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CARBON-PHOSPHORUS HETEROCYCLES. SYNTHESIS OF SUBSTITUTED 2,3,4,5-TETRAHYDRO-5-OXO-2,2-DIPHENYL-1*H*-2-BENZOPHOSHEPINIUM SALTS VIA INTRAMOLECULAR ACYLATION WITH 115% POLYPHOSPHORIC ACID

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CARBON-PHOSPHORUS HETEROCYCLES. SYNTHESIS OF SUBSTITUTED 2,3,4,5-TETRAHYDRO-5-OXO-2,2-DIPHENYL- 1H-2-BENZOPHOSHEPINIUM SALTS VIA INTRAMOLECULAR ACYLATION WITH 115% POLYPHOSPHORIC ACID

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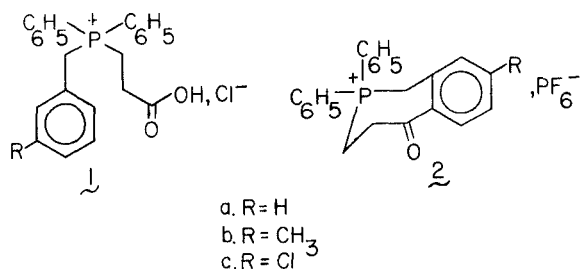
Department of Chemistry, University of Oklahoma, Norman, OK 73019

(Received July 30, 1977)

Intramolecular acylation involving three ω -carboxyalkylphosphonium salts **1a-c** has been achieved in the presence of 115% polyphosphoric acid (PPA) to yield the heretofore unknown 2,3,4,5-tetrahydro-5-oxo-2,2-diphenyl-1H-2-benzophosphepinium salts **2a-c**. The open-chain precursors were easily prepared by quaternization of the corresponding tertiary arylmethyl-substituted phosphines with 3-chloropropanoic acid. Cyclization of the carboxy-substituted salts was accomplished at 200°C with PPA in modest yields (37-64%). A mechanism reminiscent of a classic electrophilic acylation process was tentatively proposed. An x-ray crystallographic analysis of a single crystal of **2a** showed the phosphepin ring to exist in a twisted-chair conformation.

INTRODUCTION

Polycyclic, carbon-phosphorus (C-P) heterocycles possessing a carbonyl function in the ring system have been rare in the literature.³ To date, the synthetic methods available for the synthesis of many keto-containing C-P heterocycles have usually been laborious and often required difficulty accessible precursors.³ We herein report both the synthesis of ω -carboxyphosphonium salts **1a-c** from readily available starting

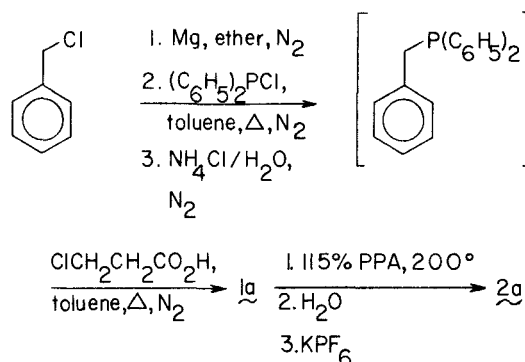


materials and the subsequent PPA-catalyzed intramolecular acylation to give phosphepinium salts **2a-c**.⁴

RESULTS AND DISCUSSION

A typical synthesis of the open-chain salts is illustrated

SCHEME I



for **1a** in Scheme I and discussed in detail in the Experimental section. Benzylmagnesium chloride was treated with diphenylphosphinous chloride to yield, after hydrolysis, benzyltriphenylphosphine. Quaternization *in situ* of the crude phosphine with 3-chloropropanoic acid in boiling toluene gave salt **1a**, the physical and spectral properties of which can be found in Tables I and II, respectively.

Cyclization of **1** (Scheme I) consisted of adding **1a** to 115% PPA at 200°C followed by aqueous hydrolysis and precipitation of crude **2a** with a saturated aqueous KPF₆ solution. Purification was easily accomplished by

TABLE I
 Physical data for phosphonium salts

Cpd	R	mp (°C)	Yield (%)	Mol. for.	Anal. (% P)
1a	H	223–5	58	C ₂₂ H ₂₂ ClO ₂ P	Calc. 8.05 Fd. 8.04
1b	CH ₃	167–71	34.5	C ₂₂ H ₂₄ ClO ₂ P · CH ₂ Cl ₂	Calc. 6.44 Fd. 6.20
1c	Cl	225–9	40	C ₂₀ H ₂₁ Cl ₂ O ₂ P · H ₂ O	Calc. 7.08 Fd. 6.95
2a	H	126–9	64	C ₂₂ H ₂₀ F ₆ OP ₂	Calc. 13.00 Fd. 12.99
2b	CH ₃	187–90	37	C ₂₃ H ₂₂ F ₆ OP ₂	Calc. 12.63 Fd. 12.67
2c	Cl	186–8	58	C ₂₂ H ₁₉ ClF ₆ OP ₂	Calc. 12.13 Fd. 12.15

 TABLE II
 Ir, ¹H nmr, and ³¹P nmr data for phosphonium salts

Cpd	Ir-principal maxima (cm ⁻¹) ^a	¹ H nmr spectral assignments, chemical shifts, δ ^b	³¹ Pmr, δ ^c
1a	3370(m) 1720(s), 1233(s) 1440(s), 1112(s)	2.50–3.24 [m, CH ₂ CH ₂ , 4H] 4.20 [d, J _{POCH} = 14 Hz, ArCH ₂ , 2H] 6.72–6.94 [m, ArH, 2H] 7.10–7.40 [m, ArH, 3H] 7.40–7.98 [m, ArH, 10H]	+25.05 ^d
1b	3390(m) 1730(s), 1234(s) 1447(s), 1115(s)	2.14 [s, CH ₃ , 3H] 2.46–3.24 [m, CH ₂ CH ₂ , 4H] 4.17 [d, J _{POCH} = 14 Hz, ArCH ₂ , 2H] 6.46–6.84 [m, ArH, 2H] 7.00–7.26 [m, ArH, 2H] 7.40–8.00 [m, ArH, 10H]	+26.04 ^e
1c	3380(m) 1720(s), 1220(s) 1110(s), 997(m)	2.56–3.34 [m, CH ₂ CH ₂ , 4H] 4.32 [d, J _{POCH} = 14 Hz, ArCH ₂ , 2H] 6.66–7.00 [m, ArH, 2H] 7.00–8.04 [m, ArH, 12H]	+26.72 ^e
2a	1670(m), 1115(m) 998(w), 840(b)	3.16 [s, CH ₂ P, 2H] 3.25 [d of m, J _{PCCCH} = 23 Hz, CH ₂ CO, 2H] 4.35 [d, J _{POCH} = 14 Hz, ArCH ₂ , 2H] 6.96–7.02 [m, ArH, 1H] 7.42–7.98 [m, ArH, 13H]	+21.51 ^d
2b	1660(s), 1439(s) 1112(s), 844(b)	2.35 [s, CH ₃ , 3H] 3.19 [s, CH ₂ P, 2H] 3.28 [d of m, J _{PCCCH} = 24 Hz, CH ₂ CO, 2H] 4.34 [d, J _{POCH} = 14 Hz, ArCH ₂ , 2H] 6.89 [s, ArH, 1H] 7.30–8.06 [m, ArH, 12H]	+21.48 ^e
2c	1710(s), 1437(s) 1114(s), 840(b)	3.40 [d of m, J _{PCCCH} = 24 Hz, CH ₂ CO, 2H] 3.45 [s, CH ₂ P, 2H] 5.06 [d, J _{POCH} = 14 Hz, ArCH ₂ , 2H] 7.08–8.32 [m, ArH, 14H]	+21.04 ^f

^aThe IR spectra were obtained on samples (4 mg) with KBr (400 mg) pellets.

^bNMR spectra were obtained on DCCl₃ solutions [except 2c (DMSO-*d*₆ and no F₃CCO₂H)] with F₃CCO₂H added to give a clear solution and tetramethylsilane (TMS) as internal standard. Peak positions quoted in the case of doublets were measured from the approximate center.

^c³¹P resonance signals were relative to 85% H₃PO₄; chemical shifts are reported as positive downfield from the standard.

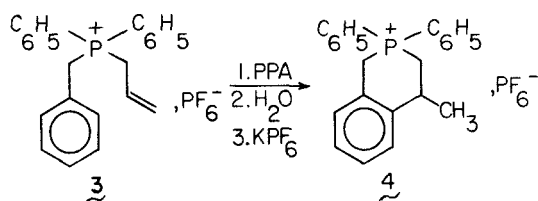
^dThe spectra were obtained on samples in DCCl₃:F₃CCO₂H(4:1).

^eThe spectra were obtained on samples in DMSO-*d*₆:F₃CCO₂H(10:1).

^fThe spectra were obtained on samples in acetone-*d*₆.

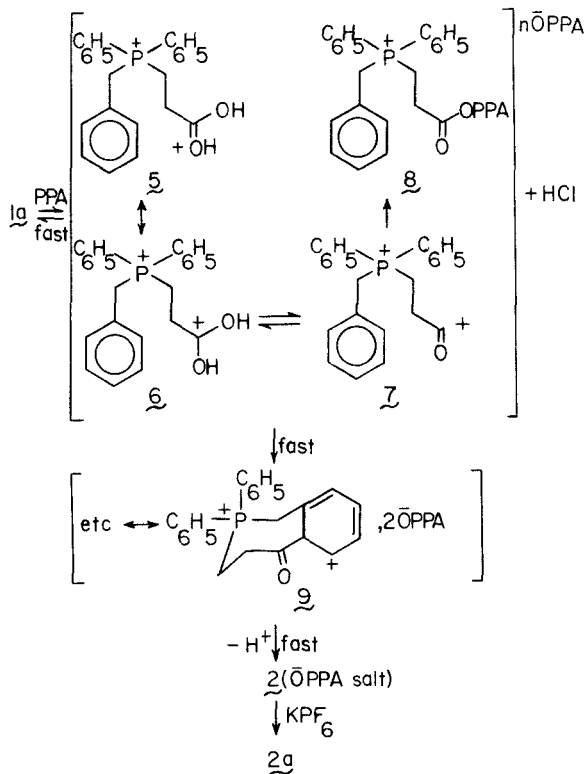
dissolution of **2a** in 95% ethanol and reprecipitation by the slow addition of ether. Physical and spectral data for **2a-c** have been listed in Tables I and II.

A ^{31}P NMR analysis of the PPA-catalyzed cyclization of **1a** \rightarrow **2a** revealed only two ^{31}P signals (+25.4 ppm and +22.5 ppm) throughout the course of the reaction. The addition of authentic samples of starting material **1a** and product **2a** increased the relative intensity of the signal at +25.4 ppm and at +22.5 ppm, respectively, confirming the assignments. A similar experiment⁵ had proven useful for the related alkenylphosphonium salt **3** which gave isophosphinolinium salt **4**.



Addition of **1a** to preheated (190°C) PPA caused immediate expulsion of a gas, presumably HCl .⁶ This extremely fast protonation could give rise to any

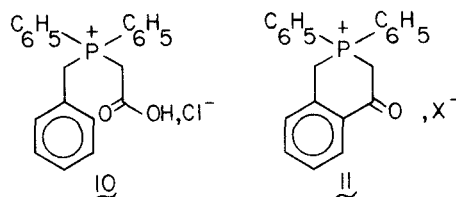
SCHEME II



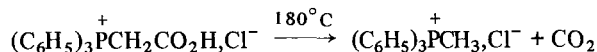
number of PPA anion-associated cations (a ^{31}P signal was observed at +25.4 ppm relative to 85% H_3PO_4 in the mixture) such as **5-8** shown in Scheme II. A fast cyclization followed by immediate proton loss would result in product **2** (^{31}P : +22.5 ppm rel. to 85% H_3PO_4) as the $^-\text{OPPA}$ salt.

Indeed, this tentative mechanism was similar to a classic electrophilic substitution process in which substitution and rearomatization have been assumed to occur rapidly.^{5,7} Therefore the absence of a ^{31}P signal for an intermediate would not be unreasonable.

Attempts to cyclize related open-chain salt **10** to isophosphinolinium salt **11** gave only simple benzylmethylphenylphosphonium hexafluorophosphate



(**12**) (see Experimental section). This was reminiscent of the thermal decarboxylation of



(carboxymethyl)triphenylphosphonium chloride observed previously.⁸ It was noteworthy that the loss of the elements of CO_2 proceeded even upon boiling benzyl-diphenylphosphine and chloroacetic acid in benzene.⁹

Characterization of the novel phosphhepinium salts **2** consisted of elemental, infrared, mass spectral,¹⁰ and nmr analyses and chemical degradation studies as well as an x-ray crystallographic analysis of **2a**. The ^1H nmr spectra of salts **2a-c** proved quite unusual. A solvent dependency was detected for the doublet for the H(1) protons and the single, broad line for the H(3) protons was apparent. Downfield shifts were observed for these same protons in acetone- d_6 (δ 5.01 and δ 3.54, respectively) and DMSO- d_6 (δ 5.08 and δ 3.34, respectively) compared to the shifts (δ 4.35 and δ 3.16, respectively) observed in an equally concentrated solution of DCCl_3 : trifluoroacetic acid.¹¹ Chemical shift differences of +0.66 and +0.73 ppm were observed for the H(1) resonances in acetone- d_6 and DMSO- d_6 , respectively. Smaller differences of +0.38 (acetone- d_6) and +0.18 ppm (DMSO- d_6) were observed for the H(3) proton resonances. An increase in $^2J_{\text{PCH}}$ from 14 to 16 Hz for the H(1) protons as well as broadening of the "singlet" for the H(3) protons was also noted with a change in solvent from DCCl_3 : trifluoroacetic acid to DMSO- d_6 . Similar observations have been made regard-

ing chemical shifts and coupling constants for benzyl-substituted phosphonium salts¹² and α -methylene-substituted phosphonium salts.^{13, 14}

The assignment of the signals for the H(3) and H(4) protons was based on the observed coupling (^1P - ^1H) and solvent shifts in representative **2a**. A doublet of multiplets ($^3J_{\text{PCH}} = 23$ Hz) at δ 3.48 was observed for the H(4) protons, and a doublet ($^2J_{\text{PCH}} = 12$ Hz) at δ 3.56 for the H(3) protons appeared only after deuteration *in situ* of salt **2a** (saturated solution of **2a** in 0.5 ml of acetone- d_6 with 1 drop of 40% NaOD in D_2O added). One hour after mixing salt **2a** with NaOD/ D_2O , exchange of the H(1) and H(4) protons had proceeded and a doublet appeared for the H(3) protons in the ^1H nmr spectrum. After 20 hours, a nearly quantitative exchange of the H(1) and H(4) protons had occurred while the doublet at δ 3.56 (about 80% of this proton had been exchanged) remained. $^1\text{H}\{^1\text{P}\}$ double resonance collapsed the H(3) doublet to a single line supporting the original assignment. Based on these observations, it has not been possible to eliminate a conformational change in deuterated **2a** as the cause of $^2J_{\text{PCH}}$ to increase. However, it appeared unlikely that replacement of hydrogen by deuterium at C(1) and C(4) could change the conformation at phosphorus and C(3) sufficiently to account for the dramatic increase of $^2J_{\text{PCH}}$ from *ca.* 0 to 12 Hz.¹⁵ Another possibility which cannot be ruled out was that the single line observed for the H(3) protons was the result of a complex multiplet with $^2J_{\text{PCH}} = 12$ Hz. Further delineation of the spin-spin couplings of the five nuclei [P , CH_2 (3), CH_2 (4)] via $^1\text{H}\{^1\text{H}\}$ double resonance experiments were unsuccessful due to the small chemical shift difference (8 Hz in acetone- d_6) between the H(3) and H(4) resonances.

Variable-temperature experiments were conducted with **2a** over a temperature range of 260°C. Cooling a solution of **2a** to -110°C resulted only in slight line broadening, and heating a solution to $+150^\circ\text{C}$ did not produce a detectable change. From this data and from examination of molecular models (Courtald), it was assumed that the seven-membered ring was conformationally rigid in solution over the temperature range studied.

^{13}C NMR chemical shifts and ^1P - ^{13}C coupling constants for phosphopepin representative **2a** are listed in Table III. The assignments made were based on analogous systems reported previously.¹⁶ The ^{13}C resonance for C(5a) at 137.83 ppm was considered to result from the deshielding effect of the carbonyl group and the reduced ^1P - ^{13}C coupling (compared to $^1J_{\text{PC}}$ or $^2J_{\text{PC}}$). The atoms C(9) and C(9a) were assigned on the basis of the shielding effect of the positive phosphorus

TABLE III^a
 ^{13}C chemical shift^b and ^1P - ^{13}C coupling constants^c for **2a**

Carbon atom(s)	Chemical shift	Coupling constant
1	24.64	47.60
3	13.83	56.00
4	34.78	d
5	200.04	d
5a	137.83	3.72
6	128.89 ^e	d
7	130.32 ^e	d
8	132.56 ^e	d
9	131.29	7.72
9a	126.79	7.72
10, 16	118.24	82.60
11, 15, 17, 21	132.37	9.62
12, 14, 18, 20	129.71	12.01
13, 19	134.61	d

^a 240 mg of **2a** in 1.5 ml of DMSO- d_6 at 37°C .

^b Chemical shifts in ppm downfield from TMS.

^c Coupling constants in hertz.

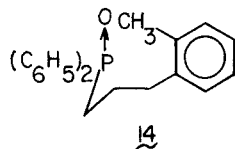
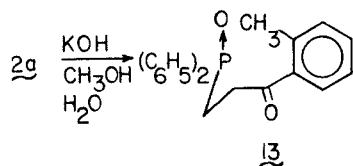
^d Not resolvable.

^e May be interchanged.

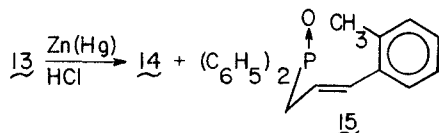
as well as their ^1P - ^{13}C coupling of 7.72 Hz. Carbon atoms 6, 7, and 8 could not be differentiated due to their proximity in chemical shift as well as the non-resolvable ^1P - ^{13}C coupling.

^1P nmr spectra of **1a-c** and **2a-c** exhibited broad signals (non- ^1H decoupled) which compared favorably with related compounds **3** and **4**.¹⁷ However, the slightly shielded signals of **2a-c** (**2a**: +21.51 ppm), compared to **1a-c** (**1a**: +25.05 ppm), probably reflect a difference in geometric as well as electronic environment about the phosphorus atom. It has been suggested that ^1P chemical shifts can be related to the internal C-P-C bond angle in cyclic phosphorus compounds.¹⁸ Comparison of ^1P chemical shifts of **2a** and **4**⁵ gave a $\Delta\nu$ of -4.34 ppm in going from a seven-membered ring to a six-membered ring. However, the validity of the comparison must be considered tentative since no comparable oxoisophospholinium salts have reported ^1P values. It remains only speculative that this $\Delta\nu$ is due to bond angle effects,¹⁸ as a result of the paucity of ^1P shifts values for cyclic phosphonium salts and the lack of x-ray data for those compounds for final confirmation of bond angles.

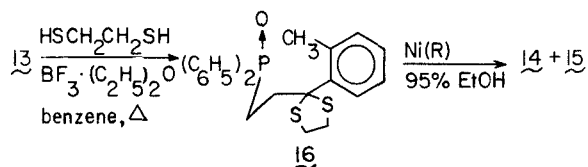
Further characterization of the cyclic nature and ring size of **2a-c** was achieved via basic hydrolysis of **2a** to **13**¹⁹ which was subsequently reduced to **14**. Clemmenson reduction²⁰ of **13** and desulfurization by Raney nickel²¹ of the thioketal of **13** were employed for the preparation of **14**. However, only the desulfurization procedure proved useful as the strongly acidic



conditions in the Clemmensen process promoted dehydration to yield mainly **15**. Thioketalization of **13** with 1,2-ethanedithiol followed by desulfurization with

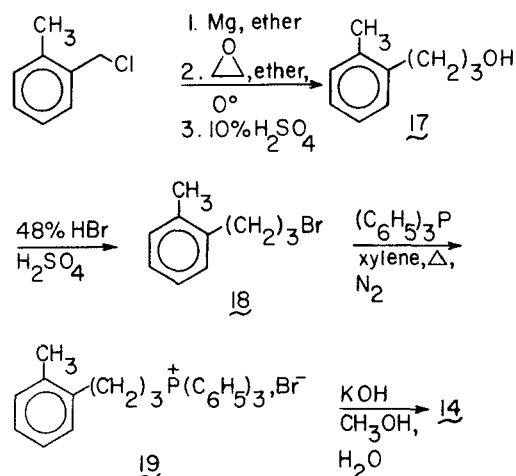


Raney nickel gave a mixture (7:3 via ^1H nmr) of oxides **14** and **15**, respectively. Separation of the mixture was accomplished with preparative tlc (see Experimental section).



Additional proof of structure for **14** (and therefore **2a**) was accomplished by an independent synthesis (Scheme III). Physical and spectral data for key intermediates **17** and **18** were identical with that reported

SCHEME III



previously.²² Pertinent data for **19** can be found in the Experimental section.

SINGLE CRYSTAL ANALYSIS

A stereoview of a single molecule of **2a** is shown in Figure 1, the numbering scheme and bond distances in Figure 2 and bond angles in Figure 3. Some additional bond angles are given in Table IV. The seven-membered heterocycle is in an approximate C_2 (twist-chair) conformation with the two-fold axis passing through the P(2) atom and the midpoint of the C(5a)–C(5) bond. The internal torsion angles for the ring are as follows: C(1)–P(2), 48.1; P(2)–C(3), 41.4; C(3)–C(4), –78.0; C(4)–C(5), 8.4; C(5)–C(5a), 53.6; C(5a)–C(9a), –0.4; C(9a)–C(1), –76.5°.

The phenyl groups are attached to the P atom such that the planes of the two groups are approximately

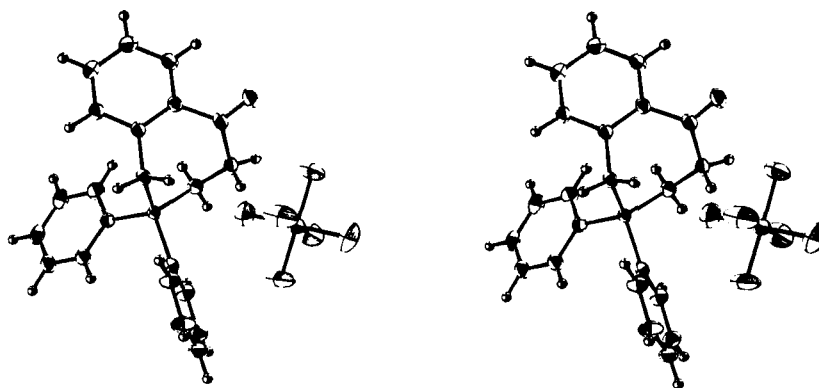


FIGURE 1 Stereoview of a single molecule for **2a**. (C. K. Johnson, ORTEP, Oak Ridge National Laboratory Report ORNL-3794, 1965.

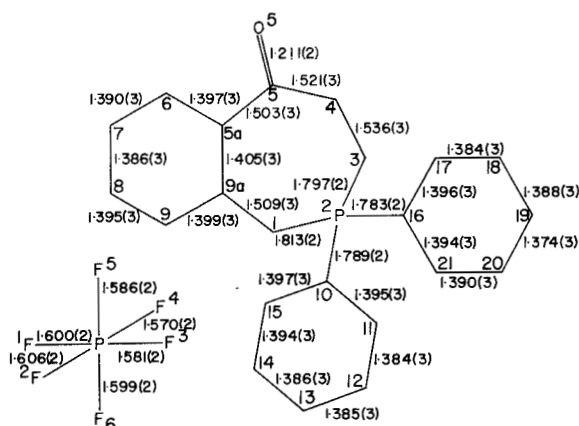


FIGURE 2 Bond distances for **2a**. Calculated standard deviations are given in parentheses.

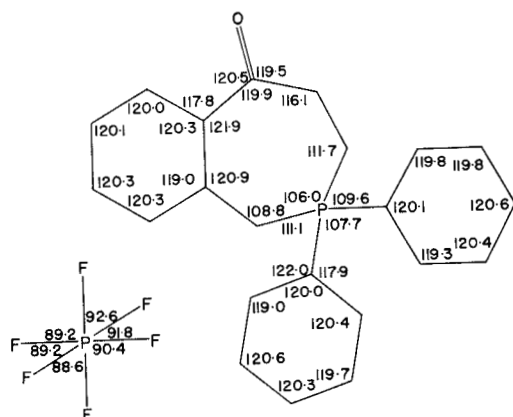


FIGURE 3 Bond angles for **2a**. Standard deviations range from 0.1° for bonds involving a P atom to 0.20 for those involving only C atoms. Additional bond angles are given in Table III.

perpendicular. The bond distances of 1.783 and 1.789 Å for the P(2)–C(16) and P(2)–C(10) bonds are consistent with values for other systems containing

P⁺–C (phenyl) bonds.²³ Because P–C bond distances have been shown to vary greatly depending on such factors as valency, ionization and hybridization²⁴ one

TABLE IV

Additional bond angles for **2a** calculated standard deviations are in parentheses

C(1)–P(2)–C(16)	111.3(1)	F(2)–P(1)–F(3)	89.5(1)
C(3)–P(2)–C(10)	111.2(1)	F(2)–P(1)–F(4)	178.1(1)
		F(2)–P(1)–F(5)	88.8(1)
F(1)–P(1)–F(3)	178.6(1)	F(3)–P(1)–F(5)	90.5(1)
F(1)–P(1)–F(4)	89.6(1)	F(4)–P(1)–F(6)	90.0(1)
F(1)–P(1)–F(6)	89.8(1)	F(5)–P(1)–F(6)	177.2(1)

must be cautious in making comparisons. Values ranging from 1.771–1.792 Å have been reported for the ring P⁺–C bond in three compounds containing six-membered rings.^{23,27} In the present structure the values of 1.797 and 1.813 Å are somewhat larger than the average with both values falling completely outside the range and, in fact, are closer to the values observed for an acyclic P⁺(sp³)–C(sp³) bond distance.²⁵ A possible explanation is that the increase in size of the ring allows a reduction of strain and more closely resembles the conditions in an acyclic compound. The relatively large difference between the two distances within a compound was also observed in all three compounds containing six-membered P⁺-heterocycles.^{23,27}

The C(1)–P(2)–C(3) endocyclic bond angle was found to have a relatively large value of 106.0°.²⁶ This approach towards the tetrahedral bond angle may be taken as a further indication of reduction of strain in the phosphepin ring as compared to a typical six-membered system.

In the present structure the counter-ion is the PF₆[−] anion. Although such groups are notorious for disorder and high thermal motion in the solid state, no such problems were encountered at −135°C with the aver-

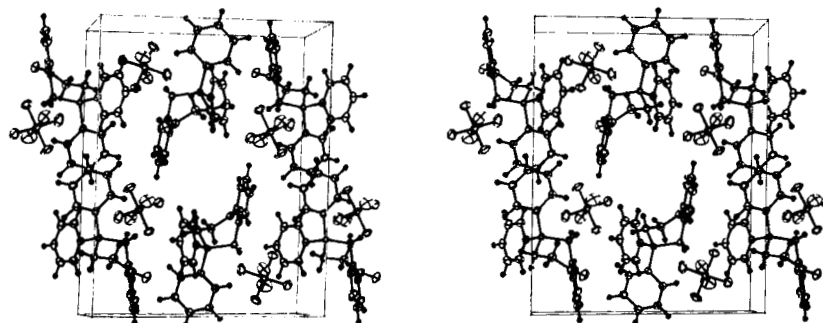


FIGURE 4 Stereoview of a unit cell of **2a** looking down the *a* axis. The remaining directions are *b*→ and *c*↑.

age isotropic B value of about 4.6 \AA^2 . It is interesting to point out that in this case the PF_6^- group shows two different groups of three bond distances having average values of 1.602 and 1.579 Å. This C_{3v} distortion of the octahedral PF_6^- anion has also been observed in the crystal structure of 1,2,3,4-tetrahydro-4,4-dimethyl-1-methyl-1-phenyl-phosphinolinium hexafluorophosphate in which case the values are 1.608 and 1.580 Å.²⁷

A packing diagram viewing a unit cell down the a axis is shown in Figure 4. The cation-anion stacking is primarily along the two-fold screw axis. The large hole seen in the center of this view of the unit cell forms a channel through the crystal structure in the a direction. In the CH_2Cl_2 solvate of this compound, this channel is filled with solvate molecules.

Herein we have reported the synthesis of three novel phosphhepinium salts prepared easily from readily available starting materials. Proof of structure for one member **2a** was based on physical, spectral, and chemical data as well as x-ray crystallographic analysis. A ^{31}P nmr analysis of the reaction tentatively suggested a classic electrophilic substitution process for the intramolecular acylation of **1a-c** to **2a-c** via 115% polyphosphoric acid. The x-ray analysis is the first recorded for a seven-membered, phosphorus-containing cyclic ketone.

EXPERIMENTAL

General data. Melting points were obtained on a Thomas-Hoover melting point apparatus and were uncorrected. ^1H nmr, ^{13}C nmr, and ^{31}P nmr data were obtained on a XL-100(15) Varian spectrometer with a TT-100 PFT accessory operating at 100.1 MHz with tetramethylsilane (TMS) as the internal standard for ^1H nmr, 25.2 MHz with TMS as the internal standard for ^{13}C nmr, and 40.5 MHz with 85% H_3PO_4 as the external standard for ^{31}P nmr. Infrared and mass spectral data were collected on a Beckman IR-5A unit and a CEC Model 21 HR unit, respectively. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Starting materials. Reagents (commercially available) were purified before use as necessary. Solvents used were reagent grade and were dried over sodium where required.

Preparation of open-chain salts 1a-c. A typical preparation is exemplified in the synthesis of benzyl(2-carboxyethyl)diphenylphosphonium chloride (**1a**). In a 500 ml, round-bottom flask under N_2 was placed 1.2 g (0.05 g-atom) of Mg and 10 ml of anhydrous ether. Into an attached 125 ml addition funnel was placed 6.3 g (0.05 mol) of benzyl chloride in 100 ml of anhydrous ether. The reaction flask containing the Mg was charged with approximately 5 ml of the benzyl chloride solution. When the reaction had begun, the remaining benzyl chloride solution was added dropwise over a 2-hr period, and then the solution was stirred for 4 hr. To the addition funnel was added 11.0 g (0.05 mol) of diphenylphosphinous chloride

in 100 ml of anhydrous toluene. This solution was added dropwise over a 1-hr period to the Grignard solution. When the addition was complete, the ether was distilled off, and the remaining heterogeneous mixture was boiled 12 hr. After cooling to room temperature, the mixture was hydrolyzed with 2.7 g (0.05 mol) of NH_4Cl in 50 ml of degassed (N_2 bubbled through for 0.5 hr) H_2O . Two layers separated (under N_2), and the organic layer was dried (MgSO_4). The dried organic layer was filtered (under N_2) and delivered to a 500 ml, round-bottom flask (under N_2) containing 6.5 g (0.06 mol) of 3-chloropropanoic acid in 25 ml of anhydrous toluene. The solution was then boiled for 24 hr, after which cooling caused formation of an oil. Toluene was evaporated to give an extremely viscous white oil. The oil was dissolved in a minimum amount of hot H_2CCl_2 , and the phosphonium salt **1a** was precipitated by the dropwise addition of anhydrous ether. After standing 12 hr, the white solid was collected by vacuum filtration and dried *in vacuo* (110°/5 mm) to yield 11.05 g (58%) of **1a**, mp 223–225°. Physical and spectral data have been given in Tables I and II, respectively.

Preparation of benzyl(carboxymethyl)diphenylphosphonium chloride (10). The procedure was the same as for all other open-chain salts except for the quaternization conditions. Benzyl-diphenylphosphine (prepared from 2.4 g, 0.1 g-atom Mg; 12.6 g, 0.1 mol benzyl chloride; and 22.1 g, 0.1 mol diphenylphosphinous chloride, as before) in 100 ml of toluene was delivered to a 250 ml round bottom flask containing 10.0 g (0.11 mol) of chloroacetic acid dissolved in 50 ml of ether. The reaction mixture was allowed to stand 2 weeks at 0°C. A white crystalline solid precipitated which was collected by vacuum filtration and air dried to give 6.94 g (18.9%) of **10**, mp 144° dec; ir (KBr) ν 1710 ($\text{C}=\text{O}$), 1438 ($\text{P}-\text{C}_6\text{H}_5$), 1270, 1183, 1103 cm^{-1} ($\text{P}-\text{C}_6\text{H}_5$); ^1H nmr (DCCl_3 :TFA, 20:1) δ 4.06 [d, $J_{\text{PCH}} = 13 \text{ Hz}$, $\text{CH}_2\text{CO}_2\text{H}$, 2H], 4.37 [d, $J_{\text{PCH}} = 15 \text{ Hz}$, ArCH_2 , 2H], 6.76–7.98 [m, ArH , 15H].

Anal. Calcd. for $\text{C}_{21}\text{H}_{20}\text{ClO}_2\text{P} \cdot \text{H}_2\text{O}$: P, 7.97. Found P, 7.81.

Cyclizations. The general cyclization procedure will be illustrated with the preparation of **2a**. In a 100 ml beaker was placed 60 ml of 115% PPA which was then heated and mechanically stirred on a hot plate to 200°. Compound **1a** (2 g, 5.2 mmol) was slowly added with the expulsion of a gas, presumably HCl .⁶ After the addition was complete (ca. 10 min.), the solution was maintained at $200 \pm 10^\circ$, with stirring, for 90 min. Cooling the solution to approximately 120° and pouring it into 300 ml of ice-water, with stirring, produced a homogeneous solution. Addition of 60 ml of saturated aqueous KPF_6 precipitated **2a**. The crude salt was collected by vacuum filtration and washed (H_2O). Dissolution of crude **2a** in 95% ethanol was followed by clarification of the solution with carbon black. Filtration and evaporation of solvent produced a white solid which was stirred in 100 ml of ether. Vacuum filtration gave a solid which was dried (110°/5 mm) to yield 1.59 g (64%) of **2a**, mp 126–129°. Physical and spectral data were given in Tables I and II, respectively.

Reaction of salt 10 with PPA. Salt **10** (500 mg, 1.35 mmol) was added slowly, with the expulsion of gas,⁶ to 30 ml of 115% PPA warmed to 100°C. The light tan reaction mixture was stirred at 100°C for 90 min. and then poured into 200 ml ice-water to give a homogeneous solution after stirring. Crude **12** was precipitated by the addition of ca. 30 ml satd. aqueous KPF_6 . The solid was collected by vacuum filtration, washed

with water, and air dried (300 mg, 51%). Recrystallization (acetonitrile/ether, 1:1) gave **12**, mp 173–174°C: ir (KBr) ν 1436 (P–C₆H₅), 1117 (P–C₆H₅), 997 (P–C₆H₅), 840 cm⁻¹; ¹H nmr (DCCl₃:TFA, 20:1) δ 2.76 [d, J_{PCH} = 14 Hz, CH₃, 3H], 4.96 [d, J_{PCH} = 14 Hz, ArCH₂, 2H], 7.00–8.12 [m, ArH, 15H].

Anal. Calcd. for C₂₀H₂₀F₆P₂ · H₂O: P, 13.65. Found: P, 13.89.

Base hydrolysis of 2,3,4,5-tetrahydro-5-oxo-2,2-diphenyl-1H-2-benzo-phosphepinium hexafluorophate (2a). Ketone **2a** (900 mg, 1.9 mmol) was added to 60 ml of CH₃OH/H₂O (4:1) in which 6 g of KOH had been dissolved. The resulting solution was boiled for 12 hr, cooled, and 50 ml of H₂O was added. The aqueous solution was extracted (6 × 25 ml HCCl₃); the extracts were combined, dried (MgSO₄), and filtered. Evaporation of solvent gave a light green oil which, after standing for 2 hr at room temperature, deposited light green crystals. Two recrystallizations (hexane/H₂CCl₂, 4:1) gave 480 mg (73%) of **13**, mp 114–116°C: ir (KBr) ν 1670 (C=O), 1438, (P–C₆H₅), 1190 cm⁻¹ (P=O) 1120; ¹H nmr (DCCl₃) δ 2.45 [s, CH₃, 3H], 2.58–2.92 [m, CH₂P, 2H], 3.06–3.42 [m, CH₂CO, 2H], 7.06–7.94 [m, ArH, 14H].

Anal. Calcd. for C₂₂H₂₁O₂P: C, 75.85; H, 6.08; P, 8.89. Found: C, 75.99; H, 6.01; P, 9.02.

2,4-Dinitrophenylhydrazine (0.4 g) was dissolved in 10 ml of 95% ethanol, 3 ml of H₂O, and 2 ml of conc. H₂SO₄. Ketone **13** (19 mg, 0.55 mmol) in 5 ml of 95% ethanol was then added, and the reaction mixture warmed on a steam bath for 30 min. Water (5 ml) was then added and the mixture was extracted with 3 × 25 ml of benzene. The benzene solution was dried (MgSO₄) and filtered; to the filtrate was added 5 ml of petroleum ether (bp 40–60°C). After standing at 0°C for 24 hr, an oily residue formed. The liquid was decanted, and the oil was dissolved in HCCl₃:hexane (1:1) which stood overnight at 0°C during which time yellow needles formed. The solid was filtered and dried to yield 11.3 mg (38%) of the 2,4-dinitrophenylhydrazone of **13**, mp 165–166°C: ir (KBr) ν 3390, 1620, 1580, 1500, 1420, 1335, 1182 cm⁻¹; ¹H nmr (DCCl₃) δ 2.15 [s, CH₃, 3H], 2.73–4.39 [m, CH₂CH₂, 4H], 7.00–7.10 [m, ArH, 1H], 7.26–7.99 [m, ArH, 13H], 8.25–8.37 [m, ArH, 2H], 9.02–9.05 [m, ArH, 1H], 10.76 [s, NH, 1H].

Anal. Calcd. for C₂₈H₂₅N₄O₅P · 0.5H₂O: C, 62.56; H, 4.84. Found: C, 62.92; H, 4.85.

Thioketalization of (3-Diphenylphosphinyl)-2-propionophenone (13). To 544 mg (1.56 mmol) of ketone **13** in 25 ml of benzene was added 1.5 ml of 1,2-ethanedithiol and 2 ml of freshly distilled boron trifluoride-etherate. The solution was boiled 3 hr and cooled, and 5 ml of petroleum ether (bp 40–60°C) was added. The reaction flask was transferred to a refrigerator and allowed to stand at 0°C for 1 week. A crystalline solid formed and was filtered, washed with petroleum ether (bp 40–60°C), and then recrystallized (benzene) to yield, after drying over P₂O₅ at 5 mm, 620 mg (94%) of **16**, mp 107–110°C: ir (KBr) ν 1475, 1440 (P–C₆H₅), 1110 b (P=O, P–C₆H₅), 889 cm⁻¹ (CH₂–S); ¹H nmr (DCCl₃) δ 2.32 [s, CH₃, 3H], 2.44–2.90 [m, CH₂CH₂P, 4H], 3.29 [s, SCH₂CH₂S, 4H], 7.02–7.24 [m, ArH, 3H], 7.40–7.92 [m, ArH, 11H].

Several attempts to obtain ketal **16** in an analytically pure state failed and **16** from above was used for the desulfurization with Raney nickel.

Desulfurization of ketal 16. To 1.5 g of Raney nickel²⁸ (3g

alloy) in 15 ml of 95% ethanol was added 500 mg (1.22 mmol) of **16** dissolved in 10 ml of 95% ethanol. The reaction mixture was boiled 6 hr and filtered hot. Ethanol was evaporated to leave an oil which was dissolved in benzene and this solution was dried (MgSO₄). After standing overnight (0°C), a gummy solid formed and was repeatedly recrystallized (benzene) to give 54 mg of oxides **14** and **15** (7:3 via ¹H nmr). Separation was performed by spotting an acetone solution of **14** and **15** onto a pre-coated (Brinkmann, Sil G-200 UV₂₅₄, 20 × 20 cm, 2 mm layer thickness) preparative thin-layer plate and eluting with acetone. The plate was dried and developed in an iodine chamber. The spot (**14**: R_f = 0.76) was scraped, and oxide **14** was extracted (acetone). The acetone was evaporated and the resulting solid was dissolved in benzene (ca. 2 ml); petroleum ether (bp 40–60°C, ca. 2 ml) was added to turbidity. After standing 12 hr (0°C), the precipitated white solid was filtered and dried (P₂O₅, 60°C/5 mm) to give 11 mg of **14**, mp 100–101°C: ir (KBr) ν 3020, 2920, 1442 (P–C₆H₅), 1184 (P=O), 1120 cm⁻¹; ¹H nmr (DCCl₃) δ 1.66–2.28 [m, CH₂CH₂P, 4H], 2.20 [s, CH₃, 3H], 2.72 [t, ArCH₂, 2H], 7.00–7.22 [m, ArH, 4H], 7.28–7.84 [m, ArH, 10H]. Oxide **14** prepared herein was identical to that obtained starting from **17**→**18**→**19**→**14**.

Clemmenson reduction of ketone 13. A mixture of 2.5 g (0.038 g-atom) of granular Zn, 1.5 g (5.5 mmol) of HgCl₂, 1 ml of conc. HCl and 5 ml of H₂O was placed in a 150 ml, round-bottom flask and stirred for 5 min. The supernatant liquid was decanted, and the solid material was covered with 25 ml of conc. HCl and 25 ml of H₂O. To this was added 1.35 g (3.88 mmol) of ketone **13**, and the mixture was boiled for 24 hr and then cooled. The resulting solid was filtered off and dissolved in HCCl₃, and the aqueous phase was extracted (3 × 50 ml HCCl₃). The HCCl₃ portions were combined, washed (2 × 50 ml of satd. NaHCO₃), dried (MgSO₄) and filtered; HCCl₃ was evaporated. The resulting oil was chromatographed on acidic alumina (Merck activity I) employing HCCl₃ as the eluent to give a mixture of products. The crude solid produced after HCCl₃ removal was recrystallized from hexane/ether (2:1) to give 400 mg of a white compound. Initial ¹H nmr (DCCl₃) analysis indicated this to be predominately unsaturated **15**. Recrystallization (ether) followed by drying over P₂O₅ (110°C/5 mm) gave 110 mg of **15**, mp 147–148°C: ir (KBr) ν 1438 (P–C₆H₅), 1190 (P=O), 1118 (P–C₆H₅), 976, 880 cm⁻¹; ¹H nmr (DCCl₃) δ 2.14 [s, CH₃, 3H], 3.32 [dd, (J_{HCHH} = 7 Hz, J_{PCH} = 14 Hz), CH₂P, 2H], 5.80–6.20 [m, =CH, 1H], 6.50–6.74 [m, =CH, 1H], 6.98–7.92 [m, ArH, 14H]; ms (70 eV) m/e 332 (M⁺, 50.5%), 215, 202 (25.3%), 201 (100%), 131, 91, 77 (28.4%). In spite of many recrystallizations, attempts at sublimation, and chromatography there were found traces of oxide **14** via mass spectral analysis and this precluded a good elemental analysis.

3-(2-Methylphenyl)propanol (17). In a 500 ml, 3-necked, round-bottom flask (with N₂) was placed 2.4 g (0.1 g-atom) of Mg and 10 ml of anhydrous ether. To this, 14.0 g (0.1 mol) of α -chloro-*o*-xylene in 100 ml of anhydrous ether was added dropwise. After complete addition (ca. 2 hr), the Grignard solution was stirred 12 hr. Ethylene oxide (6.6 g, 0.15 mol) in 100 ml of anhydrous ether was added slowly to the cooled (0°C) Grignard solution. After complete addition (ca. 2 hr), the reaction mixture was warmed to room temperature and stirred for 4 hr. Hydrolysis was accomplished with 100 ml of 10% H₂SO₄. The layers were separated and the aqueous layer was extracted with ether (3 × 100 ml). The ether extracts were combined, dried (MgSO₄) and filtered. Ether was evapor-

ated to give a liquid which was distilled under reduced pressure to yield 9.24 g (61.5%) of 17, bp 96–98°C/0.8 mm, $n_D^{25} = 1.5291$ [lit^{22a} bp 126–128°C/10 mm, $n_D^{25} = 1.5270$].

1-Bromo-3-(2-methylphenyl)propane (18). To 39.6 g (0.214 mol) of 48% HBr in a 250 ml, round-bottom flask was added 0.5 ml of conc. H_2SO_4 and 8 g (0.0534 mol) of alcohol 17. The mixture was gently boiled for 18 hr, cooled, and diluted with 50 ml of benzene. The layers were separated and the aqueous phase was extracted (3 x 75 ml) with benzene. The combined benzene extracts were washed (satd. $NaHCO_3$), dried ($MgSO_4$) and filtered. The benzene was evaporated and the resulting liquid was distilled under reduced pressure to yield 6.46 g (56.8%) of 18, bp 69–71°C/0.5 mm, $n_D^{25} = 1.5502$ [lit^{22b} 1H nmr data were identical for 19 as found in this reference].

3-(2-Methylphenyl)propyltriphenylphosphonium bromide (19). Bromide 18 (2.40 g, 1.13 mmol) and 2.58 g (1.02 mmol) of triphenylphosphine, in 25 ml of xylene, were boiled vigorously under N_2 for 24 hr. A solid precipitated during the course of the reaction. After cooling, the crude salt was filtered, recrystallized from H_2CCl_2 /ether (1:1), and dried over P_2O_5 (110°C/5 mm) to yield 2.75 g (58%) of 19, mp 186–188°C: ir (KBr) ν 1440 (P–C $_6$ H $_5$), 1112 (P–C $_6$ H $_5$), 995 (P–C $_6$ H $_5$), 739, 638 cm^{-1} ; 1H nmr ($CDCl_3$) δ 1.70–2.10 [m, CH_2 , 2H], 2.18 [s, CH_3 , 3H], 3.03 [t, Ar CH_2 , 2H], 3.76–4.14 [m, CH_2 P, 2H], 7.02–7.20 [m, ArH, 4H], 7.46–7.96 [m, ArH, 15H].

Anal. Calcd. for $C_{28}H_{28}BrP$: C, 70.74; H, 5.94; P, 6.51. Found: C, 70.80; H, 5.92; P, 6.47.

Base hydrolysis of 19. Salt 19 (500 mg, 1.05 mmol) was added to 20 ml of aqueous 1N KOH and 10 ml of CH_3OH . The reaction mixture was boiled 48 hr and cooled, the solution was then extracted with $HCCl_3$ (5 x 25 ml), the organic phase dried ($MgSO_4$) and filtered; $HCCl_3$ was evaporated to yield 350 mg (100%) of crude 14. The oil was passed through a column of alumina (Brinkmann 1077) with benzene as eluent. The benzene was evaporated to give, after recrystallization (ether/hexane, 1:1) pure 14 (168 mg, 48%), mp 100–101°C; ir and 1H nmr data were identical to 14 prepared from 16.

Anal. Calcd. for $C_{22}H_{23}OP$: C, 79.02; H, 6.93; P, 9.26. Found: C, 79.23; H, 7.01; P, 9.34.

The melting point of 14 prepared from 19 was not depressed by admixture of 14 obtained from 16.

Structure determination of 2,3,4,5-tetrahydro-5-oxo-2,2-diphenyl-1H-2-benzophosphepinium hexafluorophosphate (2a). Initial attempts to grow suitable crystals of 2a from H_2CCl_2 and petroleum ether (bp 40–60°C) resulted in the formation of the H_2CCl_2 solvate with the H_2CCl_2 site at 50% occupancy. The structure reported here was determined from crystals which were obtained by slow evaporation from a mixture of acetone, chloroform, and H_2O (2:1:1), yielding a H_2CCl_2 free crystal form.

Preliminary measurements on the data crystal (0.12 x 0.17 x 0.46 mm) showed the space group to be $P2_1/c$ with four molecules per unit cell and no H_2CCl_2 . The unit cell dimensions are $a = 7.958(2)$, $b = 14.924(2)$, $c = 18.732(3)$ Å, $\beta = 97.38(2)^\circ$ and $V = 2206.3$ Å³ at $-135^\circ C$. The volume is about 60 Å³ smaller than that of the unit cell for the H_2CCl_2 solvate at the same temperature. The calculated density is 1.434 g cm^{-3} at $-135^\circ C$. Integrated intensity data and crystallographic data were collected on a Nonius CAD-4 auto-

matic diffractometer at $-135^\circ C$. For the unit cell parameters $CuK\alpha_1$ radiation ($\lambda = 1.54051$ Å) was used to measure the $+2\theta$ and -2θ values of 57 reflections distributed through all octants of reciprocal space followed by a least-squares fit to the averaged 2θ values. For the intensity data Ni filtered $CuK\alpha$ radiation was used. A maximum of 50 seconds was used for scanning each intensity with $\frac{2}{3}$ of that time spent on the peak and $\frac{1}{3}$ of the time spent on each the left and right background. In addition the total time was divided into two scans. If the results of these two scans differed by more than 3σ up to three additional scans were made. Less than 50 seconds were used for those intensities in which 40,000 counts could be obtained at a faster scan speed. The scans were made using $\theta-2\theta$ techniques with a variable scan width of $(1.10 + 0.11 \tan \theta)^\circ$. A receiving aperture of variable width calculated as $(4.0 + 0.86 \tan \theta)$ mm and constant height of 6.0 mm was located 173 mm from the crystal. A monitor reflection which was measured after every 25 observations throughout the data collection showed no systematic variation with time. Three orientation control reflections were recentered after every 100 measurements so that a new orientation matrix could be automatically calculated if the crystal position changed by more than 0.1° in any of the Θ , Φ , χ , or Ω angles. It was not necessary to determine a new matrix during the extent of this data collection. Of the 4529 reflections with $2\theta \leq 150^\circ$, 731 were considered indistinguishable from the background having a net intensity, $I < 2\sigma(I)$. For the purpose of further data analysis these reflections were assigned a value of $1.0 T^{1/2}$ where $T = PK + 2(LB + RB)$ and PK = peak height, LB = left background and RB = right background. Lorentz and polarization corrections were made followed by absorption corrections ($\mu = 23.70$ cm^{-1}) and determination of individual structure factor amplitudes. For the absorption corrections the program of Coppens and Leiserowitz and Rabinovich was used.²⁹ This program used the numerical integration method of Gauss and in this case 216 sampling points were employed. Each amplitude was assigned an experimental weight, based on counting statistics, using a scheme which has been previously described.³⁰

The structure of 2a was determined using direct methods and the program MULTAN.³¹ The positions of the 31 non-hydrogen atoms were among the 34 highest peaks in an E -map calculated from the phase set which showed the highest figures of merit. The structure was initially determined from a data set measured from a crystal form containing H_2CCl_2 . Although this data yielded the same structure it was abandoned when attempts to refine the structure failed. The hydrogen atoms were located in a difference Fourier map based on the partially refined position of the non-hydrogen atoms.

The structure was refined using 9 x 9 block-diagonal least-squares methods in which the quantity $\sum w_F(kF_0 - F_c)^2$ was minimized. Least-squares refinement using isotropic temperature factors for H atoms and anisotropic temperature factors for P, F, O and C were terminated when all shifts were less than the corresponding estimated standard deviation. The R value ($\sum |kF_0 - F_c| / \sum |kF_0|$) based on final parameters given in Tables V and VI³⁵ is 0.053 for all 4529 data.

The final difference Fourier map showed several negative peaks around the phosphorous atoms. All other peaks were between 0.2 and $-0.2 e \cdot A^{-3}$. All least-squares refinements were done with the block diagonal program of Ahmed.³² The atomic scattering factors for P, F, O and C atoms were taken from the *International Tables for X-ray Crystallography*³³ while scattering factors for the H atoms were those of Stewart, Davidson and Simpson.³⁴ In the structure factor analysis the average values of $w_F \Delta F^2$ did not show a significant variation

TABLE V

Positional parameters ($\times 10^4$) and anisotropic temperature factors ($\times 10^4$) for non-hydrogen atoms. Temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Calculated standard deviations are given in parentheses

	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
C(1)	6137(2)	8414(1)	7476(1)	201(9)	191(8)	254(9)	-11(7)	-15(7)	4(7)
P(2)	6542.1(6)	9592.8(3)	7338.8(2)	175(2)	168(2)	187(2)	7(2)	4(1)	4(1)
C(3)	8299(3)	9885(1)	7999(1)	257(10)	226(9)	259(9)	-38(7)	-4(7)	13(7)
C(4)	9665(2)	9152(1)	8075(1)	179(9)	291(10)	339(10)	-15(7)	1(7)	40(8)
C(5)	9297(2)	8332(1)	8513(1)	209(9)	258(9)	276(9)	-5(7)	-39(7)	7(8)
O(5)	10415(2)	7795(1)	8688(1)	222(8)	372(9)	488(9)	70(6)	-17(6)	107(7)
C(5a)	7579(2)	8217(1)	8754(1)	209(9)	206(9)	269(9)	1(7)	-2(7)	34(7)
C(6)	7508(3)	8060(1)	9485(1)	281(10)	318(10)	281(10)	-13(8)	-35(8)	64(8)
C(7)	5949(3)	7964(2)	9737(1)	371(12)	380(12)	266(10)	-26(9)	35(9)	71(8)
C(8)	4466(3)	7997(2)	9260(1)	273(10)	364(11)	346(10)	-47(9)	66(8)	55(9)
C(9)	4526(2)	8128(1)	8527(1)	205(9)	270(10)	327(10)	-31(7)	-7(7)	42(8)
C(9a)	6082(2)	8252(1)	8268(1)	203(9)	194(8)	252(9)	-10(7)	-12(7)	18(7)
C(10)	4717(2)	10256(1)	7443(1)	221(9)	205(9)	248(9)	0(7)	27(7)	14(7)
C(11)	3643(3)	10492(1)	6824(1)	261(10)	322(10)	280(10)	46(8)	17(7)	7(8)
C(12)	2193(3)	10988(1)	6874(1)	249(10)	311(10)	409(12)	47(8)	10(9)	46(9)
C(13)	1811(3)	11252(1)	7543(1)	239(10)	227(9)	512(12)	14(8)	108(9)	8(8)
C(14)	2868(3)	11019(2)	8161(1)	326(11)	354(11)	379(12)	11(9)	117(9)	-76(9)
C(15)	4330(3)	10517(2)	8119(1)	312(11)	353(11)	280(10)	23(9)	38(8)	-41(8)
C(16)	7087(2)	9795(1)	6459(1)	204(9)	234(9)	236(9)	34(7)	25(7)	27(7)
C(17)	7645(3)	10652(1)	6306(1)	333(11)	261(10)	273(9)	-42(8)	41(8)	-9(8)
C(18)	8027(3)	10848(1)	5622(1)	348(11)	305(10)	292(10)	-56(9)	43(8)	43(8)
C(19)	7855(3)	10191(2)	5094(1)	367(11)	358(11)	229(9)	13(9)	47(8)	43(8)
C(20)	7280(3)	9350(2)	5240(1)	583(15)	297(10)	240(10)	13(10)	69(9)	-23(8)
C(21)	6894(3)	9141(1)	5923(1)	425(12)	246(10)	264(9)	-7(9)	53(9)	1(8)
P(1)	1524.4(7)	7530.9(4)	6299.7(3)	257(3)	284(2)	231(2)	-67(2)	-25(2)	60(2)
F(1)	2193(2)	7110(1)	7070(1)	529(9)	427(8)	304(7)	-22(7)	-131(6)	97(6)
F(2)	-237(2)	7768(1)	6590(1)	387(9)	652(11)	733(10)	98(7)	161(8)	201(8)
F(3)	819(2)	7949(1)	5545(1)	698(11)	600(10)	353(7)	-249(8)	-148(7)	251(7)
F(4)	3278(2)	7315(2)	6039(1)	513(11)	1046(16)	752(12)	150(10)	335(9)	121(11)
F(5)	763(2)	6583(1)	6049(1)	908(13)	337(8)	432(9)	-176(8)	-198(8)	18(6)
F(6)	2224(2)	8490(1)	6578(1)	652(10)	342(8)	647(10)	-166(7)	-186(8)	54(7)

with either $|F_0|$ or $\sin \theta/\lambda$ indicating that the weighting scheme used was reasonable.³⁵ A comparison of observed and calculated structure factors in the final least-squares refinement cycle indicated the presence of minor extinction effects for which no correction was made.

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Supplementary material available. Listing of the hydrogen atom parameters (Table VI) and F_0 and F_c tables may be obtained from the senior authors upon request.

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A

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B

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