The Crystal and Molecular Structure of a Bicyclic Dioxyphosphorane, $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

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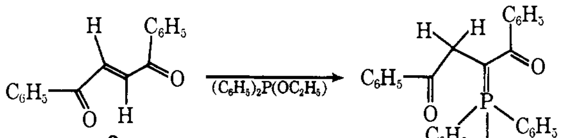
Abstract: A stable bicyclic dioxyphosphorane was made from the stepwise reaction of ethyl diphenylphosphinite, *trans*-dibenzoylethylene, and *p*-bromobenzaldehyde. X-Ray crystallographic analysis showed that the molecule was a trigonal bipyramid with two oxygens in apical positions, three carbons in equatorial positions, a five-membered unsaturated ring in an apical–equatorial plane, and a six-membered unsaturated ring in another apical–equatorial plane. The $\partial^{31}P$ nmr shift was +50.2 ppm *vs.* H_3PO_4.

The isolation of a crystalline ethoxydiphenylalkylidenephosphorane, **3**, from the reaction of ethyl diphenylphosphinite (**1**) with *trans*-dibenzoylethylene (**2**) was reported in a preliminary communication.[2] This paper describes that work in detail.



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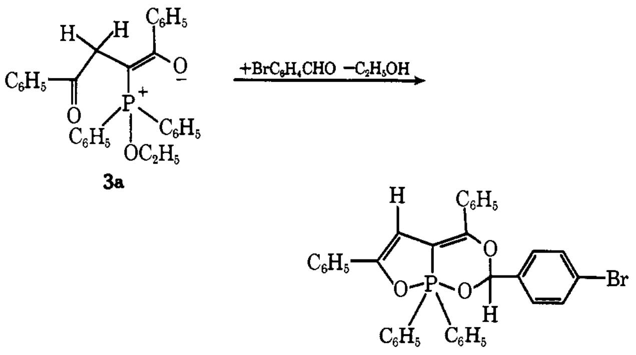
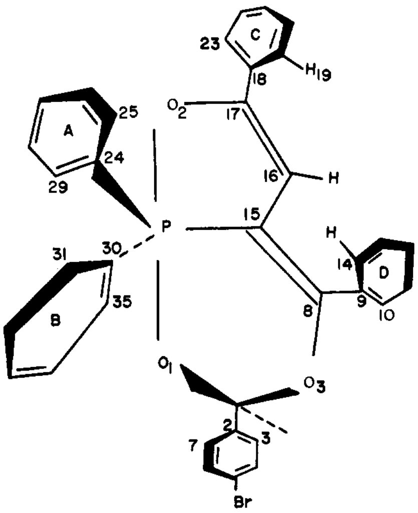
3, $\partial^{31}P = -54.2$ ppm
(CH_2Cl_2) *vs.* H_3PO_4

The alkylidenephosphorane formula **3** is one of the several resonance forms that can be drawn to represent this stabilized β-ketophosphonium ylide.[3] A closer approximation to the structure of the molecule in its ground state is probably the enolate phosphonium betaine formula **3a**. We have found that this type of ylide reacts with *p*-bromobenzaldehyde to give a striking example of a stable bicyclic *dioxyphosphorane*, **4**, in which the phosphorus atom became pentacoordinated while a molecule of ethanol was extruded from the 1:1 adduct formed from the ylide and the aldehyde.



4, $\partial^{31}P = +50.2$ ppm
(benzene)

The oxyphosphorane formula **4** would seem to represent a "strained" molecule, or, at least, a rather questionable structure for a thermally stable substance with mp 170–172°. To settle this question, and to gain further insight into the static and dynamic stereochemistry of pentavalent phosphorus,[4] we have elucidated the crystal and molecular structure of oxyphosphorane **4** by X-ray crystallography. The results are summarized in formula **4a**.



4a

Experimental Section

Reaction of Ethyl Diphenylphosphinite (1) with *trans*-Dibenzoylethylene (2). Ethyl diphenylphosphinite (34.2 g, 149 mmol) was added over a period of 15 min to the yellow-orange suspension of *trans*-dibenzoylethylene (35.1 g, 149 mmol) in 100 ml of purified 1,2-dimethoxyethane at 10° under nitrogen. The suspension gradually changed to a clear red solution. The suspension which formed after approximately 10 hr was filtered and the solid was washed with 200 ml of dry ether to afford ylide **3** in 57% yield (39.7 g, mp 115–117°) as a tan powder. Ylide **3** was very sensitive to moisture; the spectral properties reported in the text were obtained on a fresh sample under anhydrous conditions.

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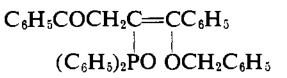
(2) F. Ramirez, O. P. Madan, and C. P. Smith, *J. Amer. Chem. Soc.*, **86**, 5339 (1964).

(3) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

(4) (a) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968); (b) F. Ramirez, J. F. Pilot, C. P. Smith, S. B. Bhatia, and A. S. Gulati, *J. Org. Chem.*, **34**, 3385 (1969).

For purposes of characterization, ylide 3 was allowed to react with benzyl bromide to yield a stable phosphine oxide enol ether



$$\begin{array}{l} C_6H_5COCH_2C{=}CC_6H_5 \\ \quad (C_6H_5)_2PO \;\; OCH_2C_6H_5 \end{array}$$

The analytical data for this derivative have been recorded.[2]

Reaction of the Ylide 3 with *p*-Bromobenzaldehyde. Preparation of 1,1,5,8-Tetraphenyl-3-*p*-bromophenyl-1-phospha-2,4,9-trioxabicyclo[4.3.0]nonadiene-5,7 (4). *p*-Bromobenzaldehyde (3.82 g, 20.6 mmol) was added all at once to a solution of the ylide 3 (9.62 g, 1 mol equiv) in 65 ml of tetrahydrofuran (previously distilled from $LiAlH_4$) under nitrogen at 25°. The original pale amber solution gradually changed to bright yellow. Infrared spectra of aliquots showed a gradual accumulation of product. After 6 days, the solvent was removed at 25° (20 mm), and finally at 0.9 mm for 1 hr, to yield a bright yellow solid. The solid was dissolved in dry CH_2Cl_2 (25 ml) and hexane (100 ml) was added to the heated solution. A thick suspension of the oxyphosphorane 4 was obtained. The analytical sample was obtained as yellow crystals, mp 170–172° from CH_2Cl_2.

Anal. Calcd for $C_{35}H_{26}O_3PBr$: C, 69.4; H, 4.3; P, 5.1; Br, 13.2. Found: C, 68.9; H, 4.4; P, 4.8; Br, 13.4.

The oxyphosphorane 4 must be protected from moisture. The spectral data given in the text were obtained on a fresh sample under anhydrous conditions. The ir spectrum in a KBr pellet had these bands: 1592 (s), 1563 (s), 1495 (s), 1385 (m), 1342 (m), 1302 (s), 1253 (s), 1161 (ms), 1129 (s), 1073 (s), 1064 (s), 990 (ms) cm^{-1}. The ir spectrum in CH_2Cl_2 had these bands, but other bands also appeared due to dissociation into *p*-bromobenzaldehyde (1701, 1203, and 819 cm^{-1}) and a second decomposition product (1513 cm^{-1}).

X-Ray Analysis of the Oxyphosphorane (4). The crystals of 4 selected for X-ray data collection had dimensions of 0.5 mm × 0.5 mm × 0.6 mm. Preliminary Weissenberg photographs showed the crystal to possess $P2_1/c$ symmetry since systematic absences were $k = 2n + 1$ for the $0k0$ reflections, $l = 2n + 1$ for the $h0l$ reflection. The lattice parameters were determined by least squares refinement of 6 2θ values measured on a diffractometer, $a = 9.432$ (5), $b = 15.854$ (5), $c = 19.094$ (6), $\beta = 102.01$ (7) at 25°. On the basis of the measured density 1.41 g/cc, there are four molecules per unit cell. The calculated density was 1.47 g/cc. The linear absorption coefficient for Cu Kα radiation is 21.08 cm^{-1}.

The intensity data were collected using a General Electric XRD-5 diffractometer equipped with a scintillation counter for detector. Independent reflections were collected by the θ–2θ scan technique (moving crystal–moving counter method) using 100-sec scans across the peak and reading the background for 50 sec on either side of peak. The scan rate was 2°/min in 2θ and the tube take-off angle was set at 4°. Nickel-filtered copper radiation was used for the data collection. A total of 4142 reflections were collected of which 3277 were considered as observed by criteria $F_o \geq 2\sigma$ (F_o)(23 of these were later removed due to secondary extinction). The data were corrected for Lorentz and polarization factors using a SDS Sigma-7 computer.[5] No absorption corrections were applied. For structure factor calculations, form factors from the literature were used.[6,7] Real and imaginary anomalous terms were used for the Br atoms.

Structure Determination and Refinement. The Br atom was easily identified in the Patterson map. The Br position was initially refined by full matrix refinement and the set of phases calculated from the refined position were used to calculate the first Fourier map. This Fourier map showed all the other atoms of the molecule.

Table I. Final Atomic Coordinates for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

Atom	x	y	z
Br	−0.45453 (8)[a]	−0.22962 (4)	−0.15446 (3)
P	−0.03874 (14)	0.03996 (7)	0.20729 (6)
O(1)	−0.16758 (34)	0.00355 (18)	0.13501 (15)
O(2)	0.08588 (37)	0.07947 (19)	0.28373 (15)
O(3)	−0.18095 (37)	0.10914 (18)	0.05175 (15)
C(1)	−0.13784 (54)	0.02423 (27)	0.06861 (22)
C(2)	−0.21582 (52)	−0.03391 (28)	0.01067 (23)
C(3)	−0.15527 (63)	−0.11210 (32)	0.00337 (28)
C(4)	−0.22421 (59)	−0.16942 (33)	−0.04629 (27)
C(5)	−0.35619 (59)	−0.14776 (31)	−0.08879 (25)
C(6)	−0.41906 (67)	−0.07055 (34)	−0.08348 (28)
C(7)	−0.34650 (62)	−0.01283 (33)	−0.03318 (28)
C(8)	−0.11363 (53)	0.16586 (28)	0.10123 (24)
C(9)	−0.13770 (53)	0.25305 (27)	0.07535 (23)
C(10)	−0.13111 (65)	0.27310 (36)	0.00519 (26)
C(11)	−0.15675 (85)	0.35531 (38)	−0.01877 (30)
C(12)	−0.19105 (92)	0.41711 (38)	0.02522 (33)
C(13)	−0.20056 (85)	0.39702 (34)	0.09501 (30)
C(14)	−0.17399 (69)	0.31576 (33)	0.11924 (27)
C(15)	−0.02989 (53)	0.14286 (27)	0.16678 (22)
C(16)	0.06877 (56)	0.19750 (29)	0.21330 (24)
C(17)	0.13097 (51)	0.15921 (27)	0.27557 (23)
C(18)	0.24419 (52)	0.19148 (30)	0.33482 (24)
C(19)	0.30926 (58)	0.26987 (36)	0.33107 (28)
C(20)	0.41417 (65)	0.29865 (42)	0.38720 (31)
C(21)	0.46185 (69)	0.24876 (44)	0.44726 (33)
C(22)	0.39821 (78)	0.17122 (45)	0.45142 (32)
C(23)	0.28833 (69)	0.14219 (36)	0.39562 (28)
C(24)	−0.16978 (52)	0.02249 (28)	0.26363 (23)
C(25)	−0.28598 (63)	0.07780 (37)	0.25906 (28)
C(26)	−0.38731 (72)	0.06691 (46)	0.30217 (33)
C(27)	−0.37138 (80)	−0.00074 (44)	0.35012 (33)
C(28)	−0.25657 (83)	−0.05577 (39)	0.35463 (32)
C(29)	−0.15488 (70)	−0.04419 (34)	0.31151 (29)
C(30)	0.08691 (54)	−0.04599 (29)	0.20166 (22)
C(31)	0.23793 (61)	−0.03236 (35)	0.21620 (28)
C(32)	0.33239 (68)	−0.09829 (40)	0.21011 (33)
C(33)	0.27885 (68)	−0.17831 (38)	0.19139 (29)
C(34)	0.13072 (67)	−0.19282 (32)	0.17755 (26)
C(35)	0.03538 (59)	−0.12682 (29)	0.18165 (25)

[a] The number in parentheses is the standard deviation and refers to the least significant digits.

The final cycles of refinement were carried out on the SDS Sigma 7 computer using the block diagonal approximation to the least squares method refining positional and anisotropic thermal parameters. A parameter shift damping factor of 0.50 was used. A total of 3254 reflections were included in the least squares refinement, 23 being excluded from the refinement since they appeared to be effected by secondary extinction. The final R index is 5.59%. The weighting scheme described by Stout and Jensen[8] was used during the final cycles with "a" equal to 0.01.

Final positional parameters are listed in Table I. Table II lists the anisotropic temperature factors and Figure 2 shows an ORTEP plot of the structure, the thermal ellipsoids representing 50% probability. Table III shows the equations for the least squares planes for the five-membered ring, the equatorial plane of the trigonal bipyramid, and for the carbon atoms of the chromophore portion of the molecule. The least squares planes are calculated according to the method described by Schomaker, *et al.*,[9] using unit weights for all atoms.[9a]

Chemical and Spectroscopic Data. The formation of the ylide 3 is pictured as an initial attack by the phosphorus of the phosphinite 1 on the olefinic carbon of *trans*-dibenzoylethylene (2) to give the dipolar ion, 5. The hydrogen next to the phosphonium group in 5 is acidic and is removed by the oxide anion to form the enol form 6 of the ylide which then tautomerizes to the stable keto ylide 3.

The characteristic features of ylide 3 are (1) the large negative value of the ^{31}P nmr shift (note that the analogous ylide with three

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(5) All programs used are from the Montana State University Crystallographic Program Library written for the SDS Sigma-7 by C. N. Caughlan, E. Enwall, D. Smith, and D. Swank or those of F. R. Ahmed, National Research Council, Ottawa, Canada.

(6) J. A. Ibers, International Tables for Crystallography, Vol. III, Kynoch Press, Birmingham, England, 1962.

(7) Initial work was carried out using J. Steward, *et al.*, "Crystal Structure Calculation System X-ray 63," Technical Report TR-64-6, University of Maryland, College Park, Md., 1964, on the IBM 7094 computer at the University of Washington, Seattle, Washington.

(8) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination, a Practical Guide," Macmillan, New York, N. Y., 1968, pp 454–458.

(9) V. Schomaker, S. Waser, R. E. Marsh, and G. Bergman, *Acta Crystallogr.*, **12**, 600 (1969).

(9a) A table of observed and calculated structure amplitudes from this analysis has been deposited as Document No. NAPS-01470 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $5.00 for photoprints or $2.00 for microfiche. Advance payment is required. Make checks or money orders payable to: CCMIC–NAPS.

Table II. Thermal Parameters for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

Atom	β_{11}[a,b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	1685 (9)[c]	0393 (2)	0327 (2)	0014 (4)	0378 (6)	−310 (9)
P	0976 (16)	0204 (4)	0135 (3)	−077 (6)	−031 (11)	−010 (14)
O(1)	1002 (43)	0278 (13)	0139 (8)	−204 (17)	−001 (30)	−047 (38)
O(2)	1309 (50)	0250 (13)	0158 (9)	−200 (17)	0139 (34)	0013 (40)
O(3)	1314 (50)	0220 (13)	0154 (9)	−068 (16)	0078 (33)	0048 (39)
C(1)	1141 (67)	0235 (18)	0135 (12)	−078 (24)	−040 (46)	−022 (56)
C(2)	1057 (65)	0258 (19)	0150 (12)	−080 (25)	0084 (46)	−043 (57)
C(3)	1372 (82)	0307 (21)	0251 (17)	−076 (30)	0026 (58)	−139 (65)
C(4)	1147 (76)	0372 (23)	0253 (16)	0013 (31)	0032 (55)	−185 (65)
C(5)	1212 (73)	0323 (21)	0187 (14)	−102 (28)	0044 (51)	−065 (63)
C(6)	1663 (92)	0343 (23)	0231 (16)	0123 (31)	−250 (62)	−139 (72)
C(7)	1345 (79)	0336 (23)	0241 (16)	0168 (30)	−209 (58)	−090 (67)
C(8)	0951 (65)	0246 (19)	0194 (13)	−032 (25)	0016 (47)	−019 (55)
C(9)	1054 (65)	0242 (20)	0173 (13)	−030 (24)	−135 (46)	0017 (53)
C(10)	1666 (87)	0383 (23)	0202 (15)	0166 (32)	0062 (56)	0127 (79)
C(11)	2586 (131)	0413 (27)	0241 (18)	0355 (35)	0142 (76)	0163 (95)
C(12)	2953 (144)	0328 (25)	0286 (19)	0288 (35)	−021 (83)	0092 (95)
C(13)	2724 (130)	0261 (22)	0249 (18)	0326 (31)	−051 (75)	−018 (84)
C(14)	1828 (95)	0289 (22)	0223 (16)	0122 (29)	−013 (61)	−038 (72)
C(15)	1027 (66)	0228 (18)	0155 (13)	−016 (24)	0009 (46)	0044 (56)
C(16)	1202 (72)	0249 (19)	0186 (14)	0116 (26)	0092 (50)	−049 (58)
C(17)	0908 (63)	0225 (18)	0184 (13)	0011 (25)	0019 (46)	−074 (53)
C(18)	0892 (65)	0312 (20)	0202 (14)	0046 (27)	0103 (48)	−140 (58)
C(19)	1150 (72)	0419 (23)	0279 (17)	−292 (35)	0270 (55)	−269 (73)
C(20)	1151 (80)	0636 (33)	0309 (19)	−455 (40)	0239 (62)	−349 (80)
C(21)	1345 (85)	0675 (37)	0328 (20)	−075 (42)	−032 (64)	−374 (86)
C(22)	1815 (106)	0624 (34)	0271 (19)	0207 (40)	−437 (72)	−170 (95)
C(23)	1645 (91)	0415 (25)	0215 (16)	0159 (33)	−284 (61)	−072 (77)
C(24)	1065 (66)	0257 (19)	0154 (13)	−183 (25)	0072 (46)	0085 (56)
C(25)	1218 (78)	0483 (27)	0235 (16)	0094 (33)	0106 (57)	−014 (73)
C(26)	1419 (92)	0685 (36)	0313 (20)	−222 (43)	0381 (68)	−098 (92)
C(27)	1979 (108)	0600 (33)	0292 (20)	−741 (40)	0527 (73)	−192 (98)
C(28)	2364 (119)	0426 (28)	0292 (19)	−506 (36)	0644 (77)	−041 (91)
C(29)	1819 (94)	0343 (23)	0256 (16)	−179 (32)	0412 (63)	0064 (76)
C(30)	1152 (68)	0273 (19)	0142 (12)	0011 (25)	0092 (46)	0058 (58)
C(31)	1152 (74)	0429 (25)	0263 (16)	0025 (33)	0101 (56)	−056 (70)
C(32)	1377 (91)	0518 (30)	0335 (20)	0202 (38)	0126 (68)	−136 (81)
C(33)	1547 (91)	0477 (28)	0247 (17)	0188 (35)	0158 (63)	0038 (80)
C(34)	1805 (93)	0308 (21)	0187 (15)	0117 (28)	0316 (58)	0046 (72)
C(35)	1346 (77)	0258 (20)	0192 (14)	−001 (27)	0207 (54)	0018 (61)

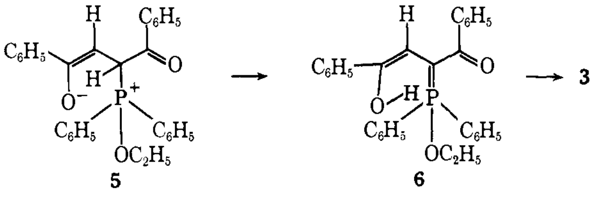
[a] The β_{ij}'s have been multiplied by 10^5. [b] The form of the anisotropic ellipsoids is $\tau = \exp[-\{\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl\}]$. [c] The number in parentheses is the standard deviation and refers to the least significant digit.

Table III. Equations of Least Squares Planes Referred to Orthogonal Axes for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$[a]

Atoms	*a*	*b*	*c*	*D*, Å	*S*, Å²
PO(2)C(15)C(16)C(17)	−0.7156	0.2743	0.6424	2.339	6.9×10^{-4}
PC(15)C(24)C(30)	0.5778	0.3951	0.7142	3.326	2.6×10^{-3}
C(8)C(9)C(15)C(16)C(17)C(18)	−0.7089	0.1305	0.6931	2.167	1.3×10^{-2}
C(8)C(9)C(10)C(14)	0.9719	0.2163	−0.0925	−0.248	3.8×10^{-4}
C(17)C(18)C(19)C(23)	−0.6797	0.3600	0.6391	2.609	1.3×10^{-5}

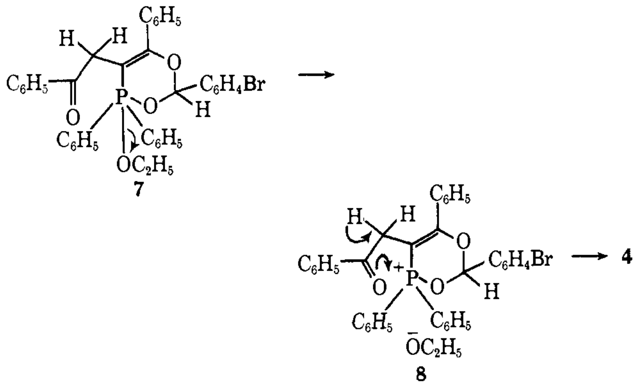
[a] $X = x + z\cos\beta$; $Y = y$; $Z = z\sin\beta$, $D = a\bar{X} + b\bar{Y} + c\bar{Z}$, S = sum of squares of deviations of atoms from plane, D = origin to plane distance in ångströms. All atoms are given equal weight.

phenyl rings on phosphorus[10] had $\delta^{31}P = -16.9$ ppm, *i.e.*, a much more shilded P nucleus); (2) the presence of a doublet, $\tau = 6.33$ ppm (*vs.* TMS = 10), $J_{HCCP} = 21$ cps, in the ¹H nmr spectrum of **3**



due to the two equivalent phenacyl protons; (3) the strong and broad ir band at 1504 cm⁻¹ due to β-ketophosphonium ylides,[2,10] in addition to the normal carbonyl band at 1675 cm⁻¹.

The formation of dioxyphosphorane **4** may involve the initial formation of an intermediate with pentacoordinated phosphorus **7**



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(10) (a) F. Ramirez, O. P. Madan, and C. P. Smith, *J. Org. Chem.*, 30, 2284 (1965); (b) F. Ramirez, O. P. Madan, and C. P. Smith, *Tetrahedron*, 22, 567 (1966).

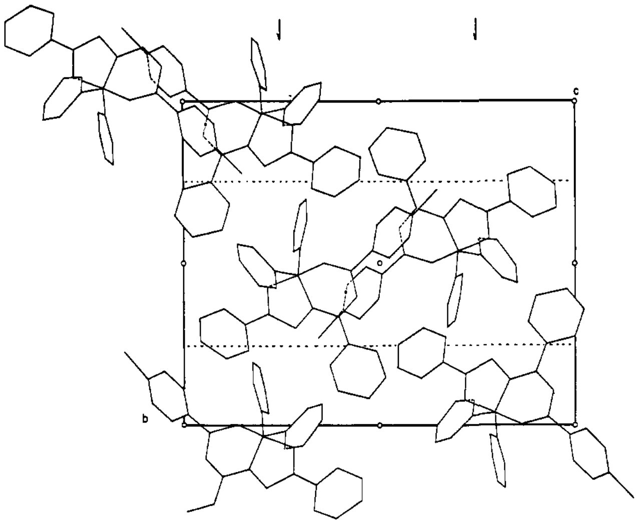
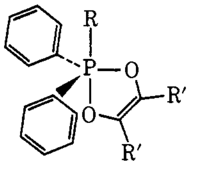


Figure 1. Projection of the crystal structure of $PO_3(C_6H_5)_4$-$(C_6H_4Br)C_5H_2$ onto the *bc* plane.

from the insertion of the aldehyde into the enolate phosphonium betaine **3a**. The intermediate **7** is well suited for the intramolecular interaction of oxygen with the γ-ketophosphonium function as shown in **8**. The ethoxide ion acting as the base should remove the activated proton to yield the stable oxyphosphorane **4**.

The oxyphosphorane **4** is characterized by the following properties: (1) a large positive ^{31}P nmr shift, +50.2 ppm (in fact, the P nucleus of this oxyphosphorane **4** is shielded much more effectively than those of related monocyclic oxyphosphoranes, **9**, **10**, having the same number of oxygen atoms and of carbon atoms attached to the pentavalent phosphorus);[11] (2) the presence of a proton doublet



9, R = C_2H_5; δ^{31}P +9.3 ppm (benzene)
10, R = C_6H_5; δ^{31}P +15.6 ppm (benzene)
R'COCOR' = phenanthrenequinone

in **4** at τ 3.54 ppm with a very large HCCP coupling, J = 37.0 cps, due to the vinyl proton at C16 (see numbering in **4a**) (the large coupling is probably related to the particular molecular geometry.[10,12] There was also a doublet at τ 3.90, J_{HCOP} = 12.3 cps due to the proton at C1); (3) the ir spectrum of **4** is given in the Experimental Section. The spectrum was examined best in the solid phase since the oxyphosphorane **4** tends to dissociate partially into *p*-bromobenzaldehyde and other products in dilute solutions.

The β,α-diketophosphonium ylide **3** did not undergo the usual Wittig olefination reaction with aldehydes.[3,13] This reaction would have involved the nucleophilic addition by the α-carbon rather than by the oxide anion of ylide, **3**, **3a**, on the carbonyl carbon of the aldehyde.

X-Ray Crystallographic Analysis. The results are shown in Figures 1 and 2. A simplified formula is given in **4a**. The bond distances are listed in Table IV and the bond angles in Table V.

The phosphorus is at the center of a nearly regular trigonal bipyramid. The apical–equatorial bond angles ranged from 87.3 (2)° to 93.5 (2)°, while the diequatorial bond angles ranged from 116.8 (2)° to 124.0 (2)°, which are not large deviations from the ideal 90 and 120°, angles, respectively.

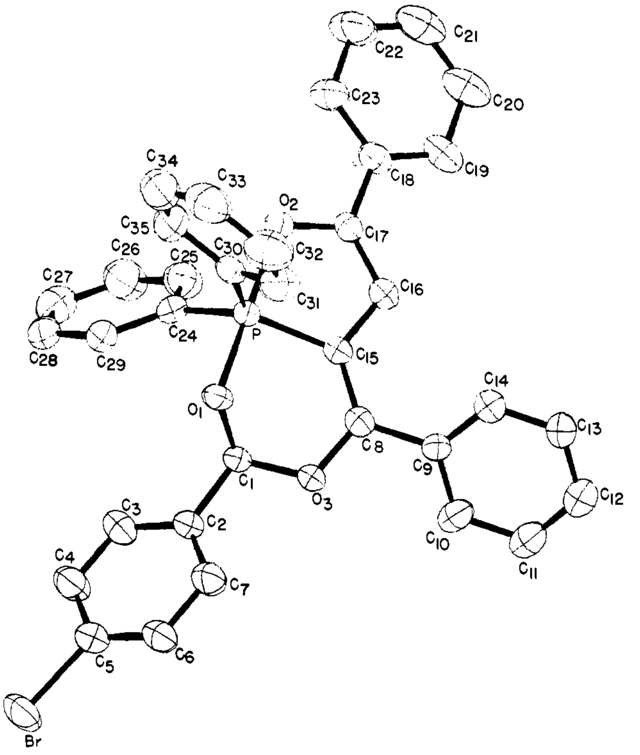


Figure 2. Molecular structure of $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$ showing orientation and magnitude of thermal ellipsoids representing 50% probability.

The five-membered oxaphospholene ring occupies an apical–equatorial position; the O2–P–C15 angle is 87.3 (2)°. The ring is planar as can be seen by the data for atoms O2–P–C15–C16–C17 in Table III. The five-membered ring of 2,2,2-triisopropoxy-4,5-(2',2''-biphenyleno)-2,2-dihydro-1,3,2-dioxaphospholene is also in the apical–equatorial plane of a trigonal bipyramid.[14] Apparently, the 90° apical–equatorial angle accommodates the O–P–C as well as the O–P–O angles in a five-membered ring better than the 120° diequatorial angle in trigonal bipyramidal phosphorus. These experimental results are consistent with the configurations assigned to a number of five-membered cyclic oxyphosphoranes in solutions,[4,15] from the results of variable-temperature ^{1}H nmr spectroscopy.[4,15,16] The apical–equatorial position had been postulated as the most favorable placement of a 1,3,2-dioxaphospholane ring in the hypothetical intermediate[17] or transition state[17a] for the hydrolysis of five-membered cyclic phosphate esters.

The six-membered dioxaphosphorinene ring occupies an apical–equatorial plane and is puckered at the tetragonal C1. The two oxygens attached to the phosphorus occupy the apical positions, O1, O2. The two phenyl rings and the trigonal C15 occupy the equatorial positions. This is in agreement with suggestions concerning the preference of elements of high electronegativity for the apical positions of trigonal bipyramidal phosphorus.[18]

The substance was yellow, and this chromophore is probably due to the *S-trans*-1,4-diphenyl-1,3-butadiene system, (C9)–C8–C15–C16–C17–(C18). The conjugation of this system is reflected in the bond lengths; the bond orders[19] are indicated also. In spite of the

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Table IV. Bond Distances for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

Atoms	Distance, Å
Br-C(5)	1.905 (9)[a]
P-O(1)	1.737 (6)
P-O(2)	1.786 (6)
P-C(24)	1.821 (7)
P-C(15)	1.815 (6)
P-C(30)	1.824 (7)
O(1)-C(1)	1.402 (7)
O(2)-C(17)	1.354 (7)
O(3)-C(1)	1.430 (8)
O(3)-C(8)	1.362 (10)
C(1)-C(2)	1.514 (12)
C(2)-C(3)	1.384 (10)
C(2)-C(7)	1.380 (13)
C(3)-C(4)	1.375 (14)
C(4)-C(5)	1.380 (13)
C(5)-C(6)	1.374 (11)
C(6)-C(7)	1.398 (14)
C(8)-C(9)	1.470 (9)
C(8)-C(15)	1.383 (11)
C(9)-C(10)	1.390 (8)
C(9)-C(14)	1.388 (11)
C(10)-C(11)	1.386 (12)
C(11)-C(12)	1.373 (14)
C(12)-C(13)	1.392 (11)
C(13)-C(14)	1.374 (12)
C(15)-C(16)	1.436 (12)
C(16)-C(17)	1.356 (12)
C(17)-C(18)	1.476 (12)
C(18)-C(19)	1.395 (10)
C(18)-C(23)	1.389 (12)
C(19)-C(20)	1.376 (15)
C(20)-C(21)	1.389 (16)
C(21)-C(22)	1.378 (14)
C(22)-C(23)	1.402 (16)
C(24)-C(25)	1.392 (11)
C(24)-C(29)	1.386 (11)
C(25)-C(26)	1.396 (12)
C(26)-C(27)	1.399 (15)
C(27)-C(28)	1.379 (15)
C(28)-C(29)	1.400 (13)
C(30)-C(31)	1.410 (10)
C(30)-C(35)	1.396 (10)
C(31)-C(32)	1.394 (12)
C(32)-C(33)	1.389 (14)
C(33)-C(34)	1.386 (12)
C(34)-C(35)	1.393 (11)

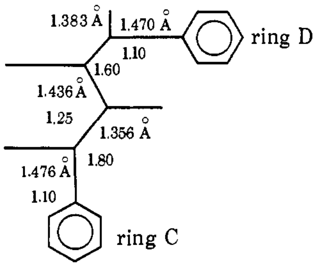
[a] The number in parentheses is the standard deviation and refers to the least significant digits.

Table V. Bond Angles for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

Atoms	Degrees
O(1)-P-O(2)	176.9 (1)[a]
O(1)-P-C(24)	88.3 (1)
O(1)-P-C(15)	92.7 (2)
O(1)-P-C(30)	93.5 (2)
O(2)-P-C(24)	89.0 (1)
O(2)-P-C(15)	87.3 (2)
O(2)-P-C(30)	89.1 (2)
C(15)-P-C(24)	119.1 (2)
C(24)-P-C(30)	116.8 (2)
C(15)-P-C(30)	124.0 (2)
P-O(1)-C(1)	113.3 (2)
P-O(2)-C(17)	113.8 (2)
P-C(15)-C(8)	123.7 (4)
P-C(15)-C(18)	111.1 (3)
P-C(30)-C(31)	121.1 (3)
P-C(30)-C(35)	120.6 (4)
O(1)-C(1)-O(3)	108.4 (3)
O(1)-C(1)-C(2)	110.5 (3)
O(2)-C(17)-C(16)	115.5 (4)
O(2)-C(17)-C(18)	115.5 (3)
O(3)-C(1)-C(2)	109.2 (4)
C(1)-O(3)-C(8)	113.1 (3)
C(1)-C(2)-C(3)	117.7 (4)
C(1)-C(2)-C(7)	122.8 (4)
C(3)-C(2)-C(7)	119.4 (4)
C(4)-C(3)-C(2)	121.0 (4)
C(3)-C(4)-C(5)	118.7 (4)
C(4)-C(5)-C(6)	121.9 (4)
C(5)-C(6)-C(7)	118.5 (5)
C(2)-C(7)-C(6)	120.4 (5)
C(8)-C(9)-C(10)	120.3 (4)
C(8)-C(9)-C(14)	120.7 (4)
C(10)-C(9)-C(14)	118.9 (4)
C(9)-C(10)-C(11)	119.6 (4)
C(10)-C(11)-C(12)	121.1 (5)
C(11)-C(12)-C(13)	119.6 (5)
C(14)-C(13)-C(12)	119.6 (5)
C(9)-C(14)-C(13)	121.3 (5)
C(8)-C(15)-C(16)	125.1 (4)
C(15)-C(16)-C(17)	112.3 (4)
C(16)-C(17)-C(18)	129.0 (4)
C(17)-C(18)-C(19)	121.7 (4)
C(17)-C(18)-C(23)	119.3 (4)
C(19)-C(18)-C(23)	119.1 (4)
C(18)-C(19)-C(20)	120.5 (5)
C(19)-C(20)-C(21)	120.7 (5)
C(22)-C(21)-C(20)	119.1 (5)
C(21)-C(22)-C(23)	120.8 (5)
C(18)-C(23)-C(22)	119.8 (5)
C(25)-C(24)-C(29)	119.5 (4)
C(24)-C(25)-C(26)	120.8 (4)
C(25)-C(26)-C(27)	119.2 (5)
C(26)-C(27)-C(28)	120.2 (5)
C(27)-C(28)-C(29)	120.4 (5)
C(24)-C(29)-C(28)	120.0 (5)
C(31)-C(30)-C(35)	118.3 (4)
C(30)-C(31)-C(32)	120.4 (4)
C(31)-C(32)-C(33)	120.2 (5)
C(32)-C(33)-C(34)	120.0 (5)
C(35)-C(34)-C(33)	120.1 (4)
C(30)-C(35)-C(34)	120.9 (4)
Br-C(5)-C(6)	119.8 (4)
Br-C(5)-C(4)	118.2 (3)
Br-C(5)-C(2)	177.6 (3)
Br-C(5)-C(3)	148.8 (3)
Br-C(5)-C(7)	150.8 (3)

[a] The number in parentheses is the standard deviation and refers to the least significant digits.

strong conjugation in the diphenylbutadiene system, the two phenyl rings D and C were not coplanar with the oxaphospholene ring, *i.e.*, with respect to the double bond system. The phenyl at C8 (ring D) was twisted 136° 32′, while the phenyl at C17 (ring C) was twisted 13° 40′ with respect to the double bond system. However, note that each set of atoms C9–C8–C15–C16–C17–C18, C8–C9–C10–C14, and C17–C18–C19–C23, fell in one plane, respectively (Table III).

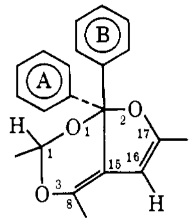


One consequence of the twisting of rings C and D with respect to the apical–equatorial planes is to prevent interference among the hydrogen at C16 and the *o*-hydrogens of the two rings (on C14 and C19). It is noteworthy that the *p*-bromophenyl ring at C1 was nearly perpendicular to the apical–equatorial planes. Moreover, one of the phenyls on phosphorus, ring B, was twisted with respect to the equatorial plane, while the other ring A was nearly coplanar with the equatorial plane. *These appear to be further manifestations*[4,15] *of the severe intramolecular crowding which exists in trigonal bipyramidal phosphorus and which plays an extremely important role in determining the stability of pentacoordinated vs. tetra-*

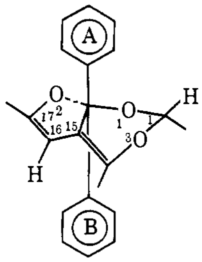
coordinated phosphorus. Probably, one of the main reasons for the stability of this oxyphosphorane **4** is the ability of the flat double bond system and of the five aromatic rings to arrive at an accommodation of their mutual steric interactions to minimize the intramolecular crowding in the bipyramid.

The phosphorus–phenyl bond distances are 1.82 Å, which should be compared with the mean distance of 1.85 Å reported for the equatorial phosphorus–phenyl rings in pentaphenylphosphorane.[20] The third P–C distance in **4** was also 1.82 Å. This is normal for a P–C single bond[21] (1.82 Å). The apical P–O bond distances are 1.79 Å for the bond in the five-membered ring, and 1.74 Å for the bond in the six-membered ring. These correspond to P–O single bonds (1.76 Å), and we surmise that the π bond character of these apical bonds is nearly zero.

It is interesting to speculate on the possible motions of the atoms in the bicyclic oxyphosphorane **4a** in solution. The groups attached to pentacoordinated phosphorus can exchange positions by an intramolecular bond-bending process (pseudorotation[4,15,16,18,22,23]) and by a bond rupture–recombination mechanism,[4] depending on the stability of the molecule and on the experimental conditions. The consequences of one pseudorotation of oxyphosphorane **4a** using the phenyl ring A as pivot would be[22c] the bipyramid **11**. For steric reasons alone this pseudorotation **4a** → **11** seems unlikely. One pseudorotation of **4a** using ring B as pivot would have analogous consequences. One pseudorotation of **4a** using C15 as pivot would give bipyramid **12**. Again, for steric reasons alone the pseudorotation **4a** → **12** seems unlikely. Moreover, note that in both cases pseudorotation moves both oxygens to equatorial positions. We conclude that **4a** is essentially incapable of pseudorotation. In fact, the molecule slowly falls apart in solution on standing at 20°; this decomposition prevents studies of variable temperature ^{1}H nmr at higher temperatures.



11



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(23) NOTE ADDED IN PROOF. It has been recently suggested that the positional exchange of the ligands in pentacoordinated phosphorus can take place by the *turnstile rotation* mechanism. It was claimed that cyclic phosphoranes can undergo permutational isomerizations only by the turnstile rotation, while acyclic phosphoranes can do so, in many cases, by both mechanisms, *turnstile rotation* and *Berry pseudorotaton.* See: (a) F. Ramirez, S. Pfohl, E. A. Tsolis, J. F. Pilot, C. P. Smith, I. Ugi, D. Marquarding, P. Gillespie, and P. Hoffmann, *Phosphorus*, **1**, 1 (1971); (b) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Accounts Chem. Res.*, **4**, 288 (1971); (c) F. Ramirez and I. Ugi, "Advances in Physical Organic Chemistry," Vol. 9, V. Gold, Ed., Academic Press, London, 1971.

Polymerization of Unprotected 2′-Deoxyribonucleoside 5′-Phosphates at Elevated Temperature[1a,b]

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Abstract: Polymerization of unprotected thymidine 5′-phosphate and 2′-deoxyribonucleoside 5′-phosphate (disodium salts) in *N,N*-dimethylformamide at reflux temperature for 30 min has been observed and studied. This reaction is catalyzed by proton(s) or a proton donor and is involved with P^1,P^2-dinucleosidyl 5′-pyrophosphate as a key intermediate. The main products are two series of oligomers with structural formulas of $(pN)_n$ and $(pN)_np$; 5–10% of the oligonucleotides consist of at least one 5′–5′ phosphodiester linkage (or less likely pyrophosphate linkage) as indicated by their resistance to spleen phosphodiesterase; no 3′–3′ phosphodiester linkage has been found since all materials are hydrolyzable by venom diesterase. With the best catalysts (β-imidazolyl-4(5)-propanoic acid or triethylamine hydrochloride), the yield of dimer to hexamer of thymidine oligonucleotides ranges from 12 to 5% of each species. The mechanisms of the synthetic and degradative processes are discussed. The study of this polymerization process may provide additional understanding about the prebiotic synthesis of polynucleotides.

In recent years, chemical polymerization of deoxynucleotides has been successfully achieved in two laboratories.[2-4] The synthetic procedure generally adopted involves the activation of the phosphate moiety of the suitably protected nucleotides in the polymerization mixture. This procedure inadvertently yields pyrophosphates and cyclic phosphates as side products. The pyrophosphates could be eliminated by an improvement of the reaction conditions as well as by a subsequent degradation which involves treatment with car-

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