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SPIROOXYPHOSPHORANES[1]

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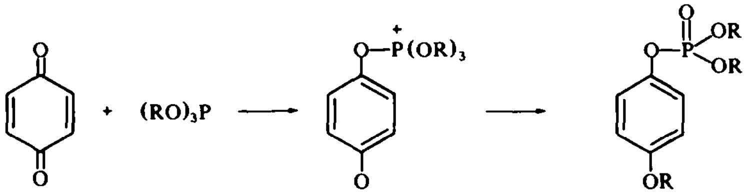
Abstract—*Spirooxyphosphoranes* with quintuply-connected phosphorus were made from the reaction of phenanthrenequinone, benzil, biacetyl, and 1-phenylpropanedione with 5-membered and 6-membered cyclic phosphite esters and amides. The P^{31} NMR spectra were compared with those of the oxyphosphoranes derived from open-chain trimethyl and triphenyl phosphites. Further comparisons were made with spiroaminooxyphosphoranes previously reported. The introduction of an additional 5-membered ring into the oxyphosphoranes resulted in a large decrease in the positive value of the P^{31} NMR shift, $\Delta \cong 20$ to 23 ppm. The effect of a 6-membered ring was negligible. The replacement of an endocyclic oxygen by a nitrogen in the 5-membered spirooxyphosphoranes led to a small increase in the positive value of the shift, $\Delta \cong 5$ ppm. The replacement of an exocyclic oxygen by a nitrogen resulted in a small decrease in the positive value of the shift, $\Delta \cong 2$ to 4 ppm. The phenyl esters of ethylenephosphite and of 2,2-dimethyl-1,3-propanediol cyclic phosphite were less reactive than the corresponding methyl esters toward α-dicarbonyl compounds.

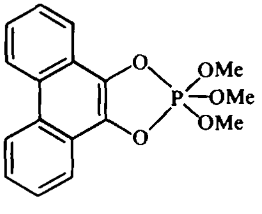
The formation of a P—O bond in the reaction of trialkyl phosphites with *p*-quinones was first reported[3,4,5] in 1957. Red colors and electron spin resonance spectra were observed in these reactions. The free radicals resulted from further oxidation of the quinone–phosphite adducts by quinones.[6,7] The colors were due to the same free radicals and also to charge-transfer complexes formed between the quinones as acceptors and the phosphites as donors.



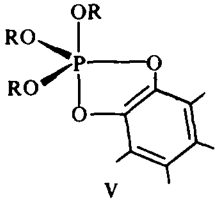
I II III, R= Me

$\delta P^{31} = +3{\cdot}7$ ppm
vs H_3PO_4

The reaction of trialkyl phosphites with *o*-quinones led also to the formation of P—O bonds; however, in this case the adducts were 2,2,2-trialkoxy-1,3,2-dioxaphospholenes[8] (IV). The X-ray analysis of one of these showed that the phosphorus was at the center of a trigonal bipyramid,[9] as in V. The H^1 NMR spectrum disclosed that the three alkoxy groups were magnetically equivalent[10] or indistinguishable in solutions at 20° and at −60°.

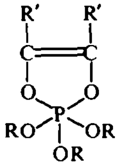


IV, $\delta P^{31} = +44{\cdot}7$ ppm

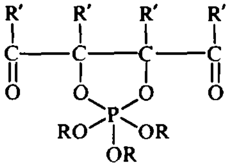


V

Some α-diketones behaved like the *o*-quinones toward trialkyl phosphites and gave pentaoxyphosphoranes VI. This was reported, independently, by three groups of investigators.[8,11,12] Other diketones, however, formed 2:1-adducts (VII) when treated with phosphites.[13]



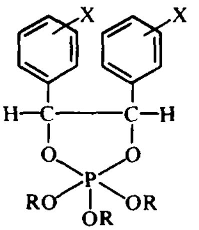
VI



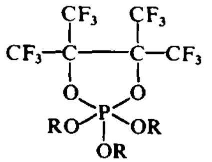
VII

Nucleophilic additions of 1,3,2-dioxaphospholenes (VI) to a large variety of carbonyl compounds gave rise to new families of oxyphosphoranes related to VII. This constitutes a new approach to the formation of C—C bonds.[8,14]

Pentaoxyphoranes of types VIII and IX have been made from the reactions of trialkyl phosphites with monocarbonyl compounds in which the carbonyl function was activated by electron-withdrawing groups.[15,16] Pentaoxyphosphoranes of type VII were prepared also from α-ketoesters and trialkyl phosphites.[17]

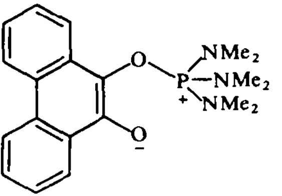


VIII: X = *p*-NO_2
o-NO_2
o-CHO

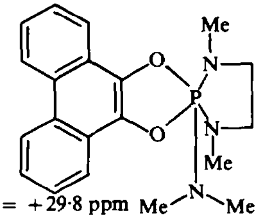


IX

The formation of P—O bonds from the reactions of *tris*dialkylaminophosphines, $(R_2N)_3P$, with *o*-quinones, α-diketones and vicinal triketones was reported recently.[18,19] Some of these adducts had quadruply-connected phosphorus, as in X; others, however, had quintuply-connected phosphorus as in XI.



X: $\delta P^{31} = -38{\cdot}5$ ppm

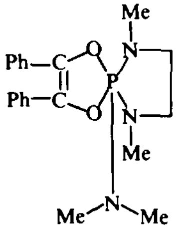


XI: $\delta P^{31} = +29{\cdot}8$ ppm

The adduct made from benzil and *tris*dimethylaminophosphine existed as an equilibrium mixture of the two forms, XIIa and XIIb, in solutions.[18] On the other hand, the related adduct made from a 5-membered cyclic triaminophosphine was a spirotriaminodioxyphosphorane, XIII. The steric effects observed in these cases are probably due to the extreme intramolecular crowding revealed by the X-ray analysis of a cyclic oxyphosphorane, V.[9] This crowding is due to interactions between the oxygen atoms in certain positions of the trigonal bipyramid and the carbon atoms attached to the oxygens in other positions of the bipyramid.


XIIa XIIb

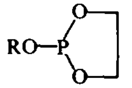
$\delta P^{31} = +13{\cdot}1$ ppm (CH_2Cl_2)
$+29{\cdot}9$ ppm (benzene)

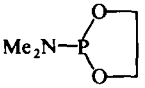

XIII: $\delta P^{31} = +37{\cdot}0$ ppm

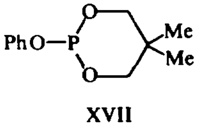
To provide more information on the molecular structure of the oxyphosphoranes[20] we undertook the preparation of a series of adducts made from the reactions of 5-membered and 6-membered cyclic phosphite esters[21] and amides with *o*-quinones and with α-diketones. This paper describes the results of this investigation.

RESULTS

The cyclic phosphite esters and amides included in this study were methyl ethylenephosphite[21] (XIV) phenyl ethylenephosphite (XV) dimethylaminoethylenephosphoroamidite (XVI),[22,23] phenyl-(2,2-dimethyl-1,3-propanediol) cyclic phosphite (XVII) and dimethylaminotrimethylene phosphoroamidite (XVIII),[22] The P^{31} NMR shifts of these compounds are given in Table 1.


XIV: R = Me
XV: R = Ph


XVI


XVII

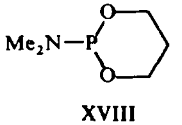
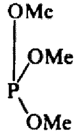
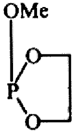
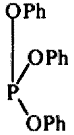
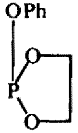
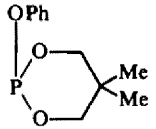
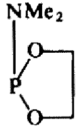
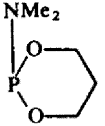

XVIII

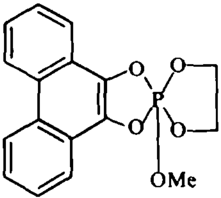
TABLE 1. P^{31} NMR SHIFTS[a] OF 1:1 ADDUCTS[b] AND OF 2:1 ADDUCTS[c] FROM THE REACTION OF CYCLIC PHOSPHITES AND PHOSPHOROAMIDITES (P^{III}) WITH PHENANTHRENEQUINONE (PQ)[d], BENZIL (BZ)[d], BIACETYL (BI)[e] AND 1-PHENYLPROPANEDIONE (PD)[e]

														
Compd.	M.p.°	δP^{31}	M.p.°	δP^{31}	M.p.°	δP^{31}	M.p.°	δP^{31}	M.p.°	δP^{31}	M.p.°	δP^{31}	M.p.°	δP^{31}
P^{III}	111 (760)	−140·0	58 (25)	−131·6	184 (0·2)	−127·1	133 (11)	−128·1	115 (0·5)	−114·8	81 (38)	−140·0	69 (28)	−143·4
P^{III}·PQ	74	+44·7	62	+23·0	147	+58·6	155	+27·0	176	+48·7	157	+21·3	136	+40·7
P^{III}·BZ	49	+49·5	75	+28·1[f]	99	+62·5	129	+32·2	94	+53·7	90	+26·4	—	—
P^{III}·BI	45 (0·5)	+48·9	73 (0·1)	+27·0	—	+64·7[h]	—	+30·8	—	—	94 (0·2)	+26·1	—	—
	31	+54·8[g]	—	—	—	+66·1	—	+36·7[i]	—	+56·6[j]	—	—		
P^{III}·PD	117 (0·2)	+49·5	148 (0·3)	+28·0	—	—	—	—	—	—	149 (0·2)	+26·9	—	—
	—	—	—	—							—	—		

[a] δP^{31} in ppm *vs* 85% H_3PO_4 at 40·5 Mc/s. Solvent: CH_2Cl_2 except as shown. [b] Spiro-1,3,2-dioxaphospholene-(1,3,2-dioxaphospholane) or (1,3,2-dioxaphosphorinane). [c] Spiro-1,3,2-dioxaphospholane-(1,3,2-dioxaphospholane) or (1,3,2-dioxaphosphorinane). [d] Forms only 1:1 adducts. [e] Forms both 1:1 *adducts* (upper values in Table) and 2:1 adducts (lower values). [f] δP^{31} = +28·1 ppm in benzene; +28·1 in tetrahydrofuran; +27·8 in dimethylformamide. [g] *Meso*-isomer of 2:1 *adduct*, with *cis*-acetyl groups. *Racemic*-isomer has δP^{31} = +52·6 ppm. [h] A 1:1 mixture of phosphite and biacetyl gave 1·0 parts of 1:1 *adduct* (+64·7 ppm), 5·2 parts of *meso*-2:1 adduct (+66·1 ppm), and 0·5 parts of *racemic*-2:1 adduct (+65·3 ppm) after 2 hr at 75°. [i] A 1:1 mixture of phosphite and biacetyl gave 9 parts of 1:1 adduct (+30·8 ppm), 10 parts of *meso*-2:1 adduct (+36·7 ppm) and 2 parts of *racemic*-2:1 adduct (35·3 ppm) after 4 hr at 80°. [j] No 1:1 *adduct* was observed; 3 parts of *meso*-2:1 adduct (+56·6 ppm) and 1 part of *racemic*-2:1 adduct (+54·9 ppm) after several hr at 80°.

Reaction of methyl ethylenephosphite (XIV) with carbonyl compounds

The 5-cyclic phosphite XIV reacted with phenanthrenequinone at 20° and gave a pale yellow oxyphosphorane XIX. This substance crystallized with considerable difficulty, however, it showed remarkable thermal stability. It was recovered unchanged from boiling diglyme solution and when heated to 120° in the absence of solvents. It was very sensitive to moisture.



XIX

The phosphorane structure XIX was based on the P^{31} NMR shift listed in Table 1. The H^1 NMR spectrum is reproduced in Fig. 1. Signals 1 and 2 were due to the OMe group. Signals 3, 4 and 5 were due to the methylene protons; signal 3 could be resolved into a more complex pattern. The separation between signals 3 and 4 and between 3 and 5 were field-independent, but the separation between 4 and 5 was field-dependent. Therefore, the four methylene protons were not magnetically equivalent. The spectrum did not change significantly at −60°.

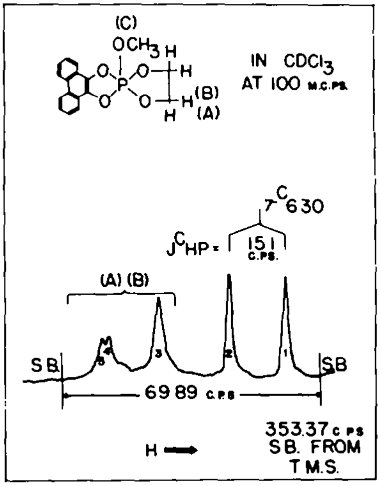
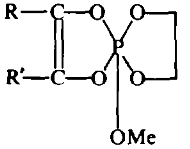


FIG. 1 H^1 NMR spectrum of the phenanthrenequinone–methyl ethylene phosphite 1:1-adduct at 30° in $CDCl_3$. At *100 Mc/s*, signals 1, 2, 3, 4, and 5 were at 362·8, 378·0, 396·8, 410·1, and 412·0 c/s, respectively, to low field of TMS. At *60 Mc/s*, these signals were at 214·3, 228·3, 233·9, 248·0 and 248·9 c/s to low field of TMS. S.B. = side bands from TMS, for calibration. The spectrum in CH_2Cl_2 solution was the same at −60° and at +30°.

The reaction of methyl ethylene phosphite (XIV) with benzil was exothermic at 20° and gave the pentaoxyphosphorane (XX). The P^{31} NMR shift is included in Table 1 and the H^1 NMR spectrum is reproduced in Fig. 2. This phosphorane was, again, thermally stable in boiling diglyme.



XX: R = R' = Ph
XXI: R = R' = Me
XXII: R = Ph, R' = Me

The spiropentaoxyphosphorane (XXI) derived from biacetyl was prepared in excellent yield; cf. Table 1. The H^1 NMR spectrum was analogous to that in Fig. 2; in addition there was a 6 H^1 singlet at τ 8·42, due to the two Me groups on the phospholene ring. These were, therefore, magnetically equivalent or indistinguishable. The spectrum was examined at −60°, −40°, −20°, +40°, +55°, +75°, +90° and +110°, without significant variations.

The spirooxyphosphorane (XXII) was made from 1-phenylpropanedione and the phosphite XIV.

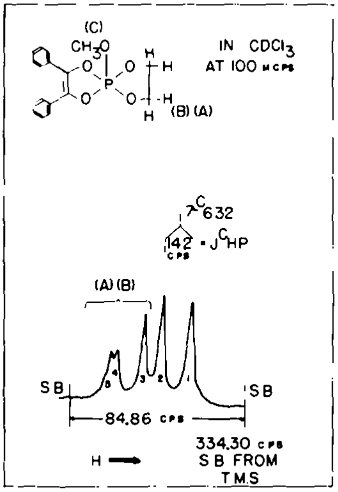
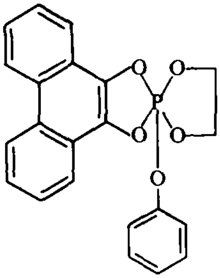


Fig. 2 H^1 NMR spectrum of the benzil–methyl ethylene phosphite 1:1-adduct, XX, at 30° in dilute $CDCl_3$. At *100 Mc/s*, signals 1, 2, 3, 4, and 5 were at 361·0, 375·2, 384·3, 398·3 and 400·3 c/s, respectively, to low field of TMS. At *60 Mc/s*, these signals were at 217·7, 231·6, 247·7, and 248·9 c/s to low field of TMS. In concentrated $CDCl_3$ solution, signals 2 and 3 merged. In CCl_4 solution, signal 2 was at lower field than 3 (at 60 Mc/s). The spectrum in CH_2Cl_2 solution was the same at −20° and at +30°.

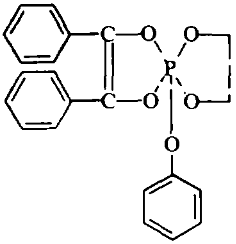
Reaction of phenyl ethylenephosphite (XV) with carbonyl compounds

This phosphite was less reactive than the Me analogus (XIV). The oxyphosphorane XXIII was made from phenanthrenequinone at 140°. The H^1 NMR spectrum was very similar to that shown in Fig. 1, except that it lacked signals 1 and 2.

The phosphorane XXIV was prepared from benzil at 100°.



XXIII



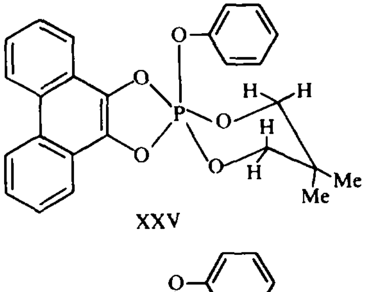
XXIV

A slightly exothermic reaction was noted when biacetyl and phenyl ethylenephosphite (XV) were mixed at 20°. When the reagents were heated to 80° a mixture of 1:1 adduct and of diasteromeric 2:1 adducts were produced. The course of this reaction will be described elsewhere;[24] however, for comparison purposes the P^{31} NMR shifts of these phosphoranes are included in Table 1.

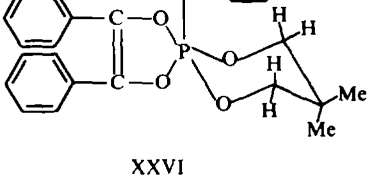
Table 1 lists the P^{31} NMR shifts of 1:1- and 2:1-adducts made from the reaction of biacetyl and triphenyl phosphite,[24] $(PhO)_3P$. Note the differences in the shifts due to the presence of the rings.

Reaction of 6-membered cyclic phosphites with carbonyl compounds

Spirooxyphosphoranes, XXV* and XXVI, were made from the reaction of a phenyl ester of a 6-membered phosphite (XVII) with an *o*-quinone and with benzil; cf. Table 1. The H^1 NMR spectrum of one of these phosphoranes is shown in Fig. 3. Signals 1 and 2 were due to the Me groups on the 6-membered ring; the signals were field-dependent showing that the two Me's were not magnetically equivalent. Signals 3, 4 and 5 were due to the methylene protons. The separation between 3 and 5, and between 4 and 5 were field-independent. The separation between 3 and 4 was field-dependent; i.e., the methylene protons were not magnetically equivalent.



XXV



XXVI

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* Formulas XXV and XXVI, and others in this paper, have no stereochemical connotation. A detailed discussion of the geometry of these molecules is deferred until the x-ray data becomes available.

The reaction of biacetyl with the phenyl ester, XVII, was complex.[24] In this case, no 1:1-adduct could be detected; the P^{31} NMR shifts of the isomeric 2:1-adducts are listed in Table 1.

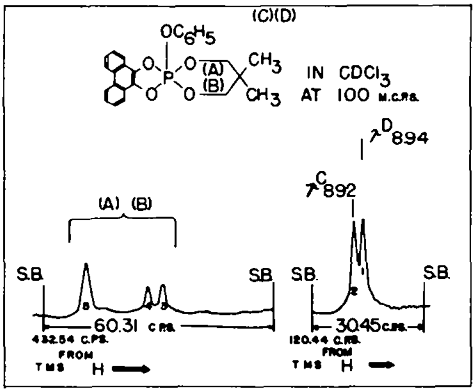
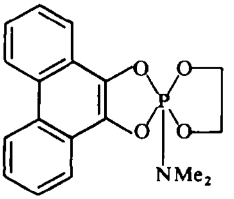


FIG. 3 H^1 NMR spectrum of the phenanthrenequinone-(phenyl 2,2-dimethyl-1,3-propanediol cyclic phosphite) 1:1-adduct at 30° in $CDCl_3$. At *100 Mc/s* signals 1, 2, 3, 4, and 5 were at 106·1, 108·6, 401·1, 404·8, and 420·9 c/s, respectively, to low field of TMS. At *60 Mc/s*, these signals were at 63·9, 65·2, 236·3, 238·1, and 255·3 c/s to low field of TMS. S.B. = side bands from TMS for calibration.

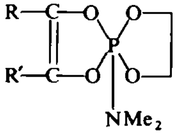
Reaction of cyclic phosphoroamidites with carbonyl compounds

The 5-membered cyclic amidite, XVI, reacted with phenanthrene quinone at 0° and gave the spirotetraoxyaminophosphorane, XXVII; cf. Table 1. The two Me groups attached to the nitrogens gave one doublet at τ 7·30, $J_{HP} = 10{\cdot}5$ c/s. The spectrum was analogous to that in Fig. 1, except that signal 3 was clearly resolved into two multiplets.

The oxyaminophosphoranes, XXVIII, XXIX and XXX were readily made from benzil, biacetyl and 1-phenylpropanedione, respectively. The two Me groups on the phospholene ring of XXIX were magnetically equivalent or indistinguishable since they gave one singlet at τ 8·30.

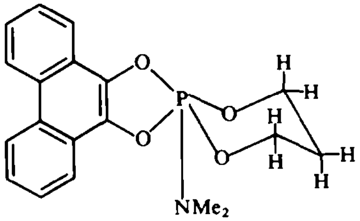


XXVII



XXVIII: R = R′ = Ph
XXIX: R = R′ = Me
XXX: R = Ph, R′ = Me

The 6-membered cyclic amidite, XVIII, gave a phosphorane XXXI with phenanthrequinone at 0°.



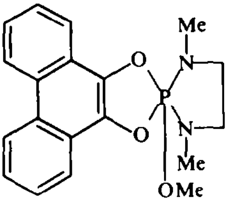
XXXI

DISCUSSION

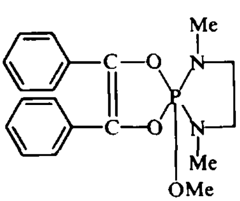
This investigation showed that 5-membered and 6-membered cyclic phosphite esters and amides are capable of forming oxyphosphoranes that are as stable as the corresponding compounds made for non-cyclic phosphites. The molecular geometry of some of these phosphoranes in the crystalline state is being studied by X-ray analysis.

Some correlations between molecular structure and P^{31} NMR shifts emerged from this and previous work.[8, 18] The P-shift of a 2,2,2-trialkoxy-1,3,2-dioxaphospholene of type IV or VI was shifted to lower magnetic field when two of the three exocyclic oxygen atoms became part of a new 5-membered saturated ring, as in the spirooxyphosphoranes XXI–XXXI. The decrease in the shift amounted to 21 ppm regardless of the nature of the carbonyl compound. This effect was not noted in the case of the introduction of a 6-membered ring.[25, 26]

The replacement of an endocyclic oxygen of a 1,3,2-dioxaphospholane by a nitrogen resulted in a small increase, $\Delta \sim 5$ ppm in the P-shift. However, when the oxygen that was being replaced by nitrogen was exocyclic, the P-shift decreased somewhat, $\Delta \sim 2$ pp. These conclusions follow from the data in Table 1 and from the values of the shifts in the related compounds XXXII and XXXIII.[8, 18]

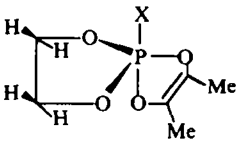


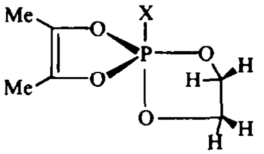
XXXII: $\delta P^{31} = +33{\cdot}5$ ppm

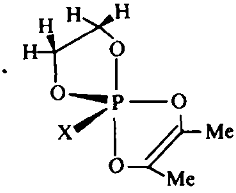


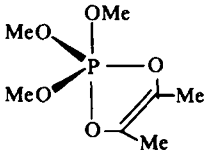
XXXIII: $\delta P^{31} = +38{\cdot}6$ ppm

A tentative conclusion can be reached from studies of the H^1 NMR spectra of the oxyphosphoranes in the temperature range −60° to +110°. This concludion can be stated with reference to formulas XXXIVa, XXXIVb and XXXIVc. In XXXIVa the phospholene ring is in an apical-equatorial plane, while the phospholane ring is in a diequatorial plane. The relative positions of the rings are reversed in XXXIVb. Both rings occupy apical-equatorial planes in formula XXXIVc. The biacetyl–trimethyl phosphite adduct can be represented as XXXVa, with the phospholene ring in the apical-equatorial plane, according to the X-ray analysis of a related compound.[9]


XXXIVa: X = OMe or NMe_2


XXXIVb: X = OMe or NMe_2

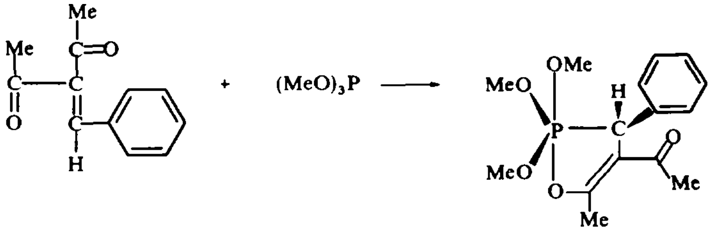

XXXIVc: X = OMe or NMe_2


XXXVa

The H^1 NMR spectrum of the biacetyl–methyl ethylenephosphite adduct (XXI) had only one singlet for the two Me groups on the phospholene ring, while the four methylene protons on the phospholane ring gave a complex pattern indicative of magnetic non-equivalency. The spectrum was very similar in the range −60° to +110°, therefore, it is probable that the molecule is not stereochemically rigid in this range. Possibly, the molecule is undergoing rapid positional exchange[10] among structures *a*, *b* and *c*. Note that in *b* the two Me groups are equivalent, and that in *a*, *b* and *c* the methylene protons are not equivalent.

It is conceivable that the positional exchange may be between *a* and *c* only, and that the difference in the H-shift associated with an apical-Me and an equatorial-Me is too small for detection. This point could be elucidated further by changes in the nature of the group X in order to magnify the difference in the shifts of the Me's on the phospholene ring. This effect, however, was not noted when $X = NMe_2$, as in adduct XXIX, which had only one singlet due to the two Me groups.

The H^1 NMR spectrum of the biacetyl–trimethyl phosphite adduct, XXXV, had only one singlet for the two Me groups on the phospholene ring and only one doublet due to the three OMe groups, in the temperature range −60° to 30°. An exchange among XXXV and the corresponding structure with the ring in the diequatorial plane would be consistent with these observations. Again, it is not known if the differences in the shifts associated with the groups in the various positions of the bipyramid are large enough for detection.


XXXVI

It was reported recently, that the cyclic tetraoxyalkylphosphorane[27] XXXVI showed a different H^1 NMR at $-65°$ and $+30°$. At $+30°$ the three OMe groups gave only one doublet,[27] while at the lower temperature, three doublets were detected.[28] Apparently, in this type of phosphorane the positional exchange can be inhibited at low temperatures and the differences in the shifts of the methoxy groups in the various positions can be detected.

EXPERIMENTAL

The P^{31} NMR spectra were determined in a Varian HR-100 instrument at 40·5 Mc/s using trimethyl phosphite as external reference; all values are referred to 85% H_3PO_4 as zero.

The H^1 NMR spectra were determined in all cases at 60 Mc/s in a Varian A-60 instrument, and in several cases also at 100 Mc/s in a Varian HR-100 instrument; all values are referred to TMS as 10 (τ values).

Analyses are by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Cyclic phosphite esters and amidites. Methyl ethylene–phosphite[21], n_D^{25} 1·4877, was made from ethylene glycol and PCl_3 followed by methanolysis as described. Phenyl ethylenephosphite was obtained from Hooker Chemicals and was freshly distilled. Phenyl 2,2-dimethyl-1,3-propanediol cyclic phosphite was obtained from Aldrich Chemicals and was purified by distillation. The Me groups in the ring gave H^1 NMR signals at τ 8·83 and τ 9·46.

2,2-Dimethylamino-1,3,2-dioxaphospholane was made as described[22, 23] from the reaction of Me_2NH with 2-chloro-1,3,2-dioxaphospholane in hexane. 2-Dimethylamino-1,3,2-dioxaphosphorinane was prepared in a similar manner.[22]

The P^{31} NMR shifts are given in Table 1.

Reaction of methyl ethylenephosphite with phenanthrenequinone

(a) The phosphite (6·8 g, 1·13 mole equiv) was added to the quinone (10·3 g) under N_2 in the following manner. A few drops of the phosphite were added to the quinone at 20°; an immediate brown color appeared, but the exothermic phase of the reaction was noted only after 5 min. The mixture was placed in an ice-bath and the rest of the phosphite was added dropwise, with stirring, at such a rate that the inside temp remained between 50 and 70°. (If the temp is allowed to drop, crystallization of product occurs too early and incomplete reaction is observed). The product was kept 1 hr at 0°, when crystallization seemed complete. Hexane (50 ml) was introduced; the mixture was stirred 15 hr at 20°, was refluxed 2 hr, and was cooled to 20°. The gummy *hexane-insoluble fraction* 1 gave IR and H^1 NMR spectra which were indistinguishable from those of the analytical sample of the adduct XIX. Fraction 1 was kept 24 hr at $-20°$ under 70 ml of hexane and afforded 4·5 g (30%) of pale yellow crystalline adduct, XIX, m.p. 61–63° (after drying at 0·1 mm and 20°). This crop 1 was submitted to analysis; see Table 1 for spectral data. The non-crystalline portion of fraction 1 was kept an additional 24 hr at $-20°$ under hexane and afforded 9·4 g (50%) of the crystalline adduct, XIX. The spectral properties of crops 2 and 1 of adduct, XIX, were indistinguishable; no additional material was found in the hexane mother liquids. Total yield of crystalline XIX: 80%.

The initial *hexane-soluble fraction* 2 deposited a nearly colourless gum upon cooling at $-20°$ for 15 hr. This crop 3 of impure adduct (1·2 g) could not be crystallized; its spectra showed all the features of the adduct XIX and traces of what seemed to be a phosphate ester.

The final hexane mother liquid afforded 0·9 g of a gummy mixture of adduct, XIX, a phosphate, and small amounts of the original phosphite, XIV.

Crystalline 1:1-adduct XIX, m.p. 61–63°. (Found: C, 61·5; H, 4·8; P, 9·4. $C_{17}H_{15}O_5P$ requires: C, 61·8; H, 4·5; P, 9·4%.)

The adduct was very susceptible to moisture. Its solubility in CCl_4, $CDCl_3$, and hexane decreased markedly when in the crystalline state. It had IR bands in CCl_4 at: 6·02 (m), 6·23 (w), 6·62 (w), 6·71 (m), 7·25 (s), 7·50 (w), 7·95 (m), 8·55 (w), 8·95 (shoulder), 9·15 (w), 9·35 (s), 9·50 (*vs*), 9·70 (s), 10·40 (w), 10·55 (w), and 11·65 (s), μ. The P^{31} NMR shift is given in Table 1.

(b) A slow reaction occurred at 20° when XIV was added to an equimolar amount of phenanthrenequinone suspended in *methylene chloride*. A clear, red-brown soln (0·4 M) resulted after 24 hr. Removal of the solvent in vacuum left a viscous red oil which was considerably more soluble in CH_2Cl_2 than both the crystalline 1:1-adduct, XIX, and phenanthrene quinone, although the IR spectrum in that solvent contained all the bands due to these two substances. Presumably, they are associated as a complex. This material easily gave clear 1·2 M solns in CH_2Cl_2; after an additional 24 hr period at 20°, most, but not all of the phenanthrene–quinone had disappeared. Removal of the solvent and recrystallization of the residue from benzene–hexane gave the crystalline 1:1-adduct with considerable difficulty.

Reaction of methyl ethylenephosphite with benzil

Compound XIV (9·53 g, 78 mmoles) was added to benzil, Ph.CO.CO.Ph, (16·27 g, 77·5 mmoles) at 20°, under N_2, with stirring. The exothermic reaction resulted in a clear yellow soln within 15 min; no red color, as in the quinone case, was noted at any time. IR spectra showed complete reaction in about 2 hr. The product was dissolved in benzene (2 ml/g); the soln was diluted with an equal volume of hexane and was kept 2 days at −20°. The first crop of nearly colorless 1:1-adduct XX, (20·0 g, m.p. 73–76°) was collected in a dry N_2 atm. From the filtrate, 4·3 g of crude XX was obtained; this gave 1·7 g of additional adduct, m.p. 74–76° after recrystallization from benzene–hexane. The yield of XX was 90%.

The analytical sample of the *methyl ethylenephosphite–benzil* 1:1-*adduct*, XX, had m.p. 75–76° from benzene–hexane. (Found: C, 60·7; H, 5·2; P, 9·2. $C_{17}H_{17}O_5P$ requires: C, 61·4; H, 5·1; P, 9·3%.) The spectral characteristics were: bands at 3·40 (w), *6·06* (*1650* cm^{-1}) (w; C=C), 6·27 (vw), 6·71 (w), 6·94 (w), 7·87 (m), 7·95 (m), 8·13 (vw), 8·47 (vw), 8·80 (m), 9·09 (shoulder), 9·48 (1055 cm^{-1}) (*vs*, POMe), 11·45 (m) μ (in CCl_4). The P^{31} NMR shift is given in Table 1.

Reaction of methyl ethylenephosphite with biacetyl

Compound XIV, (12·9 g, 105·6 mmoles) was added dropwise over a 15 min period to biacetyl, Me.CO.CO.Me, (9·55 g, 111 mmoles) at 20° under N_2 with stirring. After a few min, an exothermic reaction was noted; the liquid temp rose to 60°. IR spectra showed complete reaction in about 30 min. The mixture was distilled (6 inch Vigreaux column) after 2 hr at 20°. Four fractions were arbitrarily collected: (1) 1·02 g, b.p. 79–81° (0·3 mm), n_D^{25} 1·4623; (2) 2·29 g, b.p. 82–83° (0·4 mm), n_D^{25} 1·4622; (3) 9·75 g, b.p. 83–85° (0·4 mm), n_D^{25} 1·4620; (4) 2·50 g (b.p. 84–86° (0·4 mm), n_D^{25} 1·4620. The yield of nearly colorless *methyl ethylenephosphite–biacetyl* 1:1-*adduct* XXI, was 75%. (Found: C, 40·0; H, 6·2; P, 14·7; mol wt 280, (isothermal distillation in benzene). $C_7H_{13}O_5P$ requires: C, 40·4; H, 6·2; P, 14·9%; mol wt 208. The spectral characteristics were: bands at 3·42 (w), *5·84* (*1710* cm^{-1}) (*vw, with a shoulder at 5·78*), 6·92 (w), 7·22 (m), 7·70 (m), 8·06 (ms), 8·50 (ms), 9·22 (shoulder), *9·43* (*1060* cm^{-1}) (*vs*, MeOP), 9·66 (s), 10·05 (s), 10·50 (m), 11·55 (s), (s), and 12·1 (ms), μ (CCl_4). The H^1 NMR spectrum had a 3 H^1 doublet, J_{HP} = 13·8 c/s, at τ 6·42 (CH_3OP); a 6 H^1 singlet at τ 8·42 (MeC). The P^{31} NMR shift is given in Table 1.

Reaction of methyl ethylenephosphite with 1-*phenyl*-1,2-*propanedione*

The diketone (8·03 g, 54·2 mmoles) was added to XIV (8·27 g, 67·8 mmoles) at 0° under N_2 with stirring. The mixture was allowed to reach 20°, was kept 15 hr at this temp, and was then distilled through a 5 inch straight-head condenser. The excess phosphite was collected in the range 30–35° (0·3 mm) and the pale yellow, viscous 1:1-adduct, XXII, in the range 152–155° (0·3 mm); the yield was nearly quantitative. The analytical sample of the 1:1-adduct XXII had b.p. 148–149° (0·2 mm), n_D^{25} 1·5506. (Found: C, 53·0; H, 5·7; P, 11·5. $C_{12}H_{15}O_5P$ requires: C, 53·3; H, 5·7; P, 11·5%.) The spectral characteristics were: bands at: 3·40 (w), *5·97* (*1675* cm^{-1}) (*w*, C=C), 6·26 (vw), 6·90 (w), 7·96 (w), 7·87 (m), 8·13 (w), 8·40 (w), 8·60 (w), 8·80 (w), 9·20 (s, shoulder), *9·40* (*1065* cm^{-1}) (*vs*, POMe), 9·62 (s), 9·90 (s), 10·30 (m), and 10·60 (w) μ (in CCl_4). The H^1 NMR spectrum had a 3 H^1 doublet, J_{HP} = 13·3 c/s, at τ 6·41 (MeOP), and a 3 H^1 singlet at τ 7·88 (MeC) (in CCl_4). The P^{31} NMR shift is given in Table 1.

Reaction of phenyl ethylenephosphite with phenanthrenequinone

Compound XV (7·94 g, 43·2 mmole) was added to phenanthrenequinone (8·59 g, 40·8 mmoles) at 20° under N_2. No reaction was observed at this temp. The mixture was stirred 4 hr at 140–145°, and was then kept 10 hr at 20°. The brown solid was dissolved in hot benzene (50 ml) and the soln was allowed to crystallize at 0°. The first crop of the 1:1-adduct XXIII (13·6 g, 85% yield) had m.p. 155–157° from benzene. (Found: C, 67·2; H, 4·4; P, 8·0. $C_{32}H_{17}O_5P$ requires: C, 67·3; H, 4·3; P, 7·9%.) The spectral characteristics were: bands at 3·85 (w), 6·02 (m), 6·28 (m), 6·73 (m), 6·90 (m), *7·27* (*1375* cm^{-1}) (s), 8·26 (m), 9·26 (w), 9·52 (1050 cm^{-1}) (*vs*), 9·76 (s), 10·65 (s), and 11·55 (s) μ (in CH_2Cl_2). The substance was sparingly soluble in the usual solvents employed in H^1 NMR spectrometry.

The P^{31} NMR shift is given in Table 1.

Reaction of phenyl ethylenephosphite with benzil

A mixture of benzil, (16·71 g, 79·6 mmoles) and phenyl ethylenephosphite (14·63 g, 79·6 mmoles) gave no evidence of reaction at 20° under N_2. The mixture was stirred for 4 hr at 100° and the was kept 15 hr at 20°. The solid product was dissolved in hot benzene (5 ml/g) and the soln was allowed to stand at 20°. The first crop of nearly colorless 1:1-adduct XXIV was 22·7 g, m.p. 129–130° from benzene. (Found: C, 66·3; H, 4·9; P, 8·1; mol wt 461 (isothermal in benzene). $C_{22}H_{19}O_5P$ requires: C, 67·0; H, 4·8; P, 7·9%; mol wt 394). The spectral characteristics were: bands at 3·54 (w), *6·01* (*1665 cm*$^{-1}$) (*w, broad*), 6·28 (m), 6·74 (s), 6·92 (w), 7·78 (m), 8·26 (w), 8·85 (mw), 9·18 (m), *9·52* (*1050 cm*$^{-1}$) (*vs*), 9·80, 10·50, 10·60 (sh.), 10·80 (s), 11·50 (s), and 12·70 (s) μ (in CH_2Cl_2).

Reaction of phenyl(2,2-dimethyl)-1,3-propanediol cyclic phosphite with phenanthrenequinone

A mixture of the quinone (9·33 g, 45 mmoles) and the phosphite XVII (10·92 g, 50·8 mmoles) remained unchanged within 1 hr at 20° under N_2. A dark-brown liquid was obtained after 30 min at 115°, (stirring). This material solidified at 95° and was dissolved in 55 ml of hot benzene; crystallization of the 1:1-adduct, occurred at 20°. The pale yellow 1:1-adduct XXV, m.p. 176–177° from benzene was obtained in 92% yield. (Found: C, 69·0; H, 5·6; P, 7·0. $C_{25}H_{23}O_5P$ requires: C, 69·1; H, 5·3; P, 7·1%.) The spectral characteristics were: bands at 3·42 (w), *6·04* (*1655 cm*$^{-1}$) (*m*), 6·20 (sh.), 6·31 (m), 6·62 (sh.), 6·73 (ms), 6·90 (m), *7·27* (*s*), 7·52 (w), *8·26* (*s*), 8·97 (sh.), 9·35 (sh.), *9·50* (*1050 cm*$^{-1}$) (*vs*), 9·76 (s), 10·50 (sh.), 10·60 (s), 10·80 (sh.), and 11·90 (s) μ (in CH_2Cl_2). δ P^{31} is given in Table 1.

Reaction of phenyl (2,2-dimethyl)-1,3-propanediol cyclic phosphite with benzil

A mixture of benzil (20·3 g, 91·1 mmoles) and the phosphite XVII (20·84 g, 97 mmoles) showed no signs of reaction at 20° under N_2. A clear liquid was produced after 1 hr at 70°; it solidified at 20° and was soluble in 50 ml of hot benzene. The first crop of the pale yellow *benzil-phenyl (2,2-dimethyl)1,3-propanediol cyclic phosphite adduct*, XXVI, was 18·5 g and had m.p. 94–96^{9} from benzene. (Found: C, 68·5; H, 6·1; P, 6·8. $C_{25}H_{25}O_5P$ requires: C, 68·8; H, 5·7; P, 7·1%.) The spectral characteristics were: bands at 3·40 (w), *6·00* (*1670 cm*$^{-1}$) (w), 6·27 (m), 6·71 Mm), 6·80 (sh.), 6·90 (sh.), 7·30 (vw), 7·60 (sh.), 7·75 (sh.), 8·26 (m), 8·50 (w), 8·85 (vw), 9·22 (sh.), 9·43 (1060 cm^{-1}) (*vs*), 9·80 (s), 10·7 (s), and 11·6 (s) μ (in CCl_4). The P^{31} NMR shift is given in Table 1.

The benzene mother liquid afforded 18 g of a material m.p. 92–95°, with an IR spectrum which was very similar to that of the adduct.

The 1:1-adduct XXVI was rather unstable. Samples of it became quickly contaminated with a second material which has some of the spectral characteristics of a phosphate ester.

Reaction of 2-dimethylamino-1,3,2-dioxaphospholane XVI, with phenanthrenequinone

The quinone (15·1 g) and the amidite (10·5 g, 1·07 mole equiv) were mixed at 0° under N_2 with stirring. An instantaneous reaction led to a clear soln within 1 min; the liquid soon solidified. Recrystallization from hot benzene gave XXVII (24 g). The analytical sample had m.p. 157–159°. (Found: C, 63·2; H, 5·5; N, 3·7; P, 9·2. $C_{18}H_{18}O_4NP$ requires: C, 63·0; H, 5·3; N, 4·1; P, 9·0%.) The spectral characteristics were: *6·50* (*w*), 6·22 (vw), 6·62 (vw), 6·90 (w), 7·25 (s), 9·20 (vm), 9·45 (vs), 9·70 (s), 9·95 (m), 12·1 (vs), μ (in CH_2Cl_2). The P^{31} NMR shift is given in Table 1. The H^1 NMR ($CDCl_3$) had 8 H^1 at τ 1·14, 2·0 and 2·6; a 4 H^1 multiplet at ca. τ 6·10, and a 6 H^1 doublet, J_{HP} = 10·5 c/s, at τ 7·30.

Reaction of 2-dimethylamino-1,3,2-dioxaphospholane, XVI, with benzil

Benzil (6·7 g, 77·8 mmoles) was added to the amidite (10·6 g, 78·4 mmoles) at 0° under N_2 with stirring. The immediate reaction gave a liquid which soon solidified. Recrystallization from benzene gave the pale yellow crystalline XXVIII (13 g, m.p. 90–92°). (Found: C, 62·7; H, 6·2; N, 3·9; P, 9·2. $C_{18}H_{20}O_4NP$ requires: C, 62·6; Hm 5·8; N, 4·0; P, 9·0%.) Spectral characteristics were: bands at 6·00–6·05 (w), 6·25 (w), 6·68 (w), 6·92 (w), 7·74 (m), 7·84 (m), 8·82 (w), 9·15 (w), *9·46* (*vs*), 9·75 (w), 10·0 (w) 10·5 (m), μ (in CCl_4). The P^{31} NMR shift is given in Table 1. The H^1 NMR spectrum ($CDCl_3$) had 10 aromatic protons at τ 2·8, a 6 H^1 doublet, J_{HP} = 10·5 c/s, at τ 7·25, and a 4 H^1 multiplet at ca. τ 6·14.

Reaction of 2-dimethylamino-1,3,2-dioxaphospholane, XVI, with biacetyl

Biacetyl (4·7 g, 54·3 mmoles) was added *very slowly* over a 30 min period to the amidite (7·3 g, 54·3 mmoles) at 0° under N_2 with stirring. The liquid was allowed to reach 20°, kept 8 hr, and submitted to distillation through a 6 inch Vigreaux column. The main fraction of XXIX (6·5 g) was collected at 94 95°, 0·05 mm, n_D^{25} 1·4750. (Found: C, 43·3; H, 7·5; N, 6·4; P, 14·0. $C_8H_{16}O_4NP$ requires: C, 43·4; H, 7·2; N, 6·3; P, 14·0%.) The spectral characteristics were: bands at 5·78 (w), 6·90 (mw with shoulder at 6·80 and 6·90) 7·20 (m), 7·94 (ms), 8·07 (s), 8·32 (m), 8·70 (m), *9·20 (vs)*, and 10·5 vs, μ (in CCl_4). The P^{31} NMR shift is given in Table 1. The H^1 NMR of the pure liquid had a 6 H^1 singlet at τ 8·30, a 6 H^1 doublet, J_{HP} = 10·5 c/s, at τ 7·36, and a 4 H^1 multiplet centered at ca. τ 6·23.

Reaction of 2-dimethylamino-1,3,2-dioxaphospholane, XVI, *with 1-phenylpropanedione*

The diketone (13·3 g, 89·7 mmoles) was added dropwise over a 30 min period to the amidite (12·2 g, 90 mmoles) at 0° under N_2. The mixture was kept 10 hr at 20° and was then distilled through a 6 inch Vigreaux column. The XXX (19 g) was collected at 150–152° (0·5 mm), n_D^{25} 1·5551. (Found: C, 54·0; H, 6·6; P, 10·0. $C_{13}H_{18}O_4NP$ requires: C, 55·1; H, 6·4; P, 10·9%.) The spectral characteristics were: 5·96 (w), 6·23 (w), 6·96 (w), 7·28 (w), 7·80 (s), 8·10 (m), 8·37 (w), *9·22 (vs) 9·40 (vs)*, 9·88 (s), 10·28 (m), 10·55 (ms), μ (in CCl_4). The P^{31} NMR shift is given in Table 1. The H^1 NMR (CCl_4) had a 3 H^1 singlet at τ 7·84, a 6 H^1 doublet, J_{HP} = 10·2 c/s, at τ 7·28, and a 4 H^1 multiplet centered ca. τ 6·16.

Reaction of 2-dimethylamino-1,3,2-dioxaphosphorinane, XVIII, *with phenanthrenequinone*

The quinone (10·3 g, 49·7 mmoles) was added in small portions (ca. 1 g) to the amidite (8·9 g, 60·0 mmoles) at 0° under N_2 with stirring. Within 1 min after the addition of a 1 g-portion of the quinone, the reaction began; it became vigorous after about 3 g of the quinone had been introduced. Toward the end of the reaction, the mixture was dark brown, and it became solid. Benzene (20 ml) was introduced. The mixture was kept 10 hr at 0°, and 48 hr at 20°. The crystals were dissolved in benzene at the boiling point, the soln was cooled to 5°, and the first crop of XXXI was collected (11 g). A second crop of the same material (8 g) was obtained by concectration of the filtrate. The analytical sample of XXXI had m.p. 136–137°. (Found: C, 63·7; H, 5·9; N, 3·8; P, 8·6. $C_{19}H_{20}O_4NP$ requires: C, 63·9; H, 5·6; N, 3·9; P, 8·7%.) The spectral characteristics were: bands at *6·05* (w), 6·23 (vw), 6·90 (w), 7·28 (m), 9·12 (m), *9·45 (vs)*, 9·70 (m), 9·90 (m), μ (in CCl_4). The P^{31} NMR shift is given in Table 1. The H^1 NMR ($CDCl_3$) had aromatic protons at τ 1·4, 2·0, and 2·6. The four α protons gave a multiplet at ca. τ 5·9. The two β protons gave a multiplet at ca. τ 8·4. The 6 Me protons gave a doublet, J_{HP} = 10·2 c/s, at τ 7·25.

REFERENCES AND FOOTNOTES

[1] [a] *Organic Compounds with Pentavalent Phosphorus*—XXX; [b] Part XXIX: F. Ramirez, S. B. Bhatia and C. P. Smith, *J. Am. Chem. Soc.* **89**, 3030 (1967).

[2] This investigation was supported by Public Health Service Grant CA-04769-06 from the National Cancer Institute, and by the National Science Foundation Grant, GP 3341.

[3] [a] F. Ramirez and S. Dershowitz, *J. Org. Chem.* **22**, 856 (1957); [b] *Ibid.* **23**, 778 (1958); [c] F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.* **81**, 587 (1959); [d] F. Ramirez, E. H. Chen and S. Dershowitz, *Ibid.* **81**, 4338 (1959).

[4] V. A. Kukhtin and K. M. Orekhova, *Dokl. Akad. Nauk SSSR*, **124**, 819 (1959); *Chem. Abstr.* **53**, 16037d (1959), reported the formation of diethyl (2-ethoxy-5-hydroxy)phenylphosphonate from the reaction of triethyl phosphite with *p*-benzoquinone in benzene at 60°. They stated that the product was not an ester of phosphoric acid. This statement is in error. Subsequently, V. A. Kukhtin, N. S. Garif'yanov and K. M. Orekhova, *J. Gen. Chem. USSR* **31**, 1070 (1961), assumed rearrangements of adducts with P—C bonds to adducts with P—O bonds in the *p*-quinone-phosphite reactions.

[5] Th. Reetz, J. F. Powers and G. R. Graham, *Abstracts of Papers, A.C.S. Meeting* p. 86P. Chicago, Ill. (1958), reported that the reaction of chloranil with triisopropyl phosphite in boiling toluene gave quinone–phosphonates with replacement of some and of all of the chlorines. The effect of temp and of the structure of the phosphate on the course of these reactions is under investigation in this laboratory.

[6] [a] E. A. Lucken, F. Ramirez, V. P. Catto, D. Rhum and S. Dershowitz, *Tetrahedron* **22**, 637 (1966); [b] E. A. C. Lucken, *J. Chem. Soc.* 5123 (1963).

[7] For a discussion of this topic, see: C. Walling and M. S. Pearson in *Topics in Phosphorus Chemistry* (Edited by E. J. Griffith and M. Grayson) Vol. 3, p. 23. Interscience, New York, N.Y. (1966).

[8] [a] F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.* **82**, 2652, (1060); [b] *Ibid.* **85**, 3252 (1963); [c] F. Ramirez, *Pure and Appl. Chem.* **9**, 337 (1964); [d] F. Ramirez, *Bull. Soc. Chim. Fr* 2443 (1966).

[9] [a] W. C. Hamilton, S. J. LaPlaca and F. Ramirez, *J. Am. Chem. Soc.* **87**, 127 (1965); [b] W. C. Hamilton S. J. LaPlaca, F. Ramirez and C. P. Smith, *Ibid.* **89**, 2268 (1967).

[10] [a] R. S. Berry, *J. Chem. Phys.* **32**, 933 (1960); [b] E. L. Muetterties and R. A. Schumm, *Quart. Rev.* **20**, 245 (1966).

[11] [a] G. H. Birum and J. L. Dever, *Abstracts, Division of Organic Chemistry, 135th National Meeting of The American Chemical Society* p. 101P. Chicago, Ill., Sept (1958); [b] G. H. Birum and J. L. Dever, U.S. Patents, 2,961,455 (1960) and 3.014, 949 (1961).

[12] [a] V. A. KuKhtin, *Dokl. Akad. Nauk SSSR* **121**, 466 (1958); [b] V. A. Kukhtin and K. M. Orekhova, *J. Gen. Chem. USSR* **30**, 1229 (1960); [c] V. A. Kukhtin and K. M. Kirillova, *Ibid.* **32**, 2755 (1962); [d] K. M. Kirillova and V. A. Kukhtin, *Zh. Obshch. Khim.* **35**, 544 (1965); *Chem. Abstr.* **63**, 5236 (1965).

A discussion of the various structures proposed by these investigators at various times will be found in Ref. 8c.

[13] [a] F. Ramirez and N. Ramanathan, *J. Org. Chem.* **26**, 3041 (1961); [b] F. Ramirez, N. Ramanathan and N. B. Desai, *J. Am. Chem. Soc.* **84**, 1317 (1962).

[14] [a] F. Ramirez, A. V. Patwardhan and C. P. Smith, *J. Org. Chem.* **31**, 3159 (1966); [b] F. Ramirez, S. B. Bhatia and C. P. Smith, *J. Am. Chem. Soc.* **89**, 3026 (1967); [c] F. Ramirez, S. B. Bhatia and C. P. Smith, *Ibid.* **89**, 3030 (1967).

[15] [a] F. Ramirez, S. B. Bhatia and C. P. Smith, *Tetrahedron* **23**, 2067 (1967); [b] F. Ramirez, S. B. Bhatia, A. V. Patwardhan and C. P. Smith, *J. Org. Chem.* **32**, 2194 (1967).

[16] [a] F. Ramirez, C. P. Smith, A. S. Gulati and A. V. Patwardhan, *Tetrahedron Letters* 2151 (1966); [b] N. P. Gambaryan, Yu. A. Cheburkov and I. L. Kunyants, *Bull. Acad. Sci. USSR* **8**, 1433 (1964).

[17] F. Ramirez, N. B. Desai and N. Ramanathan, *Tetrahedron Letters* 323 (1963).

[18] [a] F. Ramirez, A. V. Patwardhan and C. P. Smith, *J. Am. Chem. Soc.* **87**, 4973 (1965); [b] F. Ramirez, A. V. Patwardhan, H. J. Kugler and C. P. Smith, *Tetrahedron Letters* 3053 (1966).

[19] [a] R. Burgada, *C.R. Acad. Sci., Paris* **158**, 4789 (1964); [b] R. Burgada, *Bull. Soc. Chim. Fr* 347 (1967). The adduct formed from *tris*dimethylaminophosphine and diethyl oxomalonate was incorrectly formulated as a cyclic triaminodioxyphosphorane. It actually has an open-dipolar structure, cf. Ref. 18.

[20] [a] D. B. Denney and H. M. Reller, *J. Am. Chem. Soc.* **86**, 3897 (1964); [b] D. B. Denney and S. T. D. Gough, *Ibid.* **87**, 138 (1965).

[21] For recent work on 5-membered cyclic phosphites see: [a] H. Goldwhite, *Chem. & Ind.* 494 (1964); [b] B. Fontal and H. Goldwhite, *Tetrahedron* **22**, 3275 (1966); [c] D. Z. Denny and D. B. Denney, *J. Am. Chem. Soc.* **88**, 1830 (1966); [d] R. Foster and C. A. Fyfe, *Spectrochim. Acta* **21**, 1785 (1965).

[22] [a] A. E. Arbuzov and V. M. Zoroastrova, *Izv. Akad. Nauk SSSR, Otdel, Khim. Nauk* 789 (1952); *Chem. Abstr.* **47**, 10461d (1953); [b] A. E. Arbuzov, V. M. Zoroastrova and N. I. Rizpolozhensky, *Bull. Akad. Sci. SSSR, Classe Sci. Chim.* **208**, 18 (1948); *Chem. Abstr.* **42**, 4932 (1948); [c] R. Burgada, *Bull. Soc. Chim. Fr* 2335 (1963).

[23] V. A. Kukhtin and I. P. Gozman, *Dokl. Akad. Khim. SSSR*, **158**, 157 (1964), reported the formation of a monocyclic tetraoxyaminophosphorane from the reaction of $(Et_2)NP(Et)_2$ with biacetyl. No spectral data were offered.

[24] F. Ramirez, M. Nagabhushanam, A. S. Gulati and C. P. Smith, *Tetrahedron* not available.

[25] For a recent description of the factors that may effect the P^{31} NMR shift of compounds with pentavalent phosphorus, see: J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.* **44**, 815 (1966); J. H. Letcher and J. R. Van Wazer, *Ibid.* **45**, 2916 (1966); J. H. Letcher and J. R. Van Wazer, *Ibid.* **45**, 2926 (1966).

[26] Spirophosphoranes with P—C bonds are known: G. Wittig, A. Maercker and D. Hellwinkel, *Angew. Chem.* **76**, 756 (1964) and G. Wittig, *Bull. Soc. Chim. Fr* 1162 (1966).

[27] F. Ramirez, O. P. Madan and S. R. Heller, *J. Am. Chem. Soc.* **87**, 731 (1965).

[28] D. G. Gorenstein and F. H. Westheimer, *Ibid.* **89**, 2762 (1967).