of the sulfenamide grouping does not derive from an asymmetric nitrogen atom. Rather the torsional barrier about the sulfenamide S–N bond gives rise to an axis of chirality along the bond. The ligands on nitrogen and sulfenyl sulfur lie in two mutually perpendicular planes as in suitably substituted allenes. Since the sulfur is divalent, the ligancy complementation rule must be used to assign a phantom atom[27] of atomic weight zero as a sulfur ligand on the side opposite to the CCl_3 group before the Cahn–Ingold–Prelog convention[27] can be used to assign absolute configuration. This done, application of the chirality rule, in the form used for chiral axes, to the stereoformula or, more conveniently, to the Newman projection (Figure 4) indicates that the configuration at the sulfenamide bond is also (*R*). It has been shown using nmr experiments that the diastereomer in the crystal is also the more stable epimer in solution.[11] Thus, the (*R*,*R*) epimer predominates over the (*R*,*S*) epimer at equilibrium in solution.

The crystal packing (Figure 6) is normal with van der Waals forces predominating. Two intermolecular distances are shorter than the sums of the corresponding van der Waals radii[28] (Cl(1)···Cl(3),[29] 3.44 *vs.* 3.6; O(1)···C(2)′′, 3.09 *vs.* 3.4 Å).[30]

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[27] R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 383 (1966).

[28] L. Pauling, "The Nature of The Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

[29] Primed atoms are related to unprimed atoms by the transformation $x, y, z \rightarrow 1 - x, y - 1/2, -z$. Double primed atoms are related to unprimed atoms by $x, y, z \rightarrow 2 - x, y + 1/2, 1 - z$.

[30] A referee suggested that short intramolecular contacts O(1)··· C(2) and O(2)···S(2) might influence the degree and direction of the deviation from planar substitution at nitrogen. The two distances, 3.06 and 2.90 Å, are, in fact, shorter than sums of van der Waals radii[28] which are 3.4 and 3.25 Å, respectively. One additional contact O(2)··· Cl(2) is also comparable to the sum of van der Waals radii 3.21 Å *vs.* 3.2 Å. While the effect of these short contacts very probably has an effect on the geometry of the molecule, examination of a scale molecular model indicated no obvious relationship between these short contacts and the degree of puckering at nitrogen.

The Crystal and Molecular Structure of a Four-Membered Cyclic Oxyphosphorane with Pentavalent Phosphorus, $PO_2(C_6H_5)_2(CF_3)_4C_3H_2$

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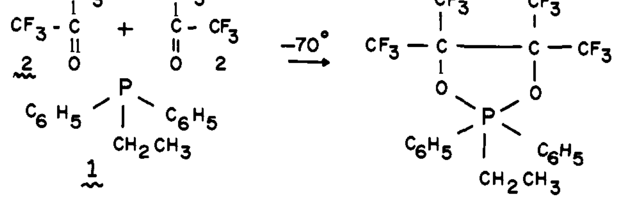
Abstract: The crystal and molecular structure of a four-membered cyclic oxyphosphorane with pentavalent phosphorus was determined by X-ray crystallography. The P atom of this intermediate in the Wittig olefin synthesis was at the center of a distorted trigonal bipyramid. The four-membered ring was in an apical–equatorial plane. Two oxygens were in apical position and three carbons were in equatorial positions. There was evidence of considerable intramolecular crowding which might contribute to the observed bending of the diapical axis (O–P–O bond angle of 165.8°) to the distortion of the ideal 120 and 90° bond angles, and to the distortion of bond angles in several tetragonal carbon atoms in the molecule.

The reaction of ethyldiphenylphosphine (**1**) with hexafluoroacetone (**2**) in hexane solution at −70° gave a five-membered cyclic oxyphosphorane[2] with pentavalent phosphorus, **3**.



3, $\delta\ ^{31}P = +6.1$ ppm (in Benzene) vs H_3PO_4

The oxyphosphorane, **3**, was relatively stable at 30°; however, it underwent a remarkable isomerization in benzene solution at 80°. The product of this isomerization was a crystalline four-membered cyclic oxyphosphorane[3] containing also pentavalent phosphorus **4**.

A possible mechanism for this unprecedented molecular transformation involves the rupture of the P–O bond of the five-membered ring of **3** to give **5**. This is followed (or accompanied) by the rupture of a C–C bond to give the dipolar ion **6** and hexafluoroacetone (**2**). The ion **6** is the same intermediate generated from

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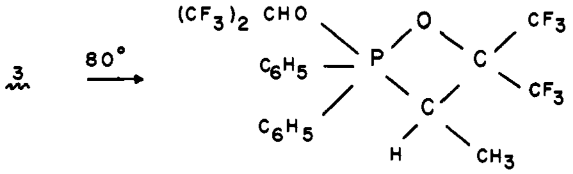
[1] (a) Montana State University. M. U. H. and C. N. C. acknowledge a grant from NIH, GM 08395-09, for partial support of this work. We are grateful to Montana State University for computing time. (b) State University of New York at Stony Brook. F. R., J. F. P., and C. P. S. acknowledge the support of this work by Grant GP-6690 from the National Science Foundation and Grant CA-04769 from the Cancer Institute of the NIH, U. S. Public Health Service.

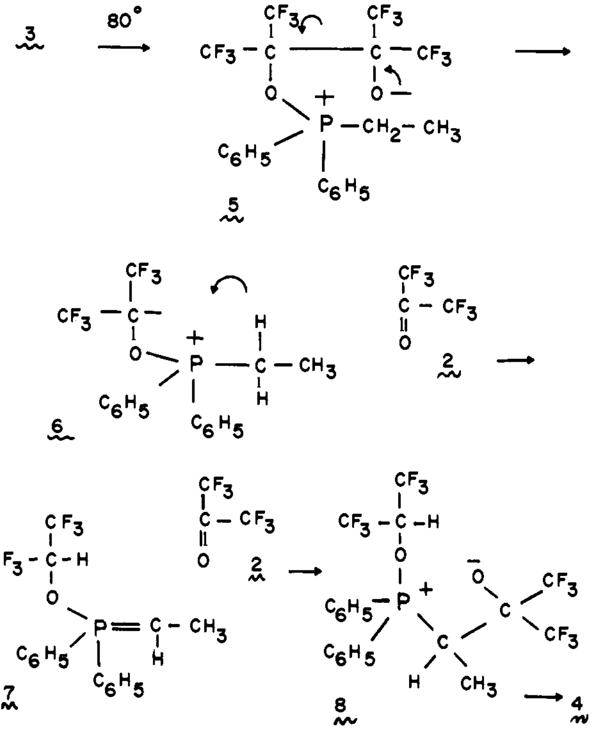
[2] F. Ramirez, C. P. Smith, J. F. Pilot, and A. S. Gulati, *J. Org. Chem.*, **33**, 3787 (1968).

[3] F. Ramirez, C. P. Smith, and J. F. Pilot, *J. Amer. Chem. Soc.*, **90**, 6726 (1968).

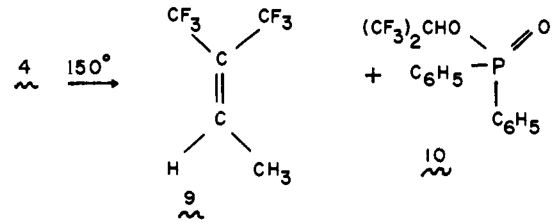


4, δ ^{31}P = + 32.1 ppm (in Benzene)

the reaction of the phosphine **1** with 1 mol of hexafluoroacetone (**2**) in the process of making the five-membered cyclic oxyphosphorane **3**. However, in that case, **6** was generated at −70°, while in the isomerization, **6** is generated at 80°. At the higher temperature, the activated proton of **6** can move to the negatively charged carbon to give the phosphonium ylide **7**. The latter reacts with hexafluoroacetone (**2**) to give **8** in what corresponds to one of the steps in the "Wittig olefin synthesis." [4] Closure of the four-membered ring in **8** gives the observed product **4**.

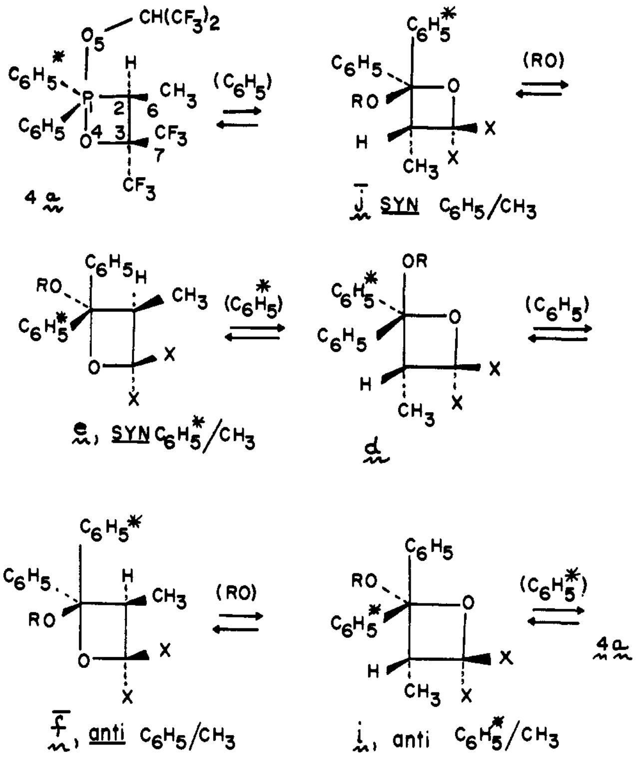


When the oxaphosphetane **4** was heated to 150°, an olefin, **9**, and a phosphinate, **10**, were produced,[3] completing the Wittig reaction.



If the oxaphosphetane **4** has the geometry of a trigonal bipyramid with the phosphorus at its center, the molecule can exist as 12 stereoisomers, *i.e.*, *six diastereomers*, each one of them consisting of a pair of enantiomers.[5] This isomer number is based on the reasonable assumption that the four-membered ring must always occupy an apical–equatorial plane where the OPC angle is 90°, and never a diequatorial plane or a diapical plane where the OPC angle would have to be 120 or 180°, respectively.[5,6] Three diastereomers, **4a**, **e**, **f̄** (Scheme I[6,7]), have the ring oxygen in an apical position; the other three diastereomers, **j̄**, **d**, **i**, have the ring oxygen in an equatorial position. Two diastereomers, **4a** and **d**, have the alkoxy group (RO) in apical positions; however, only the former, **4a**, has *both* oxygen atoms in apical positions. The pair **e**, **f̄** differ only in the relationship of the phenyl at phosphorus and the methyl at carbon (syn and anti configurations). The pair, **j̄**, **i**, differ also in the relationship of phenyl and methyl groups, but, now, both oxygen atoms occupy equatorial positions.

Scheme I



X = CF$_3$; R = (CF$_3$)$_2$CH

In Scheme I,[6,7] the six diastereomers were derived[8] by

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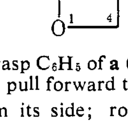
[4] (a) G. Wittig and M. Rieber, *Justus Liebigs Ann. Chem.*, **562**, 177 (1949); (b) S. Trippett, *Pure Appl. Chem.*, **9**, 255 (1964); (c) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

[5] (a) F. Ramirez, *Bull. Soc. Chim. Fr.*, 3491 (1970); (b) F. Ramirez, J. F. Pilot, C. P. Smith, S. B. Bhatia, and A. S. Gulati, *J. Org. Chem.*, **34**, 3385 (1969).

[6] The notation used in Scheme I is explained in P. C. Lauterbur and F. Ramirez, *J. Amer. Chem. Soc.*, **90**, 6722 (1968).

[7] The numbering in **4a** corresponds to the numbering of the 35 atoms located by the X-ray analysis and reported in this paper as shown in Figure 1. A systematic name for this substance is 2,2-diphenyl-2-(bis(trifluoromethyl)methoxy-3-methyl-4,4-bis(trifluoromethyl)-2,2-dihydro-1,2-oxaphosphetane. This is based on the name 2,2-dihydro-1,2-oxaphosphetane for the parent ring system



[8] To convert **a** into **j̄**, grasp C_6H_5 of **a** (the pivot), push back the two apical groups (O5, O4), and pull forward two equatorial groups (C_6H_5*, C2). This gives **j̄** lying on its side; rotate it 90° counterclockwise

successive pseudorotations.[9] One can start with bipyramid **4a** and return to it by six pseudorotations without retracing any steps;[6] *i.e.*, the six diastereomers form part of a closed cycle of six isomerizations by pseudorotation. Interconversions among isomers within this closed cycle does not require the placement of the four-membered ring in the forbidden diequatorial plane.[10]

In order to determine the molecular geometry of this substance and to make a definitive choice among the six possible diastereomers in Scheme I, we carried out an X-ray spectrometric analysis. The results are presented in this paper.

Experimental Section

The oxaphosphetane **4** was prepared as described.[3] The substance was unstable in *moist* air and thus a number of crystals were sealed in Lindemann glass capillaries in a dry argon atmosphere. Preliminary Weissenberg and precession photographs showed systematic absences were for h, k, and $l \neq 2n$ for $h00$, $0k0$, $00l$ reflections. The space group is therefore $P2_12_12_1$. Cell dimensions were obtained by least-squares method refining on twenty 2θ values measured on an XRD-5 diffractometer. Three crystals were required to collect the data since the crystals decomposed in X-rays.

The lattice parameters are $a = 8.804 \pm 0.006$, $b = 10.115 \pm 0.003$, and $c = 25.586 \pm 0.006$. Volume of the cell is 2279 Å^3; the calculated density based on four molecules per unit cell was 1.596 g cm^{-3}. The linear absorption coefficient for Mo Kα ($\lambda = 0.7107$ Å) radiation is 2.5 cm^{-1}. $F(000)$ is 1096. The intensities of 1734 independent reflections were measured by a θ–2θ scan technique on a General Electric XRD-5 diffractometer equipped with single crystal orienter and spectrogoniometer using scintillation counter and pulse height analyzer as a detector. Each peak was scanned for 100 sec, and the background for 50 sec, on each side of the peak. The scan rate was 2°/min in 2θ; the take-off angle was 4°; zirconium filtered molybdenum radiation was used. The intensities of three selected reflections were measured every 2 hr to check the stability of the crystal and to bring all intensities to a common scale. This was particularly important, since three separate crystals were required for data collection due to the decomposition of the crystals in the X-ray beam. Lorentz and polarization factors were applied using an SDS Sigma-7 computer.[11] No absorption corrections were made. For structure factor calculations, scattering factors used were from International Tables for X-ray Crystallography.[12] Extinction corrections were not applied. Anomalous terms of the form factors were not included.

Structure Determination and Refinement. The structure was solved from the Patterson map by location of the phosphorus atom followed by several successive Fourier and difference Fourier maps. Four cycles of block-diagonal least-squares refinement refining the positional parameters and individual temperature factors reduced the R to 16.2%. Additional cycles of refinement varying positional parameters and individual anisotropic temperature factors reduced the R to 12.6% for 1239 observed reflections, minimizing $\Sigma w(|F_o| - |F_c|)^2$. A weighting scheme described by Stout and Jensen[13a] was used throughout the refinement. A final difference map showed no significant features above the background.

Examination of the thermal parameters and an ORTEP plot of thermal ellipsoids showed that these probably have little physical significance, even though all were, in fact, real. Many were extremely anisotropic with very large mean displacements. The general pattern was one which indicates large and extremely anisotropic vibrations on the outskirts of the molecule with smaller vibrations of the phosphorus atoms and those atoms directly attached to it. Examples of some highly anisotropic vibrations are those of C(9), C(12), and C(23), where mean displacements are recorded as minimum, medium, and maximum; C(9), 0.03, 0.27, 0.39 Å; C(13), 0.03, 0.32, 0.39 Å; C(23), 0.02, 0.22, 0.33 Å. Although there is a general pattern of librational motion of the phenyl and fluoromethyl groups, it seems most likely that refinement of the anisotropic thermal parameters does not produce significant improvement of the structure and is really only a means of reducing the R factor by increasing the number of parameters.

The high final R factor is undoubtedly due to the fact that decomposition occurred in the X-ray beam requiring the use of three different crystals for data collection. The final atomic parameters and thermal parameters are given in Table I and Table II.[13b]

Table I. Atomic Coordinates and Their Standard Deviations (in Parentheses)

Atom	x	y	z
P(1)	0.1863 (6)	0.4957 (5)	0.3708 (2)
C(2)	0.2197 (19)	0.3989 (15)	0.4299 (6)
C(3)	0.3053 (24)	0.2995 (16)	0.3965 (8)
O(4)	0.2733 (14)	0.3462 (10)	0.3480 (4)
O(5)	0.0944 (14)	0.6151 (11)	0.4060 (5)
C(6)	0.3068 (27)	0.4684 (24)	0.4778 (8)
C(7)	0.4793 (24)	0.2902 (23)	0.4104 (10)
C(8)	0.2471 (27)	0.1511 (29)	0.4076 (11)
C(9)	−0.0547 (21)	0.6717 (17)	0.4006 (9)
C(10)	−0.1335 (21)	0.6188 (21)	0.4544 (9)
C(11)	−0.0365 (21)	0.8044 (20)	0.3992 (9)
C(12)	0.3286 (20)	0.6024 (14)	0.3482 (7)
C(13)	0.4021 (20)	0.5683 (20)	0.2984 (10)
C(14)	0.5145 (22)	0.6572 (23)	0.2756 (10)
C(15)	0.5524 (23)	0.7724 (21)	0.3067 (11)
C(16)	0.4932 (24)	0.7986 (21)	0.3559 (9)
C(17)	0.3714 (22)	0.7133 (17)	0.3772 (10)
C(18)	0.0314 (19)	0.4771 (15)	0.3245 (5)
C(19)	−0.0658 (22)	0.3721 (21)	0.3288 (8)
C(20)	−0.1784 (23)	0.3571 (21)	0.2884 (9)
C(21)	−0.1872 (24)	0.4446 (19)	0.2487 (8)
C(22)	−0.0911 (22)	0.5532 (29)	0.2437 (8)
C(23)	0.0242 (19)	0.5745 (19)	0.2849 (6)
F(24)	0.5492 (15)	0.2149 (14)	0.3682 (6)
F(25)	0.5251 (14)	0.2567 (15)	0.4537 (6)
F(26)	0.5437 (13)	0.4162 (12)	0.3960 (5)
F(27)	0.3053 (17)	0.0704 (11)	0.3706 (6)
F(28)	0.2705 (17)	0.1123 (14)	0.4548 (6)
F(29)	0.1009 (14)	0.1556 (12)	0.3968 (6)
F(30)	−0.2697 (14)	0.6586 (17)	0.4530 (6)
F(31)	−0.0669 (15)	0.6559 (15)	0.4976 (4)
F(32)	−0.1415 (14)	0.4894 (12)	0.4540 (5)
F(33)	0.0472 (13)	0.8669 (13)	0.4433 (5)
F(34)	−0.1642 (14)	0.8817 (13)	0.4019 (5)
F(35)	0.0266 (14)	0.8537 (12)	0.3560 (5)

Results

X-Ray Analysis. The interatomic distances are given in Table III, and the bond angles in Table IV.

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around the pivot axis, C_6H_5–P, and then turn it upside down (*i.e.*, rotate 180° around the 04–P axis).

[9] For documentation on pseudorotation, see ref 6 and (a) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, 20, 245 (1966); (b) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969). (c) NOTE ADDED IN PROOF. It has been recently suggested that the permutational isomerization of related cyclic oxyphosphoranes should occur by the *turnstile rotation* mechanism and not the Berry pseudorotation mechanism. See: 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); I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Accounts Chem. Res.*, 4, 288 (1971).

[10] Note that, *in this particular system*, the stereomutation of a syn into an anti isomer requires only two pseudorotations: $\mathbf{e} \rightleftarrows \mathbf{d} \rightleftarrows \bar{\mathbf{f}}$, and $\bar{\mathbf{j}} \rightleftarrows \mathbf{a} \rightleftarrows \mathrm{i}$.

[11] NRC-2, Data Reduction Program, written by F. R. Ahmed, NRC-8, Fourier Program, NRC-10, Block-Diagonal Least-Squares Program written by F. R. Ahmed of National Research Council, Ottawa, Ontario, Canada. These programs are adapted for SDS Sigma-7 computer. The rest of the programs are written by C. N. Caughlan, G. D. Smith, and E. L. Enwall.

[12] "International Tables for X-ray Crystallography," Vol. III, Birmingham, England, 1962, Table 3.3.1A, p 202.

[13] (a) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968, p 457, eq H-14. The instrument stability of 0.02 was used. (b) A table of observed and calculated structure amplitudes from this analysis has been deposited as Document No. NAPS-01469 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 and Their Standard Deviations (in Parentheses)

Atom	$\beta_{11}{}^{a}$	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
P(1)	0.0187 (10)	0.0068 (4)	0.0012 (1)	−0.0002 (4)	−0.0011 (5)	−0.0006 (15)
C(2)	0.0215 (38)	0.0079 (19)	0.0002 (3)	−0.0009 (12)	−0.0017 (16)	0.0087 (46)
C(3)	0.0300 (47)	0.0064 (21)	0.0019 (4)	0.0017 (15)	−0.0012 (24)	−0.0173 (57)
O(4)	0.0244 (27)	0.0047 (11)	0.0015 (2)	0.0008 (9)	−0.0077 (12)	0.0067 (28)
O(5)	0.0245 (27)	0.0077 (14)	0.0021 (3)	−0.0045 (11)	−0.0007 (14)	−0.0095 (33)
C(6)	0.0329 (55)	0.0260 (43)	0.0022 (5)	−0.0060 (25)	−0.0117 (27)	0.0318 (84)
C(7)	0.0249 (51)	0.0191 (38)	0.0036 (7)	−0.0085 (27)	−0.0033 (29)	0.0058 (67)
C(8)	0.0331 (11)	0.0282 (47)	0.0036 (7)	−0.0037 (23)	0.0026 (32)	−0.0034 (84)
C(9)	0.0140 (37)	0.0070 (22)	0.0041 (6)	0.0039 (20)	0.0062 (25)	−0.0134 (48)
C(10)	0.0136 (40)	0.0193 (34)	0.0035 (6)	0.0018 (25)	0.0029 (24)	−0.0124 (64)
C(11)	0.0139 (38)	0.0145 (30)	0.0032 (6)	−0.0015 (22)	−0.0021 (24)	0.0115 (55)
C(12)	0.0135 (34)	0.0055 (17)	0.0017 (4)	0.0057 (14)	0.0016 (17)	0.0067 (44)
C(13)	0.0076 (36)	0.0150 (29)	0.0044 (7)	0.0036 (23)	−0.0023 (25)	0.0192 (53)
C(14)	0.0116 (39)	0.0188 (35)	0.0048 (8)	0.0101 (28)	0.0037 (25)	0.0125 (63)
C(15)	0.0138 (41)	0.0136 (30)	0.0053 (8)	0.0046 (26)	0.0040 (30)	−0.0079 (60)
C(16)	0.0225 (48)	0.0177 (34)	0.0035 (7)	0.0087 (25)	−0.0098 (27)	0.0100 (65)
C(17)	0.0141 (40)	0.0063 (20)	0.0053 (8)	0.0074 (22)	0.0034 (26)	−0.0064 (48)
C(18)	0.0171 (34)	0.0051 (19)	0.0005 (3)	0.0011 (12)	−0.0029 (14)	0.0033 (41)
C(19)	0.0160 (40)	0.0173 (31)	0.0027 (5)	0.0020 (22)	−0.0099 (23)	0.0084 (62)
C(20)	0.0156 (39)	0.0190 (33)	0.0032 (6)	−0.0055 (23)	0.0037 (24)	0.0097 (70)
C(21)	0.0217 (43)	0.0167 (29)	0.0019 (4)	0.0009 (19)	−0.0039 (23)	0.0114 (65)
C(22)	0.0149 (44)	0.0416 (62)	0.0019 (5)	−0.0065 (28)	0.0026 (22)	−0.0096 (78)
C(23)	0.0124 (35)	0.0196 (30)	0.0002 (3)	0.0005 (15)	−0.0027 (15)	0.0072 (53)
F(24)	0.0333 (31)	0.0247 (22)	0.0041 (4)	−0.0059 (16)	0.0063 (18)	0.0135 (43)
F(25)	0.0288 (29)	0.0339 (28)	0.0035 (4)	0.0063 (16)	−0.0128 (16)	0.0038 (46)
F(26)	0.0201 (23)	0.0204 (19)	0.0042 (4)	−0.0004 (14)	0.0010 (14)	0.0046 (35)
F(27)	0.0467 (36)	0.0110 (13)	0.0057 (4)	−0.0090 (14)	−0.0133 (22)	0.0085 (41)
F(28)	0.0505 (37)	0.0257 (23)	0.0041 (4)	0.0135 (17)	−0.0169 (19)	−0.0290 (48)
F(29)	0.0314 (28)	0.0142 (16)	0.0047 (4)	−0.0012 (13)	−0.0047 (17)	0.0003 (36)
F(30)	0.0248 (27)	0.0377 (29)	0.0036 (3)	0.0067 (18)	0.0032 (14)	−0.0167 (44)
F(31)	0.0330 (27)	0.0348 (26)	0.0010 (2)	−0.0014 (13)	−0.0004 (11)	0.0022 (47)
F(32)	0.0313 (27)	0.0163 (16)	0.0046 (4)	0.0005 (15)	0.0119 (16)	−0.0199 (40)
F(33)	0.0272 (25)	0.0230 (20)	0.0026 (3)	−0.0028 (13)	−0.0032 (13)	−0.0070 (38)
F(34)	0.0301 (27)	0.0221 (20)	0.0038 (3)	−0.0040 (14)	−0.0031 (16)	0.0012 (42)
F(35)	0.0321 (28)	0.0187 (18)	0.0029 (3)	0.0057 (13)	0.0064 (14)	−0.0062 (36)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{23}kl + \beta_{13}hl + \beta_{12}hk)]$.

Some intermolecular distances are shown in Table V. Figure 1 illustrates the structure of a molecule projected on the *bc* plane.

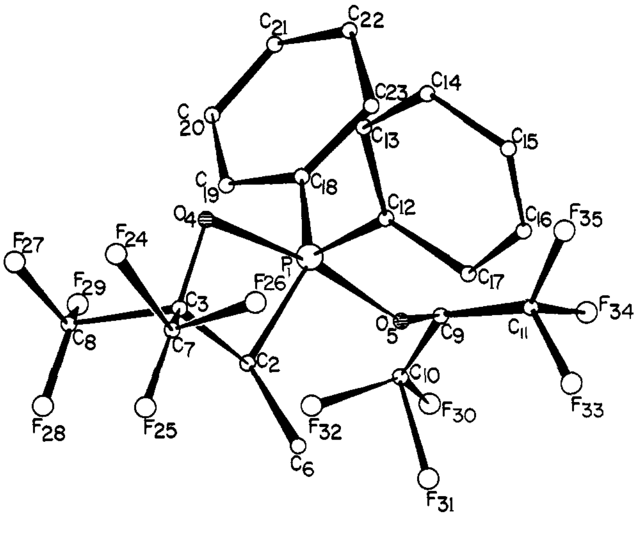

Figure 1. Molecular structure of $PO_2(C_6H_5)_2(CF_3)_4C_3H_2$ projected on the *bc* plane.

The phosphorus was at the center of a *distorted* trigonal bipyramid with the four-membered ring in the apical–equatorial plane.[14] The two apical positions were occupied by oxygen atoms. Two equatorial positions were occupied by phenyl rings and the third by an aliphatic carbon of the oxaphosphetane ring.

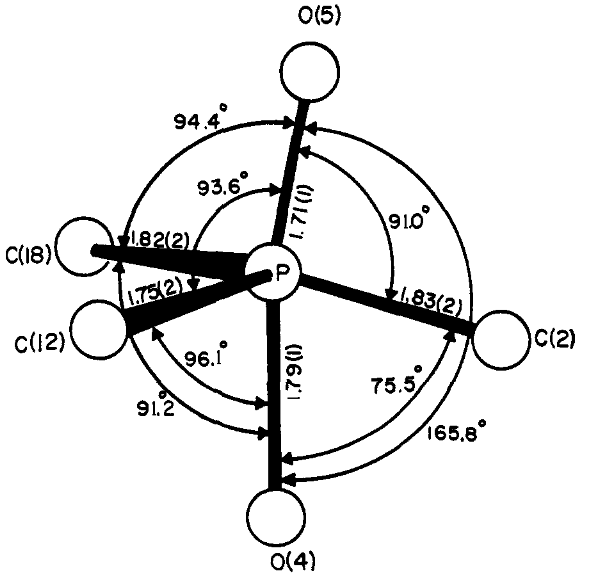

Figure 2. Trigonal bipyramidal coordination around phosphorus in $PO2(C_6H_5)_2(CF_3)_4C_3H_2$.

This distribution of atoms in the bipyramid is consistent with the view that elements of high electronegativity tend to occupy the apical positions, and elements of low

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(14) F. Ramirez, *Accounts Chem. Res.*, 1, 168 (1968).

Table III. Interatomic Distances and Their Standard Deviations (in Parentheses)

Atoms	Distance, A
P(1)–C(2)	1.83 (2)
P(1)–O(4)	1.79 (1)
P(1)–O(5)	1.71 (1)
P(1)–C(12)	1.75 (2)
P(1)–C(18)	1.82 (2)
C(2)–C(3)	1.52 (2)
C(2)–C(6)	1.61 (3)
C(3)–O(4)	1.36 (2)
C(3)–C(7)	1.58 (3)
C(3)–C(8)	1.61 (3)
O(5)–C(9)	1.44 (2)
C(7)–F(24)	1.46 (3)
C(7)–F(25)	1.23 (3)
C(7)–F(26)	1.44 (3)
C(8)–F(27)	1.35 (3)
C(8)–F(28)	1.29 (3)
C(8)–F(29)	1.32 (3)
C(9)–C(10)	1.63 (3)
C(9)–C(11)	1.35 (3)
C(10)–F(30)	1.27 (2)
C(10)–F(31)	1.31 (2)
C(10)–F(32)	1.31 (2)
C(11)–F(33)	1.49 (2)
C(11)–F(34)	1.37 (2)
C(11)–F(35)	1.33 (3)
C(12)–C(13)	1.47 (3)
C(12)–C(17)	1.40 (3)
C(13)–C(14)	1.46 (3)
C(14)–C(15)	1.45 (3)
C(15)–C(16)	1.39 (4)
C(16)–C(17)	1.48 (3)
C(18)–C(19)	1.37 (3)
C(18)–C(23)	1.42 (2)
C(19)–C(20)	1.44 (3)
C(20)–C(21)	1.35 (3)
C(21)–C(22)	1.39 (3)
C(22)–C(23)	1.48 (3)

Table IV. Bond Angles and Their Standard Deviations (in Parentheses)

Atoms	Angle, deg
C(2)–P(1)–O(4)	75.5 (6)
C(2)–P(1)–O(5)	91.0 (7)
C(2)–P(1)–C(12)	119.3 (8)
C(2)–P(1)–C(18)	127.3 (7)
O(4)–P(1)–O(5)	165.8 (6)
O(4)–P(1)–C(12)	96.1 (7)
O(4)–P(1)–C(18)	91.2 (6)
O(5)–P(1)–C(12)	94.4 (7)
O(5)–P(1)–C(18)	93.6 (7)
C(12)–P(1)–C(18)	112.7 (8)
P(1)–C(2)–C(3)	88.1 (11)
P(1)–C(2)—C(6)	118.3 (12)
C(3)–C(2)–C(6)	118.8 (15)
C(2)–C(3)–O(4)	100.5 (14)
C(2)–C(3)–C(7)	113.2 (16)
C(2)–C(3)–C(8)	111.0 (16)
O(4)–C(3)–C(7)	115.5 (16)
O(4)–C(3)–C(8)	114.8 (16)
C(7)–C(3)–C(8)	102.3 (17)
P(1)–O(4)–C(3)	94.8 (10)
P(1)–O(5)–C(9)	131.4 (11)
C(3)–C(7)–F(24)	105.9 (17)
C(3)–C(7)–F(25)	122.7 (20)
C(3)–C(7)–F(26)	105.7 (17)
F(24)–C(7)–F(25)	112.7 (19)
F(24)–C(7)–F(26)	96.1 (16)
F(25)–C(7)–F(26)	110.2 (19)
C(3)–C(8)–F(27)	108.5 (19)
C(3)–C(8)–F(28)	113.6 (20)
C(3)–C(8)–F(29)	104.0 (19)
F(27)–C(8)–F(28)	114.4 (22)
F(27)–C(8)–F(29)	104.2 (20)
F(28)–C(8)–F(29)	113.3 (21)
O(5)–C(9)–C(10)	100.2 (14)
O(5)–C(9)–C(11)	106.8 (16)
C(10)–C(9)–C(11)	113.5 (17)
C(9)–C(10)–F(30)	106.1 (17)
C(9)–C(10)–F(31)	115.4 (17)
C(9)–C(10)–F(32)	110.1 (16)
F(30)–C(10)–F(31)	110.9 (18)
F(30)–C(10)–F(32)	105.5 (17)
F(31)–C(10)–F(32)	108.4 (17)
C(9)–C(11)–F(33)	117.4 (17)
C(9)–C(11)–F(34)	117.9 (18)
C(9)–C(11)–F(35)	116.3 (18)
F(33)–C(11)–F(34)	97.1 (14)
F(33)–C(11)–F(35)	105.3 (15)
F(34)–C(11)–F(35)	99.9 (15)
P(1)–C(12)–C(13)	117.2 (13)
P(1)–C(12)–C(17)	120.8 (14)
C(13)–C(12)–C(17)	122.0 (16)
C(12)–C(13)–C(14)	120.1 (18)
C(13)–C(14)–C(15)	115.6 (20)
C(14)–C(15)–C(16)	124.4 (21)
C(15)–C(16)–C(17)	119.7 (20)
C(12)–C(17)–C(16)	117.9 (18)
P(1)–C(18)–C(19)	119.7 (13)
P(1)–C(18)–C(23)	115.4 (12)
C(19)–C(18)–C(23)	124.8 (16)
C(18)–C(19)–C(20)	116.9 (18)
C(19)–C(20)–C(21)	120.8 (20)
C(20)–C(21)–C(22)	123.5 (20)
C(21)–C(22)–C(23)	117.8 (19)
C(18)–C(23)–C(22)	116.1 (16)

electronegativity, the equatorial positions, in trigonal bipyramidal phosphorus.[14,15a,b]

The results of the X-ray analysis show that the oxaphosphetane **4** has configuration **4a** of Scheme I, in the crystalline state.

The distortion of the trigonal bipyramid can be seen in the deviation of the bond angles from the ideal ones of 180, 120, and 90°. Thus, the diapical axis is bent, since the O4–P1–O5 angle is 165.8°. The diequatorial bond angles ranged from 112.7 to 127.3°.[15c] The apical–equatorial bond angles ranged from 75.5 to 96.1°.

The shape of the four-membered oxaphosphetane ring is quite interesting as can be seen in partial formula **11**. This ring is nearly planar, with the P1 and C3 atoms 0.04 and 0.06 Å, respectively, above the plane, and the C2 and O4 atoms 0.05 and 0.06 Å, respectively, below the plane. The plane containing atoms C2–P1–O4 and the plane containing atoms C2–C3–O4 formed a dihedral angle of 11°.

The coordination around phosphorus is illustrated in Figure 2, which illustrates the pentavalent nature of phosphorus and gives some bond angles and distances. P1 is 0.07 Å above, while the C2, C12, and C18 are about 0.02 Å below the least-squares plane formed by P1, C2, C12, and C18.

The trifluoromethyl group (C7) attached to the C3 position of the oxaphosphetane ring is in the cis con-

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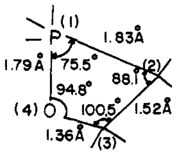
(15) (a) E. L. Muetterties, N. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963). (b) H. A. Bent, *Chem. Rev.*, **60**, 275 (1960). (c) NOTE ADDED IN PROOF. The significant deviation of the diequatorial angle C18–P–C12 = 112.7° formed by the two carbons of the phenyl rings attached to the phosphorus, from the ideal value of 120°, is particularly interesting. This angle is about 14° smaller than another diequatorial angle C18–P–C2 formed by the carbon of a phenyl ring and the carbon of the four-membered ring (Figures 1 and 2). As discussed elsewhere, this structural feature of **4a** should facilitate the *turnstile rotation* mechanism in related cyclic oxyphosphoranes; see F. Ramirez and I. Ugi, "Advances in Physical Organic Chemistry," Vol. 9, V. Gold, Ed., Academic Press, London, 1971.

Table V. Intermolecular Distances below 3.6 Å

From	To	Symmetry[a]	Distance, A
C(6)	F(33)	3	3.37
C(6)	F(34)	3	3.44
C(8)	F(33)	1	3.49
C(10)	F(28)	3	3.40
C(14)	C(21)	2	3.46
C(16)	F(30)	2	3.54
C(16)	F(34)	2	3.35
C(16)	F(27)	1′	3.23
C(17)	F(31)	3	3.51
C(20)	F(24)	2′	3.46
C(21)	F(27)	4	3.47
C(21)	F(35)	4	3.17
C(22)	F(27)	4	3.48
C(22)	F(35)	4	3.30
F(25)	F(28)	3	3.45
F(26)	F(30)	2	3.29
F(26)	F(30)	2	3.29
F(26)	F(32)	2′	3.23
F(27)	F(33)	1	3.59
F(27)	F(35)	1	3.31
F(28)	F(33)	1	3.18
F(28)	F(31)	3	3.30
F(28)	F(32)	3	2.67
F(29)	F(33)	1	3.19
F(29)	F(35)	1	3.29
F(30)	F(31)	3	3.46
F(30)	F(33)	3	3.12

[a] 1, $x, y - 1, z$; 2, $x + 1, y, z$; 1′, $x, y + 1, z$; 2′, $x - 1, y, z$; 3, $^1/_2 + x, ^1/_2 - y, -z$; 4, $-x, ^1/_2 + y, ^1/_2 - z$.

figuration relative to the methyl group (C6) on C2 of the ring. *This trifluoromethyl group is far from being tetrahedral;* the bond angles ranged from 96.1 to 122.7°. On the other hand, the trifluoromethyl group (C8) on C3, which is cis to the hydrogen on C2, is tetrahedral as expected (bond angles from 104.0 to 114.4°). There was another trifluoromethyl group (C11) which was not tetrahedral, since its bond angles ranged from 97.1 to 117.9°. This group was part of the alkoxy function in the apical position. The second trifluoromethyl group (C10) of this function, however, was tetrahedral (bond angles from 105.5 to 115.4°).



11

The apical endocyclic P–O bond length was 1.79 Å, while the corresponding apical exocyclic P–O bond length was 1.71 Å. These distances are in agreement with the values predicted[16] for apical P–O bonds (1.76 Å), and suggest that there is little pd–π bonding in the apical P–O bonds of the oxaphosphetane **4a**. The apical endocyclic P–O bond length was 1.753 Å in a 1,3,2-dioxaphospholene with a five-membered ring.[17] Comparable P–O distances, 1.74 and 1.79 Å, have been reported[18] for other apical bonds in a bicyclic oxyphorane, $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

The distances of the two phenyl rings to the phosphorus were not identical, 1.75 and 1.82 Å. The shorter distance resembles that found[19] for a similar group in 1-phenyl-1,2,2,3,4,4-hexamethylphosphetanium bromide (1.78 Å) and the triphenylphosphonium ion[20] (1.72–1.80 Å). The longer distance agrees well with the P–C (aryl) distances (1.82 Å) in the bicyclic oxyphosphorane mentioned above.[18] Other reported P–C (aryl) bond distances are pentaphenylphosphorane;[21] complexed triphenylphosphine,[22] 1.830 Å; triphenylphosphorus,[23] 1.828 Å; 1,2,3-triphenyl-1,2,3-triphosphaindan,[24] 1.825 Å; and bis(diphenylphosphino)acetylene,[25] 1.832 Å.

The P–C2 (aliphatic) bond distance in the oxaphosphetane ring (1.83 Å) agrees well with another similar bond (1.82 Å) in the phosphorane[18] $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

The average C–C single bond was 1.55 Å. The C–O single bond distance was 1.36 Å in the ring and 1.43 Å in the alkoxy group. The C–F bond scattered from 1.22 to 1.49 Å but averaged to 1.35 Å in agreement with the average C–F value of 1.35 ± 0.03 and 1.335 ± 0.015 Å found in $(PCF_3)_5$[26] and $(PCF_3)_4$,[27] respectively. The average C–C lengths in the aromatic rings were 1.41 and 1.44 Å.

The distortions found in the trigonal bipyramid of **4a** (Figure 1), *i.e.*, the deviations from the ideal 180, 120, and 90° angles, and also the distortion of the tetrahedral bond angles found in two of the trifluoromethyl groups, could result from severe intramolecular crowding in trigonal bipyramidal phosphorus. This point has been emphasized[5,14,28,29] in connection with the relative stabilities of cyclic *vs.* noncyclic oxyphosphoranes,[28] and of pentacoordinated *vs.* tetracoordinated phosphorus in related systems.[29] Certain cyclic oxyphosphoranes, in which the presence of rings of suitable size and shape results in a decrease in the intramolecular crowding in the bipyramid, are much more stable than related noncyclic oxyphosphoranes.[28,29] This phenomenon is of particular significance in connection with the mechanism of hydrolysis of five-membered cyclic saturated[30,31] and unsaturated[31c] phosphate esters where cyclic oxyphosphoranes have been postulated as intermediates.[30–32]

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[26] C. J. Spencer and W. N. Lipscomb, *ibid.*, **14**, 250 (1961).

[27] G. J. Palenik and J. Donohue, *ibid.*, **15**, 564 (1962).

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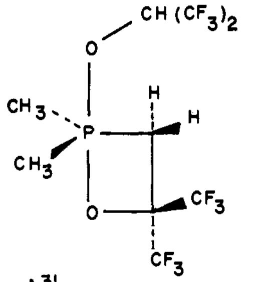
[31] (a) F. Ramirez, B. Hansen, and N. B. Desai, *J. Amer. Chem. Soc.*, **84**, 4588 (1962); (b) F. Ramirez, O. P. Madan, N. B. Desai, S. Meyerson, and E. M. Banas, *ibid.*, **85**, 2681 (1963); (c) D. Swank, C. N. Caughlan, F. Ramirez, O. P. Madan, and C. P. Smith, *ibid.*, **89**, 6503 (1967).

[32] (a) G. Aknes and K. Bergesen, *Acta Chem. Scand.*, **19**, 991 (1965); (b) **20**, 2508 (1966).

Nmr Spectrometry. The P nucleus of the oxaphosphetane **4a** was more effectively shielded (+32.1 ppm *vs.* H_3PO_4) than that of the dioxaphospholane **3** (+6.1 ppm). The parent trivalent phosphorus compound **7** had $\delta^{31}P = +12.1$ ppm.

The ^1H nmr spectrum of the oxaphosphetane **4a** in $CDCl_3$ solution at +30° had a signal at τ 8.33 ppm *vs.* TMS = 10 due to the methyl group attached to the ring. This signal was a doublet of doublets with $J_{HCCP} = 28.2$ cps and $J_{HCCH} = 7.7$ cps. The proton attached to the ring gave a signal at τ 4.83 ppm; this was a doublet of quartets with $J_{HCP} = 30.2$ cps and $J_{HCCH} = 7.7$ cps.

It has been shown[3] that the ^1H nmr spectrum of the closely related dimethyloxaphosphetane **12** did not change significantly when it was examined in $CDCl_3$ solution from −62 to +30° and in *o*-dichlorobenzene solution from +30° to *ca.* +80°. The spectrum of **12** had a doublet at τ 5.96 ppm, $J_{HCP} = 20.7$ cps, due to the two equivalent protons attached to the ring. The two equivalent methyl groups attached to the phosphorus gave a doublet at τ 8.01 ppm, $J_{HCP} = 15.0$ cps. The trigonal bipyramid **12**, and by analogy the related bipyramid **4a** (*cf.* Scheme I and Figure 1), were "frozen" in solutions from −62° to the temperatures at which they decomposed to olefins (*ca.* 90 to 150° depending on their stability). Apparently, the barrier of a pseudorotation, such as **4a** → j̄, which requires the simultaneous movement of two apical oxygens into equatorial positions, and of two equatorial carbons into apical positions, is quite high in this system. Moreover, the bond-angle deformations required to exchange the position, of the four-membered ring (which remains, however, in the apical–equatorial plane) could contribute to the high-energy barrier to pseudorotations.



12, $\delta^{31}P = +23.7$ ppm

The two trifluoromethyl groups C7 and C8, attached to the ring in the diphenylphosphetane **4a**, were not equivalent. The group that gave a ^{19}F signal at higher magnetic field should be the nontetrahedral C7 which is cis to the methyl, C6 (*cf.* Figure 1); the $\delta^{19}F = -2.0$ ppm *vs.* CF_3COOH as zero, in $CDCl_3$ at +30°. The group that gave a ^{19}F signal at lower magnetic field would then be the tetrahedral C8 which is cis to the hydrogen on the ring; the $\delta^{19}F = -7.4$ ppm. The spin–spin splitting among the fluorines of the two nonequivalent CF_3 groups had $J_{FCCCF} = 10.8$ cps. A long-range *FCCCH* spin–spin splitting with $J = 3.0$ cps was observed in the high-field ^{19}F signal attributed to C7; this presumably involves the proton at C2 trans to C7.

The two trifluoromethyl groups on the ring of the dimethylphosphetane **12** were equivalent and gave one singlet at $\delta^{19}F = +0.40$ ppm *vs.* CF_3COOH.[3]

The two CF_3 groups of the alkoxy group of **4a** (C10 and C11) were not equivalent as can be seen by examining their environment in Figure 1, and gave complex signals centered at about $^{19}F = -4.2$ and -5.0 ppm. In contrast the two CF_3 groups in the apical alkoxy of **12** were equivalent,[3] $^{19}F = -3.9$ ppm, $J_{FCCH} = 5.5$ cps.