Molecular Structure of 1-Ethoxy-1,2-diphenyl-3,3,5-tricarbethoxy-1,2-diphosphocyclopenten-5-one, a Heterocycle with Two Directly Linked Phosphorus Atoms of Different Valence States

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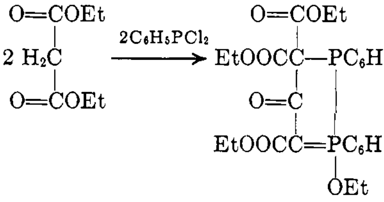
The title compound I forms when phenylphosphorus dichloride is treated with malonic acid diethyl ester in the presence of an amine. The structure of I was confirmed by X-ray diffraction analysis based on 2824 intensity data and refined to a discrepancy index of 9.7%. From this study it is concluded that two phosphorus atoms, of valence state 5 and 3, are linked together covalently and are part of a new, unusual five-membered heterocycle. A structure is proposed for the addition product of I with nickel tetracarbonyl, $Ni(CO)_3–C_{26}H_{30}O_8P_2$.

When phenylphosphorus dichloride is treated with malonic acid diethyl ester in the presence of triethylamine a colorless solid is obtained which can be recrystallized from methanol (mp 114° dec).¹ The formation of this product, 1-ethoxy-1,2-diphenyl-3,3,5-tricarbethoxy-1,2-diphosphocyclopenten-5-one (I), can be described as the result of a 2:2 addition combined with the rearrangement of one ethoxy group.



I

The structure of I, as derived by spectroscopic and chemical methods,¹ is interesting not only from a mechanistic but also from a structural chemical point of view. Thus it seemed worthwhile to undertake, in continuation of our studies on addition products of reactive organic compounds,² a detailed structural analysis of I.

The crystallographic data of the lath-shaped colorless crystals are presented in Table I. The intensities of 3248 reflections were measured with a four-circle diffractometer using Ni-filtered Cu Kα radiation. Since, when subjected to X-ray radiation, the crystals were stable only for about 4 days, a new crystal was mounted after the intensity of a reference reflection had dropped to 70% of its initial value and the data collection was then completed.

TABLE I

CRYSTALLOGRAPHIC DATA

Crystal dimensions 0.15 × 0.4 × 0.3 mm
Space group, monoclinic, $P2_1/c$
(extinctions $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$)
Cell dimensions $a = 16.774 \pm 0.003$ Å
$b = 8.078 \pm 0.002$ Å
$c = 21.122 \pm 0.005$ Å
$\beta = 108.66 \pm 0.05°$
Wavelength, Cu Kα, 1.54182 Å
Density observed (CCl_4/cyclohexane) 1.305 g/cm³
calculated ($Z = 4$) 1.303 g/cm³

After the data were corrected for this intensity change, they were converted to normalized structure factors, E_h, neglecting absorption effects. Of the 3248 measured intensities, 2824 were "observed," with F_{obsd} values above twice the background counts. The structure was solved by direct methods applying Sayre's equation³ to the 397 E_h's of magnitude greater than 1.5. The starting phase set consisted of seven E_h's. The phase angles of three of these seven E_h's served to determine the origin, and the phase angles of the other four E_h's were permuted in turn by 180°, yielding 16 phase angle sets.⁴ One of these sets, according to consistency criteria, was most promising and an E map computed from its phase angle information revealed the positions of all the 36 nonhydrogen atoms of the structure.

The initial crystallographic discrepancy index $R = \Sigma||F_{obsd}| - |F_{calcd}||/\Sigma|F_{obsd}|$ was 23.4% for the 2871 "observed" reflection data. The structure was refined in five cycles of full matrix least squares refinement minimizing $\Sigma W(F_{obsd} - F_{calcd})^2$ where W is the weighting factor computed according to Hughes' method⁵ and assigning first isotropic, then anisotropic temperature, parameters to the atoms. The scattering factors used were those given in the "International Tables of X-Ray Crystallography".⁶ The final R factor is 9.7% for the 2871 "observed" data; the average parameter shifts in the last cycle of refinement were less than $^1/_3$ the average standard deviations estimated from the variance–covariance matrix. Since the temperature factors of the benzene ring and ethyl carbon atoms, 3.5–9 Å², indicated rather intense thermal motion and/or some measure of structural disorder, perhaps radiation induced, the protons could not be located from difference Fourier syntheses.

The X-ray results confirm the previously described structure elucidation of I.⁷

A list of the observed and calculated structure factors and of the atomic parameters can be obtained on request.⁷ A projection of the structure down the b axis is illustrated in Figure 1; Figure 2 and Tables II and III contain data describing details of the molecular structure of I.

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(1) G. Bergerhoff, O. Hammes, J. Falbe, B. Tihanyi, J. Weber, and W. Weisheit, *Tetrahedron*, **27**, 3593 (1971).

(2) J. Z. Gougoutas and W. Saenger, *J. Org. Chem.*, **36**, 3632 (1971).

(3) D. Sayre, *Acta Crystallogr.*, **5**, 60 (1952).

(4) Using the FORTRAN program written by R. E. Long, UCLA, 1965.

(5) E. W. Hughes, *J. Amer. Chem. Soc.*, **63**, 1737 (1941).

(6) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

(7) Listing of structure factors and atomic parameters will appear following these pages in the microfilm edition of this volume of this journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-73-253. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

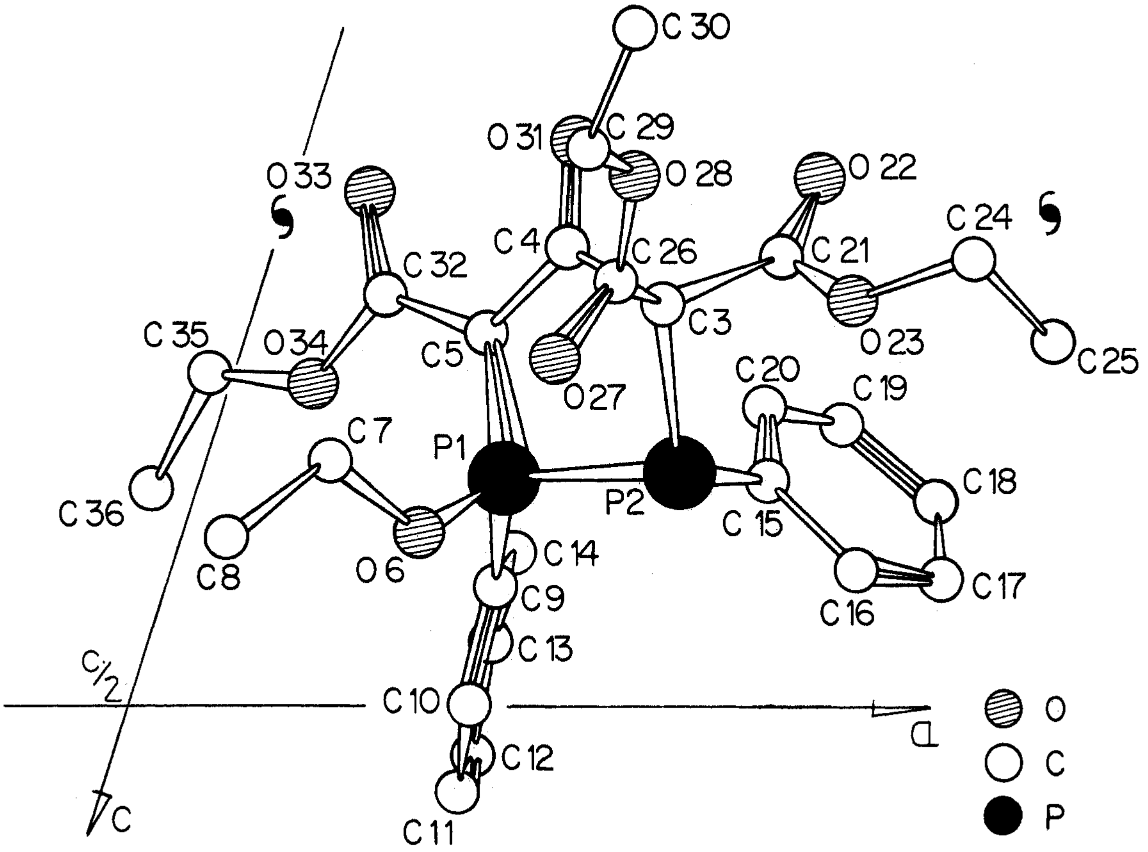

Figure 1.—The solid state structure of I as viewed down the crystallographic *b* axis, and numbering scheme used in the text.

TABLE II

DEVIATIONS OF SOME ATOMS FROM THE PLANE THROUGH ATOMS P(1), C(5), C(4)[a]

Atom	Deviation from plane, Å
C(3)	−0.149
P(2)	0.392
O(31)	−0.012
C(32)	0.013
O(33)	0.163
O(34)	−0.188
C(35)	−0.041
C(36)	−0.168
O(6)	−1.340
C(9)	1.177
C(15)	2.211
C(21)	−1.643
C(26)	0.626

[a] The equation of this plane is $0.551X - 0.821Y + 0.149Z - 2.553 = 0$, where X is along the crystallographic *a* axis, Y along *b*, and Z along c^{+}.

TABLE III

SELECTED TORSION ANGLES IN I

A. Five-Membered Ring and Substituents	
P(1)-P(2)-C(3)-C(4)	−24.0
P(2)-C(3)-C(4)-C(5)	23.1
C(3)-C(4)-C(5)-P(1)	−6.0
C(4)-C(5)-P(1)-P(2)	−10.5
C(5)-P(1)-P(2)-C(3)	18.4
C(4)-C(5)-C(32)-O(34)	171.1
C(4)-C(3)-C(21)-O(23)	−173.3
C(4)-C(3)-C(26)-O(28)	−79.8
C(5)-P(1)-O(6)-C(7)	0.3
C(5)-P(1)-C(9)-C(14)	21.7
P(2)-P(1)-C(9)-C(14)	−86.4
P(1)-P(2)-C(15)-C(16)	−129.5
C(3)-P(2)-C(15)-C(16)	139.7
B. Ethoxy Groups	
P(1)-O(6)-C(7)-C(8)	−136.4°
C(21)-O(23)-C(24)-C(25)	−104.0°
C(26)-O(28)-C(29)-C(30)	173.7°
C(32)-O(34)-C(35)-C(36)	−174.2°

The core of the molecule is formed by the five-membered heterocycle which is not planar but approximates to a half-chair conformation. Atoms P(2) and C(3) are at 0.392 and −0.149 Å distance from the plane through the atoms P(1), C(5), C(4), *i.e.*, on opposite sides (Table II); this unsymmetric puckering mode can also be visualized by the endocyclic dihedral angles which are given in Table III. Essentially coplanar with the three atom plane are the carbonyl oxygen atom O(31) and the atoms of the carbethoxy group bound to atom C(5), *i.e.*, the atoms C(32), O(33), O(34), C(35), and C(36) (Table II). The phenyl ring attached to atom P(1) is almost parallel to the bond P(1)-C(5) with an angle C(5)-P(1)-C(9)-C(14) of 21.5° and the plane through the phenyl ring bound to atom P(2) bisects the bond angle P(1)-P(2)-C(3) (Table III). The bond O(6)-C(7) of the ethoxy group linked to P(1) is cis planar with bond P(1)-C(5). The orientations of the carbethoxy groups bound to C(3) are such that the bonds C(4)-C(3) and C(21)-O(23) are trans planar but the bonds C(4)-C(3) and C(26)-O(28) are essentially gauche (Table III). Two of the four ethoxy groups are trans planar, C(26)-O(28)-C(29)-C(30), 173.7°, and C(32)-O(34)-C(35)-C(36), 174.2°, and two are gauche, P(1)-O(6)-C(7)-C(8), 136.4°, and C(21)-O(23)-C(24)-C(25), 104.0°. According to model studies, these different conforma-

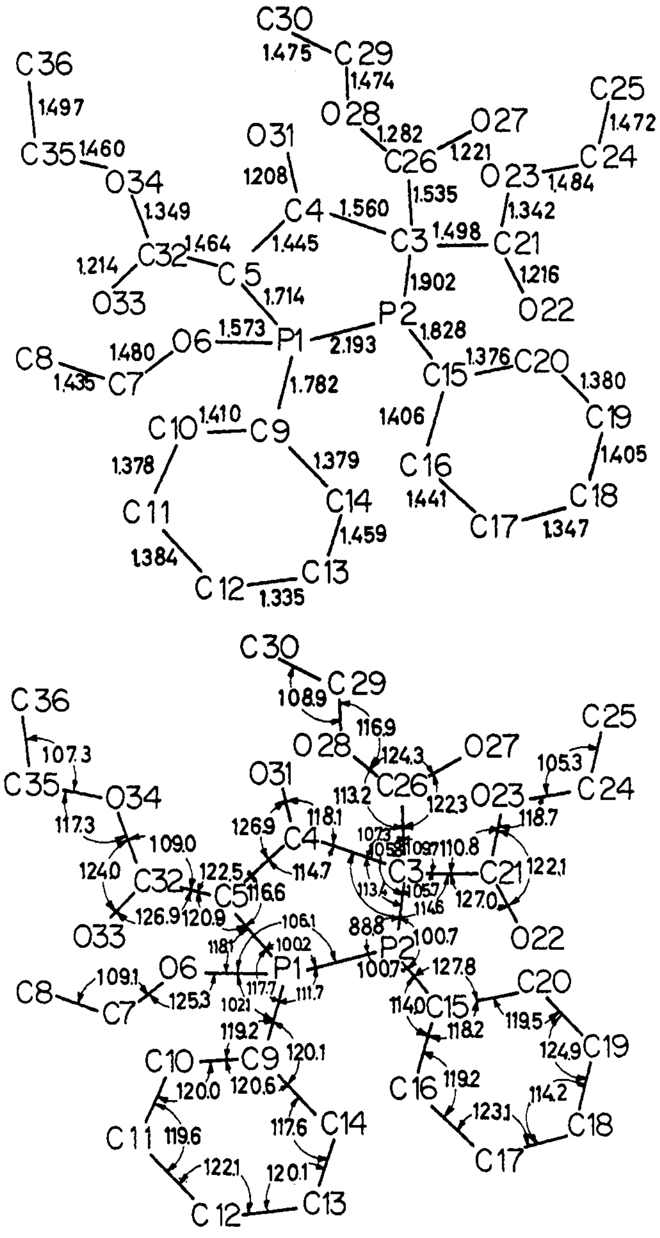

Figure 2.— Bond distances (Å) and angles in I. The standard deviations involving phosphorus atoms are 0.006 Å and 0.4°, respectively; those not involving phosphorus atoms are 0.01 Å and 0.7°, respectively.

tions of the ethoxy groups seem to be due mainly to crystal packing requirements rather than intramolecular overcrowding.

The valence states of the two phosphorus atoms are directly evident from the bond distances and angles involving these atoms. The distance P(1)–P(2), 2.193 Å, is only very slightly shorter than the P–P single distance in black phosphorus, 2.224–2.244 Å, and in other organic molecules containing P–P groups.[8,9] The P(1)–O(6) bond distance, 1.573 A, is similar to data obtained for a P–O–CH_3 group, 1.59 ± 0.01 A,[10] and the P(1)–C(5) bond has double bond character since the distance of 1.714 Å is shorter than the P–C single bond distance in $P(CH_3)_3$, 1.841 ± 0.005 Å, but similar to

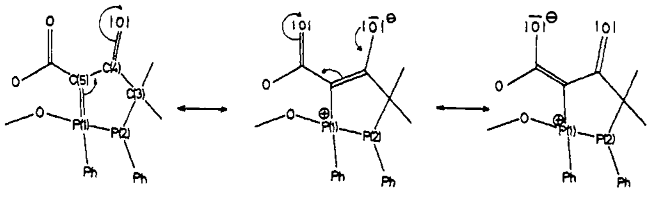

Figure 3.

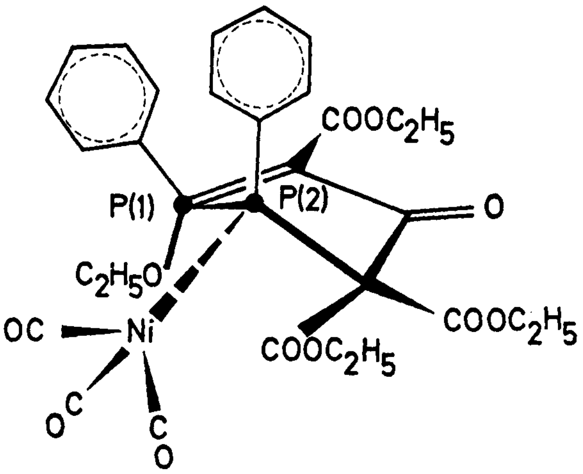

Figure 4.—Schematic drawing of the structure proposed for the complex formed between I and $Ni(CO)_4$.

the P=C double bond distance in $(C_6H_5)_3P{=}C$, 1.71 Å.[8] An isolated, "pure" P=C double bond is normally expected to be shorter than the observed P(1)–C(5) bond; conjugation, Figure 3, is indicated first by the bond distance C(4)–C(5), 1.445 Å, which is shorter than the C–C bond in the system CC=O, 1.506 ± 0.005 Å, but similar to the average C–C bond length in C=CC=O, 1.44 ± 0.01 Å,[11] and second by the short C(5)–C(32) distance, 1.464 Å, and the coplanarity of the C(32)-carbethoxy group with the five-membered heterocycle. From these considerations it follows that the valence state of the P(1) atom is 5.

On the other hand, the P(2)–C(3) and P(2)–C(15) distances, 1.902 and 1.828 Å, are in the range expected for $P{-}C_{aliphatic}$ and $P{-}C_{aromatic}$ single bonds, 1.874[12] and 1.82 Å.[13] Furthermore, the C–P(2)–C bond angles are all close to 98.9°, the C–P–C angle observed in $P(CH_3)_3$. P(2) is located on the vertex of a trigonal pyramid with the base formed by atoms P(1), C(3), C(15) and one should infer that the valence state of atom P(2) is 3.

It was observed that I forms a complex with nickel tetracarbonyl, $Ni(CO)_3{-}C_{26}H_{30}O_8P_2{}^1$. From the present structural study of I it is clear that only the trivalent phosphorus atom P(2) is able to share its lone electron pair with the Ni atom. One can assume therefore that in the complex between I and $Ni(CO)_4$ one of the tetrahedrally arranged carbon monoxide groups has been replaced by the P(2) atom of I, similar to the dimeric complex between diphenylphosphine and

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[8] D. E. C. Corbridge in "Phosphorous Chemistry," Vol. III, D. E. C. Corbridge, M. S. Pearson, C. Walling, and E. J. Griffith, Ed., Interscience, New York, N. Y., 1966.

[9] J. J. Daly, *J. Chem. Soc.*, 6147 (1964); *J. Chem. Soc. A*, 428 (1966).

[10] U. Thewalt, *Angew. Chem.*, **81**, 783 (1969).

[11] L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, Burlington House, W. 1, 1958.

[12] J. C. J. Bart, *Acta Crystallogr., Sect. B*, **25**, 762 (1969).

[13] D. L. Ward, C. N. Caughlan, G. E. Voecks, and P. W. Jennings, *ibid.*, **28**, 1949 (1972).

$Ni(CO)_4$;[14] the structure of the proposed complex is sketched in Figure 4.[15]

Registry No.—I, 25127-62-2.

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[14] R. H. B. Mais, P. G. Owston, D. T. Thompson, and A. M. Wood, *J. Chem. Soc. A*, 1744 (1967).

[15] NOTE ADDED IN PROOF.—The proposed structure of the Ni complex has been confirmed by an independent X-ray study (G. Bergerhoff, private communication).

Nucleophilic Substitution at Phosphorus[1]

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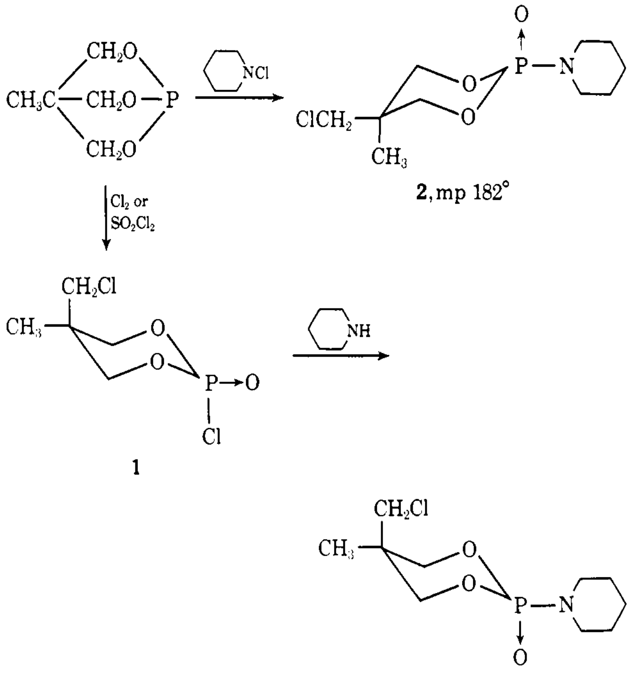
cis-5-Chloromethyl-5-methyl-2-oxo-2-chloro-1,3,2-dioxaphosphorinane was treated with a number of nucleophiles and the course of substitution at phosphorus was determined by analysis of the nmr spectra of the products. The geometry of the products with the aid of single-crystal X-ray analysis could be determined from the conformation of groups at the fifth position. In this manner the stereochemical outcome was found to be influenced by the basicity of the attacking nucleophile.

The mechanism of substitution reactions at phosphorus has been a subject of intensive study from which conflicting results have emerged. Mechanisms have been postulated on the basis of both kinetic and stereochemical results and both bimolecular, S$_N$2(P), with and without inversion, and in a few cases monomolecular, S$_N$1(P), pathways have been advanced.[2] In this paper we report results which we have obtained by means of a unique diagnostic tool which allows us to distinguish between possible stereochemical pathways.

In prior publications[3,4] we described the preparation of 2-substituted 5-halomethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinanes which entailed the treatment of a bicyclic phosphite with halogen or alkyl halide in the normal Arbuzov manner. Thus, *cis*-2-chloro-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxophosphorinane (1), which is the starting point of our study, is prepared by treating methyl bicyclic phosphite with either chlorine or sulfuryl chloride.[5] The product, a phosphorochloridate, mp 69–70°, is easily recrystallized from carbon tetrachloride. Its configuration is based upon the known configuration of 2-bromo-5-bromomethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinane,[6] and is a consequence of its mode of formation.

Two isomeric phosphoramidates were obtained by treating the bicyclic phosphate with *N*-chloropiperidine and the phosphorochloridate with piperidine.[7]



2, mp 182°

1

3, mp 152°

Single-crystal X-ray analysis[8] of the low-melting trans isomer, 3, has shown it to have the piperidinyl group equatorial and the chloromethyl group axial. The different chemical shifts of the methyl and chloromethyl hydrogens (Figure 1) indicate that the groups at the 5 position in the higher melting cis isomer, 2, have a different environment. Consequently, as a result of the mechanism of the Arbuzov reaction and the caged structure of the starting phosphite it is most likely that the piperidinyl group in 2 is also equatorial and that the

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[1] Taken in part from the Ph.D. Thesis of H. L. Horten, 1970, and M.S. Thesis of S. Larsen, 1971. Portions of this work were presented at the 5th Midwest Regional Meeting of the American Chemical Society, Kansas City, Mo., 1969, and the 4th Great Lakes Regional Meeting of the American Chemical Society, Fargo, N. D., 1970.

[2] T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," W. A. Benjamin, New York, N. Y., 1966, Chapter 5; A. I. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, Amsterdam, 1967, Chapter 10; W. E. McEwen, "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., Wiley, New York, N. Y., 1965; R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965, Chapter 8; M. J. Gallagher and I. D. Jenkins in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Wiley, New York, N. Y., 1968, Chapter 1; P. Haake and P. S. Ossip, *Tetrahedron Lett.*, 4841 (1970).

[3] W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, **84**, 610 (1962).

[4] W. S. Wadsworth, Jr., *J. Org. Chem.*, **32**, 1603 (1967).

[5] In an earlier communication, W. S. Wadsworth, Jr., and H. L. Horten, *J. Amer. Chem. Soc.*, **92**, 3785 (1970), we stated that two different isomers of the phosphorochloridate were obtained under these conditions. We have since found the material reported to have mp 59–60° to be a mixture of isomeric phosphorochloridates produced upon distillation of the pure cis isomer.

[6] T. A. Beineke, *Chem. Commun.*, 860 (1966).

[7] A third phosphoramidate, mp 136–138°, reported in our previous paper[5] has subsequently been found to be a mixture of **2** and **3**.

[8] The X-ray analyses were carried out in this laboratory under the supervision of W. Jensen. Presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., 1972.