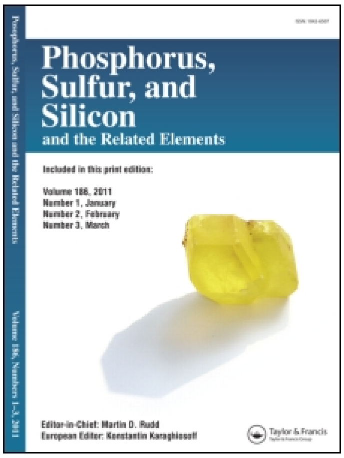


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CARBON-13 NMR STUDIES OF 1-PHENYL-4-PHOSPHORINANONE AND DERIVATIVES. SINGLE CRYSTAL X-RAY DIFFRACTION ANALYSIS OF 1-PHENYL-4-PHOSPHORINANONE 1-OXIDE AND 1-SULFIDE

S. D. Venkataramu[a]; K. D. Berlin[a]; S. E. Ealick[b]; J. R. Baker[b]; S. Nichols[b]; D. Van Der Helm[b]
[a] Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma [b] Department of Chemistry, University of Oklahoma, Norman, Oklahoma

To cite this Article Venkataramu, S. D. , Berlin, K. D. , Ealick, S. E. , Baker, J. R. , Nichols, S. and Van Der Helm, D.(1979) 'CARBON-13 NMR STUDIES OF 1-PHENYL-4-PHOSPHORINANONE AND DERIVATIVES. SINGLE CRYSTAL X-RAY DIFFRACTION ANALYSIS OF 1-PHENYL-4-PHOSPHORINANONE 1-OXIDE AND 1-SULFIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 7: 2, 133 — 141

To link to this Article: DOI: 10.1080/03086647908077457

URL: http://dx.doi.org/10.1080/03086647908077457

Phosphorus and Sulfur, 1979, Vol. 7, pp. 133–141
0308-664X/79/0702-0133$04.50/0

CARBON-13 NMR STUDIES OF 1-PHENYL-4-PHOSPHORINANONE AND DERIVATIVES. SINGLE CRYSTAL X-RAY DIFFRACTION ANALYSIS OF 1-PHENYL-4-PHOSPHORINANONE 1-OXIDE AND 1-SULFIDE

S. D. VENKATARAMU and K. D. BERLIN

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074

and

S. E. EALICK, J. R. BAKER, S. NICHOLS and D. VAN DER HELM

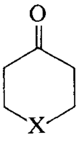
Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019

(*Received December 16, 1978; in final form February 5, 1979*)

The ^{13}C nmr spectral analysis has been recorded for the title compounds in $DCCl_3$ and all data appear to be in a accord with chair forms. Single crystal x-ray diffraction analysis of 1-phenyl-4-phosphorinanone 1-oxide and the corresponding sulfide revealed flattened chair forms in the solid state. Neither the solution data nor the x-ray data provided any evidence for a twist form for either compound as has been suggested for the carbon counterpart, namely, cyclohexane-1,4-dione.

INTRODUCTION

Active interest[1–4] in phosphorinanones attests to their potential as synthons. Quin and co-workers[4] have reported earlier ^{13}C nmr data for several 4-phosphorinanones but with a P-alkyl substituent. However, a phosphorus atom bound to an aryl substituent, as in (**1**) (as opposed to an alkyl substituent), has *d*-orbitals capable of participation in overlap with the π-bonding in the aryl group. In addition to evaluating this interaction, we have sought to assess any electrostatic interaction (field effect) resulting from the nuclear charge on the heteroatom caused by electronegative substitutents in compounds (**2–4**) and the positive end of the polarized carbonly group. Such an interaction could cause considerable distortion of the heterocyclic ring. A well known example is cyclohexane-1,4-dione which exists predominantly in a twist form both in solution and in the solid state.[5] Recently, ^{13}C nmr spectroscopy has been applied to the study of such effects in 1-hetera-4-cyclohexanones and other related systems.[6] In this paper we have addressed this possibility in the cases of (**2**) and (**3**) since it is well known that ^{13}C chemical shifts and ^{13}C–^{31}P coupling constant may be employed to probe such interactions.[7,8] We also herein report a single-crystal x-ray crystallographic analysis of oxide (**2**) and sulfide (**3**).



(**1**) $X = P{-}C_6H_5$
(**2**) $X = P(O)C_6H_5$
(**3**) $X = P(S)C_6H_5$
(**4**) $X = \overset{+}{P}(CH_3)C_6H_5, I^-$

DISCUSSION OF NMR DATA

^{13}C Nmr data for compounds (**1–4**) are presented in Table I. Examination of the data reveals an upfield shift for C(2,6) compared to that for C(3,5) regardless of the valence state at the phosphorus atom. In *N*-methyl-4-piperidone and tetrahydropyran-4-one, C(2,6) are shifted considerably downfield compared to C(3,5) whereas in tetrahydrothiopyran-4-one the shifts closely parallel that in phosphorus systems.[6] Logically, the greater electronegativity of the systems containing N and O *vs.* S and P should account for the upfield shift of C(2,6) for the latter analogs compared to that for the former systems.[9]

TABLE I

^{13}C nmr data for 1-phenyl-4-phosphorinanone and derivatives[a]

Carbon[b]	(1)	(2)	(3)	(4)[c]
PCH_3	—	—	—	6.62 (51.59)
C(2,6)	23.66 (15.47)	27.15 (66.05)	30.94 (51.58)	17.36 (50.66)
C(3,5)	38.21 (1.23)	36.35 (5.89)	36.64 (5.31)	34.63 (5.99)
C(4)	209.71 (1.60)	206.92 (8.89)	206.34 (7.76)	203.58 (8.13)
C(7)	136.98 (17.04)	131.16 (99.00)	130.37 (80.67)	119.30 (84.43)
C(8,12)	129.83 (14.17)	129.89 (9.49)	130.28 (10.39)	131.79 (9.80)
C(9,11)	128.54 (4.37)	128.82 (11.80)	128.73 (12.39)	129.37 (12.56)
C(10)	128.05 (<0.50)	132.72 (2.72)	131.97[d]	133.97[d]

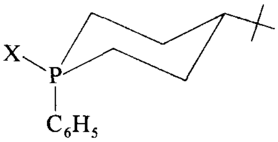
[a] Spectra recorded in $DCCl_3$ with TMS (1–5%) as internal standard; Chemical shifts are in ppm downfield from TMS; ^{31}P—^{13}C coupling constants in parentheses are in hertz.

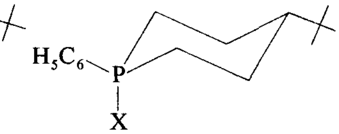
[b] See Figure 3 for number of positions.

[c] Spectrum recorded in $DCCl_3$ + DMSO (1 : 1).

[d] Coupling not clearly discernible.

More striking in the spectra of phosphorinanones (**1–4**), however, is the marked differences in $^1J_{PC}$ as opposed to $^2J_{PC}$ values (15.47 *vs.* 1.23 Hz in phosphine **1**). Quin and co-workers[4] have shown that $^2J_{PC}$ is of considerable utility in establishing the conformational preference of a phosphorus substituent in a phosphorinane system. Very recently, ^{13}C nmr data for *cis*- and *trans*-4-*tert*-butyl-1-phenyl-phosphorinane (**5a** and **5b**, respectively) have been reported.[1] The $^2J_{PC}$ values in (**5a**) and (**5b**) are 0 and 5.1 Hz, respectively.[1] In a number of phosphorinanes the same trend is seen.[3,4,11] Clearly, smaller $^2J_{PC}$ values are associated with a periplanar arrangement of the lone pair on phosphorus and P—C(3) or P—C(5) bonds. The value of 1.23 Hz found in ketophosphine (**1**) implies greater preponderance of the conformer with the axial phenyl substituent in solution which is also consistent with the x-ray data of the solid.[10]

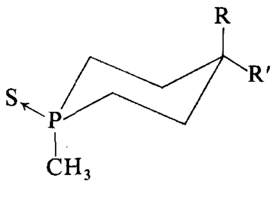




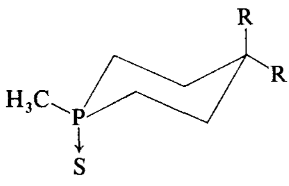
(**5a**) X = lone pair
(**6a**) X = O

(**5b**) X = lone pair
(**6b**) X = O

Interestingly, the $^2J_{PC}$ value (Table I) in oxide (**2**) and sulfide (**3**) is 5.89 and 5.31 Hz, respectively. In comparison, sharp differences exist in the $^2J_{PC}$ value of isomeric oxides (**6a**) and (**6b**) (3.8 *vs.* 5.8 Hz)[1] and several pairs of sulfides [11] such as (**7a**) and (**7b**) (5 *vs.* 6 Hz), (**8a**) and (**8b**) (4 *vs.* 6 Hz), and (**9a**) and (**9b**) (8 *vs.* 6 Hz). In our present study, x-ray analysis was performed and the data indicate that oxide (**2**) and sulfide (**3**) have an equatorial phenyl group in the solid state. Many factors have been discussed[11,12] for the preference of O and S atom to occupy an axial position on the basis of a few examples.



(**7a**) R = H; R′ = OH
(**8a**) R = OH; R′ = CH_3
(**9a**) R = OH; R′ = C_6H_5



(**7b**) R = H; R′ = OH
(**8b**) R = OH; R′ = CH_3
(**9b**) R = OH; R′ = C_6H_5

A still higher value of 5.99 Hz for the two bond P—C coupling is found in the quaternary salt (**4**). Unfortunately, ^{13}C nmr data for isomeric quaternary salts in the phosphorinane family, with which the $^2J_{PC}$ value could be compared, are unavailable. A previous ^1H nmr study of phosphorinane methiodide was indecisive.[12] Consequently, we have tentatively concluded that the similar $^2J_{PC}$ value in the series (**2–4**) implies the methyl group in the quaternary salt (**4**) also bonds from an axial position. Moreover, one must assume an equilibrium in solution resulting from ring reversal in (**2–4**) still results in a heavy favoring of the conformer with an equatorial P—C_6H_5 bond as found in the crystal analysis of (**2**) and (**3**).

With respect to the electronic interactions in phosphorinanones (**1–4**), the carbonyl carbon chemical shifts provide some insight. In ketophosphine (**1**), C(4) is situated at 209.71 ppm which, when compared with the reported[6] shifts in 1-methyl-4-

piperidone (206.2 ppm), tetrahydropyran-4-one (206.2 ppm) and tetrahydrothiapyran-4-one (208.0 ppm), it not suggestive of any P···C=O interaction. Even if such an interaction did exist, the effect must surely be more pronounced in 1-methyl- and 1-ethyl-4-phosphorinanones due to electron donating ability of the alkyl substituents. However, the C(4) atom in 1-methyl- and 1-ethyl-4-phosphorinanones is located in the same region (209.0 and 210.2 ppm respectively).[4] Of course, this does not preclude the possibility that the carbonyl carbon in these phosphorinanones may cause, in part, the lone pair to be biased in favor of one position.

Surprisingly, large carbonyl carbon upfield shifts in the compounds (**2**–**4**) are seen (Table I). These large shifts cannot be accounted for by transannular electron donation to the carbonyl carbon, since the quaternary salt (**4**) which has no free electron pair shows the maximum shift. A recent report by Hirsch and Havinga[6] describes one procedure for evaluating heteroatom group effects at C(2,6), C(3,5) and C(4) in 1-hetera-4-cyclohexanones. A plot of the chemical shifts of $^{13}C(4)$ in (**1**–**4**) relative to the chemical shift of the same carbon in cyclohexanone[13a] ($\delta^{CO}_{C_5H_8XO}-\delta^{CO}_{C_6H_{10}O}$) versus the chemical shifts of C(4) in 1-phenylphosphorinanes,[13b,c,d] relative to cyclohexane[13e] ($\delta^{C(4)}_{C_5H_{10}X}-\delta_{C_6H_{12}}$), shows some degree of scatter (Figure 1). One might tentatively conclude that these substituents on the phosphorus atom influence the carbonyl shifts in (**1**–**4**) in a non-linear fashion.

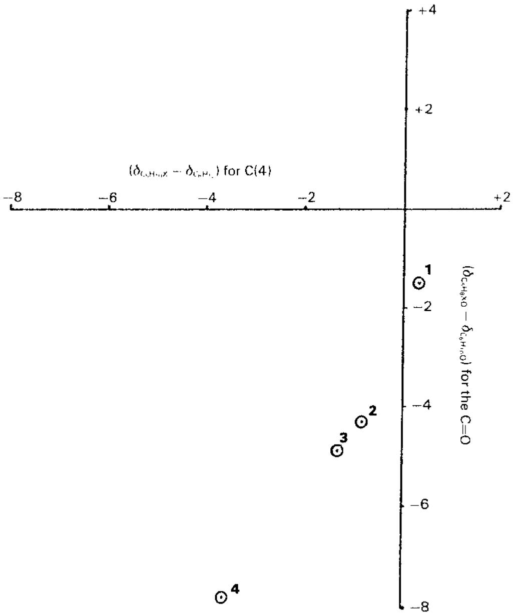


FIGURE 1 Comparison of the chemical shifts of carbonyl carbon in (**1**–**4**) (relative to cyclohexanone) with the chemical shifts of C(4) in 1-phenylphosphorinanes (relative to cyclohexane)[13] in ppm. (**1**) X = PC_6H_5; (**2**) X = $P(O)C_6H_5$; (**3**) X = $P(S)C_6H_5$; (**4**) X = $P(CH_3)C_6H_5, I^-$.

Both the chemical shifts and coupling constants of the phenyl carbons compared well with the values reported for 1-phenylphosphorinane and its derivatives.[2] Of particular interest is the C(10) of phosphine (**1**) which is shielded relative to the same carbon in other membranes of the family.

In conclusion, no transannular electron donation is detected in 1-phenyl-4-phosphorinanone (**1**). Apparently, derivatization at P in the parent phosphine (**1**) is not accompanied by much change in ring conformation in solution compared to that in the solid. Upfield carbonyl shifts [C(4)] in the compounds (**2**–**4**) is possibly a manifestiation of the substituents bound to phosphorus rather than of conformational deformation.

SINGLE CRYSTAL ANALYSIS

Stereoviews of molecules A and B of compound (**2**) and a single molecule of compound (**3**) are shown in Figures 2 and 3. In all three molecules, the six-membered ring was found to exist in a slightly flattened chair conformation as can be seen from the torsion angles reported in Table II. The major difference between molecules A and B of compound (**2**) is the orientation of the phenyl group which is in an equatorial position in both cases. In molecule A, the phenyl group is approximately parallel to the pseudo mirror plane passing through atoms P(1), O(13), C(4), O(14) and C(7) while in molecule B the phenyl group is approximately perpendicular to this plane. In compound (**3**), the phenyl group adopts an orientation similar to that of the phenyl group of molecule A of compound (**2**). The angles between the pseudo mirror planes and the plane defined by the phenyl groups are 17.8°, 77.1° and 20.7° for molecule A of (**2**), molecule B of (**2**) and (**3**), respectively.

Bond distances and numbering schemes for molecule (**2**A) and (**2**B) are given in Figure 4 and for molecule (**3**) in Figure 5. Bond angles for (**2**A) and (**2**B) are given in Figure 6 and bond angles for (**3**) are given in Figure 7. The bond distances for all three molecules are very similar with the largest differences being between the P—C(sp^3) bond distances of (**2**A) and (**2**B) (average value 1.801 Å) compared to those for (**3**) (average value 1.816 Å).

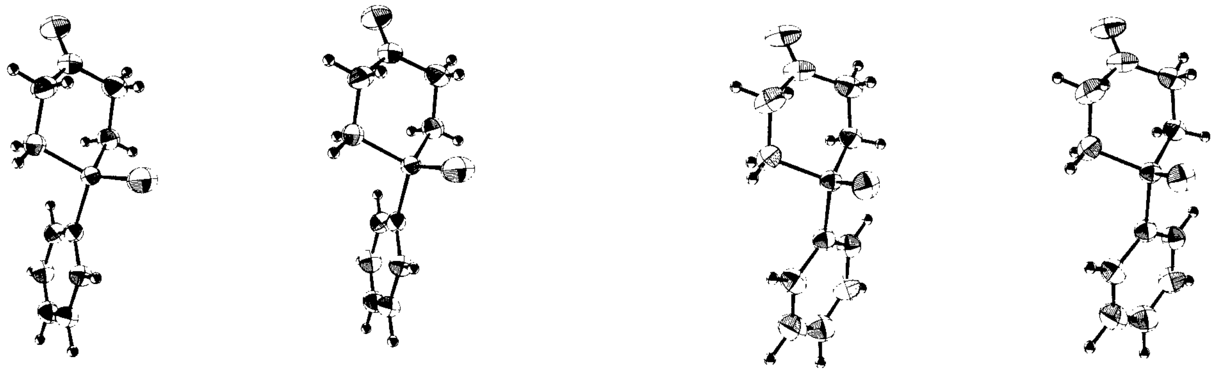


FIGURE 2 Stereoviews of molecule A and molecule B of 1-phenyl-4-phosphorinanone 1-oxide (**2**).[30]

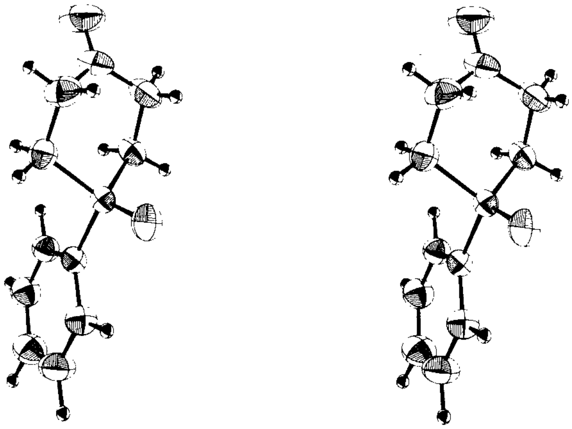


FIGURE 3 Stereoview of single molecule of 1-phenyl-4-phosphorinanone, 1-sulfide (**3**).[30]

The difference is possibly significant (4–5σ). In addition, the average value in (**2**) (1.801 Å) is slightly larger than the average of the P—C(sp^3) distances in 4-*t*-butyl-1-phenylphosphorinane 1-oxide (1.794 Å).[1] The P—C bond distances are affected by a number of factors including valency, ionization and hybridization.[14,15] Nevertheless, the values reported for the P—C (phenyl) of 1.799, 1.800 and 1.803 Å for (**2A**), (**2B**) and (**3**), respectively, compare well with the average 1.80 Å reported for a large number of compounds[16] and similar to the distances found in 4-*t*-butyl-1-phenylphosphorinane 1-oxide (1.805 Å) and 5,10-dihydro-10-methyl-5-phenylacridophosphin-10-ol 5-oxide[15] (1.806 Å). The P=O distances in the last two compounds, 1.483 Å and 1.488 Å, respectively, are slightly shorter than the average P=O distance in (**2**) (1.494 Å). The P=S distance in (**3**) [1.949(1) Å] can be compared with 1.936(5) Å and 1.947(5) Å in the structures of tri-*m*-tolyl- and tri-*o*-tolylphosphine sulfide.[17,18]

TABLE II

Torsion angles

	(**2A**)	(**2B**)	(**3**)
P(1)–C(2)–C(3)–C(4)	−56.7°	−59.8°	−59.2°
C(2)–C(3)–C(4)–C(5)	56.8	55.7	55.1
C(3)–C(4)–C(5)–C(6)	−56.9	−51.6	−53.3
C(4)–C(5)–C(6)–P(1)	57.4	51.9	56.8
C(5)–C(6)–P(1)–C(2)	−54.9	−53.0	−57.2
C(6)–P(1)–C(2)–C(3)	54.2	56.6	57.9

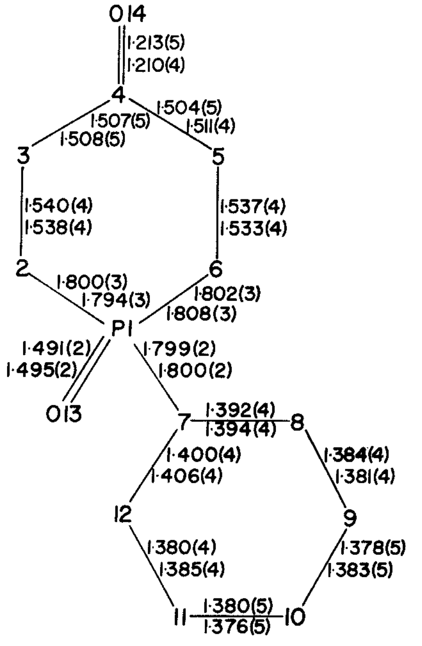


FIGURE 4 Bond distances for 1-phenyl-4-phosphorinanone 1-oxide (**2**). Top number is for molecule A and bottom number is for molecule B.

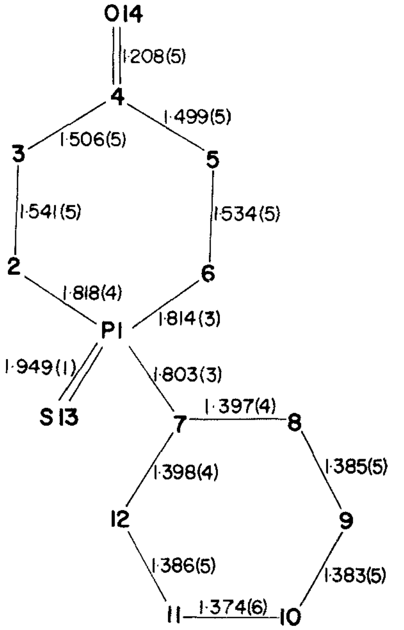


FIGURE 5 Bond distances for 1-phenyl-4-phosphorinanone 1-sulfide (3).

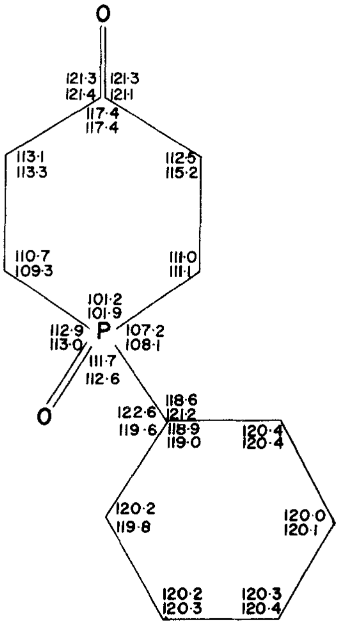


FIGURE 6 Bond angles for 1-phenyl-4-phosphorinanone 1-oxide (2). Top number is for molecule A and bottom number is for molecule B. Standard deviations are between 0.11° and 0.32°. Additional angles are C(6)–P(1)–O(13) = 114.5(113.0). C(2)–P(1)–C(7) = 108.6 (107.4)°; values for B are in parenthesis.

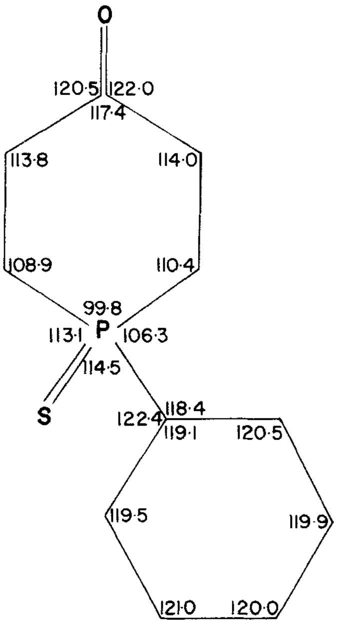


FIGURE 7 Bond angles for 1-phenyl-4-phosphorinanone 1-sulfide (3). Standard deviations are between 0.10° and 0.35°. Additional bond angles are S(13)–P(1)–C(6) = 113.7 and C(2)–P(1)–C(7) = 108.3°.

EXPERIMENTAL

General Data

Melting points were obtained with a Thomas–Hoover melting point apparatus and are uncorrected. Infrared Spectra were recorded on a Beckman IR-5A unit as KBr pellets. Proton-decoupled ^{13}C spectra were recorded on a XL-100 (15) Varian spectrometer equipped with a Nicolet TT-100 pulse-FT accessory. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Neutral alumina (EM Reagents) was employed for column chromatography.

1-Phenyl-4-Phosphorinanone Derivatives

The ketophosphine (**1**) was prepared by the literature method.[19] Recrystallization from aqueous ethanol and subsequent drying over P_2O_5 to constant weight gave pure ketophosphine (**1**), mp 43–44 (lit.[10,20,21] mp 42.5–43.5° and 43–44°). Ir, ^1H and ^{31}P nmr spectra of ketophosphine (**1**) have been reported.[19,20]

Oxidation of ketophosphine (**1**) in an improved yield (89%) was achieved by the dropwise addition of 30% H_2O_2 (11.7 g, 0.105 mole) to a stirred solution of (**1**) (19.2 g, 0.1 mole) in acetone (150 ml) with ice cooling. Usual work-up and recrystallization from acetone afforded oxide (**2**) as white crystals, mp 164–165° (lit.[22] mp 166); ir (KBr) ν 1715 cm^{-1} (C=O); ^1H nmr ($DCCl_3$) δ 2.16–3.40 (m, 8H, ring CH_2) and 7.49–7.89 (m, 5H, Ar–H).

Sulfide (**3**) was prepared by boiling a solution of the ketophosphine (**1**) (3.84 g, 20 mmoles) in benzene (100 ml) with elemental sulfur (0.68 g, 22 mmoles) for 3 h (N_2). The cooled solution was passed through a short column packed with neutral

TABLE III

Positional parameters ($\times 10^4$) for P, C and O atoms of 1-phenyl-4-phosphorinanone 1-oxide (**2**). Standard deviations for last digit in parenthesis

Molecule A

	X	Y	Z
P(1)	5583.6(1)	4262.9(6)	2625.7(6)
C(2)	4725(3)	3622(2)	3597(3)
C(3)	4334(4)	2114(3)	3220(3)
C(4)	3347(4)	1568(3)	1720(3)
C(5)	3887(4)	1980(3)	739(3)
C(6)	4230(3)	3475(3)	909(3)
C(7)	5625(3)	5990(2)	2806(2)
C(8)	6903(3)	6831(3)	3003(3)
C(9)	6960(3)	8160(3)	3090(4)
C(10)	5756(4)	8662(3)	3009(4)
C(11)	4489(3)	7846(3)	2838(3)
C(12)	4413(3)	6517(2)	2731(3)
O(13)	7086(2)	3987(2)	3012(2)
O(14)	2175(3)	807(3)	1322(3)

Molecule B

	X	Y	Z
P(1)	332.9(6)	4512.5(5)	2146.7(6)
C(2)	432(3)	3802(2)	3552(3)
C(3)	9(3)	2300(3)	3085(3)
C(4)	−1531(4)	1799(2)	1932(3)
C(5)	−1905(4)	2326(3)	654(3)
C(6)	−1556(3)	3823(2)	881(3)
C(7)	518(3)	6248(2)	2657(2)
C(8)	1236(3)	6887(2)	4029(3)
C(9)	1476(3)	8234(3)	4397(3)
C(10)	1014(4)	8959(3)	3403(3)
C(11)	292(4)	8345(3)	2045(3)
C(12)	33(3)	6995(3)	1658(3)
O(13)	1442(2)	4196(2)	1674(2)
O(14)	−2409(3)	955(2)	1998(3)

TABLE IV

Positional parameters ($\times 10^4$) for P, S, C and O atoms of 1-phenyl-4-phosphorinane 1-sulfide (**3**)

	X	Y	Z
P(1)	2265.7(7)	485.7(5)	1751.0(10)
C(2)	3810(3)	985(3)	2396(4)
C(3)	4003(4)	1661(3)	846(5)
C(4)	3827(3)	1130(3)	−954(5)
C(5)	2637(4)	601(3)	−1695(4)
C(6)	2304(3)	−141(3)	−356(4)
C(7)	2148(3)	−485(2)	3347(4)
C(8)	1025(3)	−630(2)	3756(4)
C(9)	876(3)	−1394(3)	4912(5)
C(10)	1849(4)	−2011(3)	5691(5)
C(11)	2958(3)	−1872(3)	5301(5)
C(12)	3123(3)	−1118(3)	4132(4)
S(13)	1014.1(10)	1517.5(8)	1443.5(16)
O(14)	4610(3)	1161(3)	−1778(4)

alumina (10 g) and eluted with 100 ml hot benzene. The combined benzene solutions were concentrated to about 30 ml and filtered hot. The white crystal-white solid formed was filtered, washed with cold benzene (10 ml) and dried at 80°C/5 mm to give 2.8 g of sulfide (**3**), mp 144–145°. Concentration of the mother liquor gave an additional quantity (0.7 g), mp 142–143° (total yield 78%); ir (KBr) ν 1710 cm^{-1} (C=O); ^{1}H nmr (DCCl$_3$) δ 2.14–3.52 (m, 8H, ring CH$_2$) and 7.45–8.04 (m, 5H, ArH). Anal. Calcd. for C$_{11}$H$_{13}$OPS: P, 13.83; S, 14.31; Found: P, 13.49; S, 14.09%. Salt (**3**) was prepared by the reported method.[20] mp 154–156° (lit.[20] mp 155–156°).

Techniques in the Single Crystal Analysis

Crystals of (**2**) suitable for an x-ray diffraction experiment were obtained by equilibrating a benzene solution with hexane. The crystal chosen for data collection was a plate with dimensions 0.03 × 0.28 × 0.52 mm. Crystals of (**3**) were obtained by cooling a solution in hot benzene. The data crystal was blocky with approximate dimensions 0.28 × 0.19 × 0.09 mm. All integrated intensity data and crystallographic data were collected on a Nonius CAD-4 automatic diffractometer at 24°. Preliminary measurements on the data crystal of (**2**) showed the space group to be P$\bar{1}$ with four molecules per unit cell (two crystallographically independent molecules in the asymmetric unit). The unit cell dimensions were a = 10.2293(3), b = 10.5536(3), c = 11.1003(6) Å, α = 97.967(3), β = 115.177(3), γ = 97.669(3)° and V = 1049.0 Å^3 at a temperature of 24°C. The calculated density of (**2**) was 1.318 g cm^{-3} while the density measured by flotation in a mixture of carbon tetrachloride and hexane was found to be 1.318 g cm^{-3}. The space group of (**3**) was found to be P2$_1$/c with Z = 4 and unit cell dimensions a = 11.3181(6), b = 13.3742(5), c = 7.5827(3) Å, β = 104.733(3)° and V = 1109.9 Å^3 at T = 24°. The calculated density of (**3**) was 1.342 g cm^{-3} while the density measured by flotation (carbon tetrachloride–hexane) was 1.341 g cm^{-3}. Unit cell dimensions were determined by a least squares fit of the $+2\theta$ and -2θ values of 60 reflections for each of the compounds (**2**) and (**3**).

For the intensity data Ni filtered CuK$\bar{\alpha}$ radiation was used with moving crystal–moving counter scanning techniques. A total of 4316 reflections for (**2**), of which 588 had $I \leq 2\sigma(I)$, and 2286 reflections for (**3**), of which 231 had $I \leq 2\sigma(I)$ comprising all unique data with $2\theta \leq 150°$, were measured. For each compound, a maximum of 60 s was spent on each observation. The details of the data collection method and the manner in which individual weights were obtained for the observations has been described.[23] No significant variation in the intensity of the monitor reflection was found for either data set. Lorentz and polarization corrections were made followed by absorption corrections (μ = 20.74 and 35.58 cm^{-1} for (**2**) and (**3**), respectively). *For the absorption corrections, the program of* Coppens, Leiserowitz and Rabinovich was used.[24]

Structure Determination and Refinement

An interpretation of the sharpened Patterson syntheses of (**2**) and (**3**) yielded the positions of all non-hydrogen atoms for both compounds. After several cycles of least-squares refinement, the atoms were given anisotropic thermal parameters. Difference Fourier maps were calculated which revealed the positions of all the hydrogen atoms in both compounds. Least-squares refinement using isotropic thermal parameters for H atoms was terminated when all shifts were less than 1/2 of the corresponding estimated standard deviation. The R value based on final parameters (Tables III, V and VII) was 6.6% for all

TABLE V

Anisotropic thermal parameters for 1-phenyl-4-phosphorinanone 1-oxide. Thermal parameters are of the form exp [$-2\pi^2(U_{11} h^2 a^{*2} + U_{22} k^2 b^{*2} + \ldots + 2U_{13} hla^*c^*)$]

Molecule A

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	403(3)	362(3)	372(3)	99(2)	189(2)	91(2)
C(2)	603(14)	440(13)	469(13)	134(11)	292(12)	147(10)
C(3)	848(21)	442(14)	709(19)	125(14)	388(17)	238(13)
C(4)	785(20)	357(13)	797(21)	37(13)	397(17)	99(13)
C(5)	732(19)	511(15)	600(17)	9(14)	301(15)	−56(13)
C(6)	567(14)	507(14)	431(13)	52(11)	219(11)	70(11)
C(7)	430(12)	389(11)	399(12)	68(9)	187(9)	105(9)
C(8)	461(13)	500(14)	582(16)	42(11)	253(12)	108(12)
C(9)	608(17)	458(14)	851(22)	−53(12)	323(16)	123(14)
C(10)	741(19)	357(13)	853(22)	76(13)	304(17)	131(13)
C(11)	590(16)	457(14)	757(19)	169(12)	283(14)	151(13)
C(12)	432(12)	410(12)	578(15)	92(10)	217(11)	126(11)
O(13)	480(10)	573(11)	567(11)	219(8)	244(8)	142(8)
O(14)	1039(21)	730(16)	1172(23)	−293(15)	526(18)	49(15)

Molecule B

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	376(2)	339(3)	379(3)	71(2)	202(2)	91(2)
C(2)	482(13)	447(12)	453(13)	84(10)	197(10)	154(10)
C(3)	731(18)	464(14)	671(18)	188(13)	380(15)	261(13)
C(4)	811(19)	324(12)	639(17)	48(12)	444(15)	66(11)
C(5)	689(18)	525(15)	514(15)	−90(13)	280(14)	30(12)
C(6)	437(12)	469(13)	431(13)	19(10)	191(10)	73(10)
C(7)	406(11)	397(11)	416(12)	71(9)	219(9)	99(9)
C(8)	535(14)	462(13)	425(13)	78(11)	215(11)	94(10)
C(9)	669(17)	479(14)	562(16)	58(13)	279(14)	−6(12)
C(10)	776(19)	395(13)	788(20)	146(13)	420(17)	96(13)
C(11)	700(18)	503(15)	690(19)	214(13)	344(15)	252(13)
C(12)	550(14)	498(13)	450(13)	149(11)	249(11)	164(10)
O(13)	488(9)	495(10)	591(11)	129(7)	356(9)	79(8)
O(14)	1026(18)	467(11)	866(17)	−104(11)	535(15)	126(10)

TABLE VI

Anisotropic thermal parameters for 1-phenyl-4-phosphoranone 1-sulfide. Thermal parameters are of the form exp[$-2\pi^2(U_{11} h^2 a^{*2} + U_{22} h^2 b^{*2} + \ldots + 2U_{23} hla^*c^*)$]

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	359(4)	318(4)	354(4)	17(3)	151(3)	21(2)
C(2)	353(19)	522(18)	435(16)	−184(15)	137(14)	−89(14)
C(3)	716(24)	549(21)	595(21)	−298(19)	271(18)	−68(16)
C(4)	530(18)	478(17)	501(16)	−72(14)	247(14)	47(14)
C(5)	631(22)	594(22)	358(16)	−129(16)	172(14)	3(13)
C(6)	478(16)	453(16)	350(13)	−113(13)	101(12)	−35(12)
C(7)	382(14)	343(14)	292(12)	−9(10)	85(10)	−7(9)
C(8)	364(14)	421(14)	440(15)	−8(12)	109(12)	38(12)
C(9)	486(17)	449(16)	474(16)	−77(14)	180(13)	26(13)
C(10)	665(22)	401(17)	408(16)	−56(14)	152(15)	41(12)
C(11)	524(19)	472(16)	443(16)	59(15)	53(14)	83(14)
C(12)	379(15)	452(15)	413(14)	43(12)	103(12)	9(12)
S(13)	718(7)	517(5)	898(7)	289(5)	485(6)	288(5)
O(14)	671(18)	811(20)	783(18)	−83(16)	473(15)	21(16)

TABLE VII

Positional parameters (× 10^3) and isotropic thermal parameters ($Å^2$) for H atoms of 1-phenyl-4-phosphorinanone 1-oxide. The H atoms are assigned a number corresponding to the C atom to which it is attached

Molecule A

	X	*Y*	*Z*	*B*
H(2)A	539(3)	396(3)	460(3)	5.6(7)
H(2)B	383(3)	402(3)	335(3)	5.4(7)
H(3)A	526(3)	179(3)	347(3)	6.1(8)
H(3)B	382(4)	181(3)	375(3)	6.2(8)
H(5)A	480(4)	154(3)	95(4)	7.8(10)
H(5)B	318(4)	159(3)	−18(4)	7.5(9)
H(6)A	458(3)	374(3)	27(3)	5.5(7)
H(6)B	318(4)	380(3)	68(3)	6.7(8)
H(8)	777(3)	643(3)	311(3)	5.0(7)
H(9)	787(3)	877(3)	327(3)	5.3(7)
H(10)	581(3)	962(3)	301(3)	5.3(7)
H(11)	364(4)	822(3)	283(3)	6.5(8)
H(12)	350(3)	592(3)	256(3)	4.6(6)

Molecule B

	X	*Y*	*Z*	*B*
H(2)A	140(3)	402(3)	424(3)	5.2(7)
H(2)B	−26(3)	412(2)	389(3)	3.9(6)
H(3)A	72(4)	199(3)	273(3)	7.3(9)
H(3)B	6(3)	186(3)	379(3)	5.4(7)
H(5)A	−128(3)	194(3)	20(3)	5.8(8)
H(5)B	−295(3)	199(3)	7(3)	5.6(7)
H(6)A	−166(3)	406(3)	1(3)	4.4(6)
H(6)B	−218(3)	418(3)	118(3)	4.7(6)
H(8)	158(3)	636(3)	473(3)	4.8(7)
H(9)	194(4)	862(3)	533(3)	6.1(8)
H(10)	128(3)	997(3)	364(3)	4.5(6)
H(11)	−5(4)	884(3)	133(4)	7.7(9)
H(12)	−46(3)	654(3)	68(3)	4.3(6)

TABLE VIII

Positional parameters (× 10^3) and isotropic thermal parameters ($Å^2$) for H atoms of 1-phenyl-4-phosphorinanone 1-sulfide. The H atoms are assigned a number corresponding to the C atom to which it is attached

	X	*Y*	*Z*	*B*
H(2)A	384(5)	128(4)	338(6)	7.9(15)
H(2)B	444(4)	42(3)	264(5)	4.6(9)
H(3)A	328(6)	216(5)	60(10)	10.4(19)
H(3)B	476(4)	198(4)	129(6)	6.0(11)
H(5)A	199(4)	115(4)	−197(5)	5.6(10)
H(5)B	263(4)	29(3)	−280(6)	6.2(12)
H(6)A	151(4)	−45(3)	−83(6)	4.5(9)
H(6)B	293(3)	−64(3)	−8(4)	3.7(8)
H(8)	38(4)	−22(3)	329(5)	4.6(9)
H(9)	3(4)	−146(3)	519(6)	5.3(10)
H(10)	169(4)	−253(4)	645(6)	6.1(11)
H(11)	362(5)	−232(4)	585(6)	6.1(11)
H(12)	390(3)	−102(3)	382(4)	3.8(8)

4316 data of (**2**), and 5.3% (Tables IV, VI, and VIII) for all 2288 data of (**3**).

The final difference Fourier maps showed some detail near the heavier atoms (P and S) for each structure while all other peaks were between 0.2 and −0.2e $Å^{-3}$. All least-squares refinement was done using the block-diagonal program of Ahmed.[25] The atomic scattering factors for P, S, O and C atoms were taken from the International Tables for x-ray Crystallography, Vol. III[26] while scattering factors for H atoms were those of Stewart, Davidson and Simpson.[27] The Patterson syntheses and difference Fourier maps were calculated using Ahmed's Fourier summation program.[28] In the structure factor analysis, the average value of $W_F \Delta F^2$ did not show a significant variation for either $|F_0|$ or $\sin^2\theta$ for the structure of (**2**) or (**3**) thus indicating that the weighting scheme used was reasonable.[29]

ACKNOWLEDGEMENTS

This investigation was supported by Grant No. CA 17562 (to DvdH) and CA 22770 (to KDB) awarded by the National Cancer Institute, DHEW. We also thank the University of Oklahoma for providing computer time. We are also grateful for discussions with Dr. G. D. MacDonell on several aspects of the work.

REFERENCES AND NOTES

1. G. D. Macdonell, K. D. Berlin, J. R. Baker, S. E. Ealick, D. van der Helm and K. L. Marsi, *J. Am. Chem. Soc.* **100**, 4535 (1978).
2. G. A. Gray, S. E. Cremer and K. L. Marsi, *J. Am. Chem. Soc.* **98**, 2109 (1976).
3. (a) S. I. Featherman and L. D. Quin, *Tetrahedron Letters* 1955 (1973); (b) S. I. Featherman, S. O. Lee and L. D. Quin, *J. Org. Chem.* **39**, 2899 (1974); (c) S. I. Featherman and L. D. Quin, *J. Am. Chem. Soc.* **97**, 4349 (1975).
4. J. J. Breen, S. O. Lee and L. D. Quin, *J. Org. Chem.* **40**, 2245 (1975).
5. J. B. Lambert, *Acc. Chem. Res.* **4**, 87 (1971); P. Dowd, T. Dyke and W. Klemperer, *J. Am. Chem. Soc.* **92**, 6327 (1970); A Mossel, C. Romers and E. Havinga, *Tetrahedron Letters* 1247 (1963); M. V. Bhatt, G. Srinivasan and P. Neelakantan, *Tetrahedron* **21**, 291 (1965); N. L. Allinger and C. B. Boyce, *J. Am. Chem. Soc.* **83**, 5028 (1961).
6. J. A. Hirsch and E. Havinga, *J. Org. Chem.* **41**, 455 (1976). For a reinterpretation of their earlier data see J. A. Hirsch and A. A. Jarmas, *J. Org. Chem.* **43**, 4106 (1978).
7. J. B. Stothers, *Carbon-13 NMR Spectroscopy* (Academic Press, New York, N.Y., 1972).
8. G. C. Levy and G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists* (Interscience, New York, N.Y., 1972).
9. J. B. Lambert and S. I. Featherman, *Chem. Rev.* **75**, 611 (1975).
10. A. T. McPhail, J. J. Breen and L. D. Quin, *J. Am. Chem. Soc.* **93**, 2574 (1971). For x-ray data of dimethyl ketal of phosphines 1, see A. T. McPhail, J. J. Breen, J. H. Somers, J. C. H. Steele, Jr. and L. D. Quin, *Chem. Commun.* 1020 (1971).

11. L. D. Quin, A. T. McPhail, S. O. Lee and K. D. Onan, *Tetrahedron Letters* 3473 (1974); L. D. Quin, M. D. Gordon and S. O. Lee, *Org. Magn. Reson.* **6**, 503 (1974).
12. J. B. Lambert and W. L. Oliver, Jr., *Tetrahedron* **27**, 4245 (1971).
13. (a) A value of 211.3 ppm for the carbonyl carbon in cyclohexanone was employed.[6] (b) ^{13}C NMR of 1-phenyl-phosphorinane and its oxide has been reported.[2] (c) ^{13}C NMR of 1-phenylphosphorinane sulfide has been reported.[3a] (d) A value of 24.36 ppm for C(4) reported[2] for 1-benzyl-1-phenylphosphorinanium bromide was employed. (e) A value of 27.7 ppm was employed.[6]
14. J. J. Daly, *Perspectives in Structural Chemistry*, Vol. III, p. 165 (Wiley, New York, 1969) and references therein.
15. S. E. Ealick, J. R. Baker, D. van der Helm and K. D. Berlin, submitted to *Acta Crystallographica.*
16. D. E. C. Corbridge, *The Structural Chemistry of Phosphorus* (American Elsevier, New York, N.Y., 1974).
17. T. S. Cameron, K. D. Howlett and K. Miller, *Acta Crystallographica* **B34**, 1689 (1978).
18. T. S. Cameron and B. Dahlin, *J. Chem. Soc. Perkin Trans.* **2**, 1737 (1975).
19. T. E. Snider, D. L. Morris, K. C. Srivastava and K. D. Berlin, *Org. Syn.* **53**, 98 (1973).
20. R. P. Welcher, G. A. Johnson and V. P. Wystrach, *J. Am. Chem. Soc.* **82**, 4437 (1960).
21. F. Mathey and G. Muller, *C. R. Acad. Sci. Ser. C* **269**, 158 (1969).
22. D. L. Morris and K. D. Berlin, *Phosphorus* **1**, 305 (1972).
23. D. van der Helm and M. Poling, *J. Am. Chem. Soc.* **98**, 82 (1976).
24. P. Coppens, L. Leiserowitz and D. Rabinovich, *Acta Crystallographica* **18**, 1035 (1965).
25. F. R. Ahmed, S.F.L.S. program, NRC-10 (Ottawa, National Research Council, 1966).
26. *International Table for X-ray Crystallography*, Vol. III (Kynoch Press, Birmingham, England, 1962).
27. R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.* **42**, 3175 (1965).
28. F. R. Ahmed, Fourier summation program, NRC-8 (Ottawa, National Research Council, 1966).
29. A listing of the observed and calculated structure factors can be obtained from the authors.
30. C. K. Johnson, ORTEP Report ORNL-3794 (Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965).