.0194 (2)	0.0039 (1)	0.0012 (0)	−0.0005 (1)	−0.0004 (1)	0.0002 (0)
O(1)	0.0419 (10)	0.0043 (2)	0.0018 (1)	0.0006 (4)	−0.0023 (2)	−0.0004 (1)
O(2)	0.0192 (7)	0.0053 (2)	0.0016 (1)	0.0017 (3)	0.0005 (2)	0.0005 (1)
O(3)	0.0234 (7)	0.0051 (2)	0.0015 (1)	−0.0002 (3)	0.0015 (2)	0.0005 (1)
O(4)	0.0262 (8)	0.0045 (2)	0.0014 (1)	−0.0018 (3)	−0.0015 (2)	0.0000 (1)
O(5)	0.0229 (7)	0.0038 (2)	0.0015 (1)	−0.0016 (3)	−0.0011 (2)	0.003 (1)
C(11)	0.0210 (11)	0.0053 (3)	0.0013 (1)	−0.0003 (5)	−0.0005 (2)	−0.0001 (1)
C(12)	0.0228 (12)	0.0057 (3)	0.0016 (1)	0.0003 (5)	−0.0003 (3)	0.0003 (1)
C(13)	0.0201 (12)	0 0058 (3)	0.0023 (1)	0.0011 (5)	−0.0002 (3)	0.0006 (2)
C(21)	0.0158 (9)	0.0045 (2)	0.0015 (1)	0.0007 (4)	0.0001 (2)	0.0003 (1)
C(22)	0.0177 (11)	0.0062 (3)	0.0018 (1)	0.0008 (5)	−0.0007 (3)	−0.0004 (2)
C(23)	0.0219 (13)	0.0044 (3)	0.0029 (1)	0.0010 (5)	−0.0002 (3)	−0.0006 (2)
C(41)	0.0154 (10)	0.0046 (2)	0.0013 (1)	0.0005 (4)	0.0003 (2)	0.0001 (1)
C(42)	0.0189 (11)	0.0037 (2)	0.0019 (1)	−0.0002 (4)	0.0007 (3)	−0.0004 (1)
C(43)	0.0213 (12)	0.0041 (3)	0.0024 (1)	0.0002 (5)	0.0016 (3)	0.0003 (1)
C(51)	0.0127 (9)	0.0042 (2)	0.0014 (1)	0.0001 (4)	−0.0000 (2)	0.0000 (1)
C(52)	0.0137 (10)	0.0057 (3)	0.0014 (1)	0.0004 (4)	0.0001 (2)	0.0005 (1)
C(53)	0.0193 (12)	0.0052 (3)	0.0021 (1)	0.0008 (5)	0.0006 (3)	0.0012 (1)

[a] All hydrogen atoms were assigned isotropic thermal factors of 6.0 A². Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Scheme III

7, δ^{31}P-84
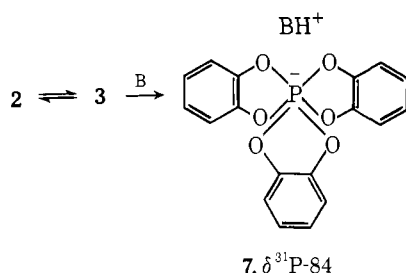
geometry, which accompany the formation of the hydroxy-phosphorane.

Solutions containing the phosphorane **2** in equilibrium with the phosphate **3** in aprotic solvents undergo remarkably rapid and complex transformations in the presence of traces of bases, even of a base as weak as dimethyl sulfoxide. The base causes the disappearance of the ^{31}P NMR signals of the structures with penta- and tetracovalent phosphorus and the appearance of the signal at −83.5 ppm which is analogous to the value found for the tris-*o*-phenylenedioxyphosphoride anion[32] **7**. An interpretation of the mechanisms which operate in these base-promoted transformations of compounds **2** and **3** is beyond the scope of the present paper, but the observation emphasizes the need to avoid all bases in dealing with the crystalline compound **3** and its solutions. This accounts for the development of the acid-catalyzed desilylation depicted in Scheme I for the preparation of *o*-hydroxyphenyl-*o*-phenylene phosphate.

Supplementary Material Available: Table VIII, structure factors (11 pages). Ordering information is given on any current masthead page.

References and Notes

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