polymer was collected on a sintered glass funnel and dried under vacuum at room temperature for 48 hr. The polymer was weighed, and solutions were prepared in chloroform for determination of inherent viscosity (0.5% in chloroform) and pmr spectrum.

A number of samples of the homopolymer were selected randomly for elemental analysis. *Anal.* Calcd for $(C_6H_{10}O_2)_n$: C, 63.13; H, 8.83. Found: C, 63.25; H, 8.65; C, 62.78; H, 8.23; C, 63.42; H, 8.94; C, 63.38; H, 9.01.

Hydrolysis of Acetals. A solution of 120 mg (1.05 mmol) of 6,8-DBO in 0.6 ml of acetone-d_6 was prepared. To the solution was added a trace of tetramethylsilane as internal standard. The pmr spectrum (Varian T-60) was scanned and integrated. To the solution was added 0.15 ml of D_2O. The spectrum was scanned periodically over a 24-hr period. No reaction could be detected. To the pmr solution, now 1.5 *M* 6,8-DBO in 20% (v/v) aqueous acetone, was added 1.0 ml [0.038 mmol, (297°K, 699 mm)] of anhydrous hydrogen chloride from a gas-tight syringe to give a solution 0.05 *M* in HCl. The pmr spectrum was scanned and integrated at specific intervals. The disappearance of acetal was measured and the half-life calculated.

The reaction solution was diluted with *ca.* 2 ml of dichloromethane and stirred with 50 mg of potassium carbonate and 50 mg of anhydrous magnesium sulfate. The mixture was centrifuged and the liquid decanted and concentrated. The infrared spectrum showed a strong broad absorption at 3370 cm^{-1} but no carbonyl band, indicating that the product of hydrolysis was the cyclic hemiacetal.

Exactly the same procedure was applied to 2,6-DBO. No detectable reaction in the neutral acetone–deuterium oxide occurred during several hours. However, according to a pmr scan taken immediately after the addition of the hydrogen chloride, the hydrolysis reaction to cyclic hemiacetal was complete.

The same procedure was used to determine the reactivity of methyl acetal.

Acknowledgment. We are deeply grateful to the National Institutes of Health for their support of this work under Grant GM 18595.

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Crystalline Six-Coordinate Phosphorus Compounds Derived from Spiropentaoxyphosphoranes

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Abstract: Two new types of crystalline substances having six-coordinate phosphorus have been isolated. One of the substances has the charge distribution of a zwitterion and is derived from the reaction of a spiropentaoxyphosphorane with pyridine. The second substance has the charge distribution of an ion pair and is derived from the reaction of the spiropentaoxyphosphorane with phenol and triethylamine. This P(6) adduct differs from previously reported analogs in having two monodentate and two bidentate oxygen ligands attached to P(6).

The literature on organic compounds with P(6)[2] has been developing in recent years.[3] Allcock[4] described a salt of the type $P(6)^-R_3NH^+$ with six oxygen ligands attached to the phosphorus[4,5] and more recently[6] demonstrated the octahedral skeletal symmetry of the anion by X-ray crystallography. Denney[7] prepared a related type of salt $P(6)^-Na^+$. Wolf[8] recently described P(6) compounds with three different bidentate oxygen ligands. Barrans[9] and Burgada[10] have reported a series of salts in which the anion contains one hydrogen and five oxygen ligands, or one hydrogen, one nitrogen, and four oxygen ligands.[10]

Derivatives of P(6) with six aromatic carbons as ligands have been known for some time from the work of Wittig[11] and of Hellwinkel.[12] The field of the alkyl- and arylfluorophosphates, $(RPF_5)^-$ and $(R_2PF_4)^-$, has been investigated by Schmutzler[13] who also summarized the earlier literature. An interesting type of fluorophosphate zwitterion was described by Brown and Bladon.[14]

The most distinctive feature of the P(6) derivatives is their ^{31}P nmr chemical shift[13,15] which appears in general at a much higher magnetic field than the shift of the related P(5) and P(4) structures.[3-15]

Previous work in this laboratory[16-18] led to the hypothesis that the base-catalyzed exchange of alkoxy ligands, which is observed when oxyphosphoranes are treated with alcohols, proceeds *via* octahedral P(6) species.[16-19] Related observations have been interpreted by Denney, *et al.*,[20] in analogous terms. Recent work by Archie and Westheimer[21] provided support for this hypothesis. Octahedral P(6) intermediates have also been suggested[22] to explain the slow ex-

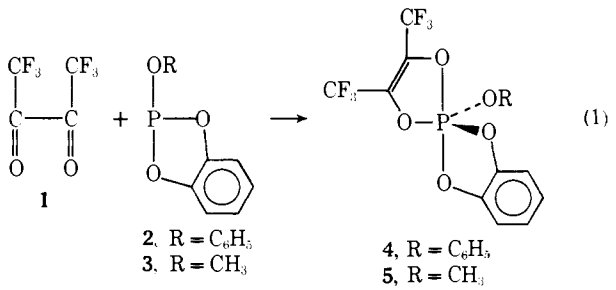
Table I. ^{31}P Nmr Shifts of Spiropentaoxyphosphoranes and of Monocyclic Pentaoxyphosphoranes in Various Solvents[a]

Compd no.	Oxyphosphorane derived from	Solvent or (solvent + reagent)	M	Mol of reagent/mol of oxyphosphorane	δ(^{31}P)
		Hexafluorobiacetyl			
4	Phenyl *o*-phenylene phosphite	$CDCl_3$	1.8	None	**+29.5**[b]
		CH_2Cl_2 + $(CF_3)_2CHOH$	0.8	5.0	+31.5
		Tetrahydrofuran	2.5	5.0	+31.2[c]
		Furan	2.8	5.0	+31.1[d]
		CH_2Cl_2 + pyridine	1.8	0.5	+45.0
			1.8	1.0	+60.0
			1.8	2.0	+69.0
		Pyridine	2.7	5.0	+82.0[e]
		γ-Collidine	1.5	5.0	+56.1
		CH_2Cl_2 + γ-collidine	1.8	1.0	+38.9
		CH_2Cl_2 + phenol	1.8	1.0	+31.3[f]
		CH_2Cl_2 + $(C_2H_5)_3N$	2.0	1.0	+32.0
		CH_2Cl_2 + phenol + $(C_2H_5)_3N$	1.0	1.0	+109.0
9	Triphenyl phosphite	$CDCl_3$	2.0	None	**+61.8**
		Pyridine	3.0	5.0	+69.7
10	Tri-*p*-tolyl phosphite	$CDCl_3$	2.0	None	**+61.0**
		Pyridine	3.0	5.0	+66.0
5	Methyl *o*-phenylene phosphite	$CDCl_3$	2.0	None	**+25.5**
		CH_2Cl_2 + $(CF_3)_2CHOH$	0.8	5.0	+25.8
		Tetrahydrofuran	3.0	4.0	+26.0
		Furan	3.5	4.0	+27.5
		CH_2Cl_2 + pyridine	2.7	0.25	+27.5
			2.7	0.5	+29.5
			2.7	1.0	+35.5
		Pyridine	3.0	4.0	+50.3
		CH_2Cl_2 + γ-collidine	2.5	1.0	+27.4
		$(C_2H_5)_3N$	2.0	4.0	+26.9
18	Trimethyl phosphite	$CDCl_3$	2.0	None	**+46.7**
		Pyridine	3.0	5.0	+47.0
		γ-Collidine	3.0	5.0	+48.0
		THF	3.0	5.0	+47.1
		Glyoxal			
21	Trimethyl phosphite	$CDCl_3$	2.0	None	**+44.2**
		Pyridine	3.0	5.0	+44.2
		γ-Collidine	3.0	5.0	+44.3
		Biacetyl			
22	Trimethyl phosphite	$CDCl_3$	2.0	None	**+48.9**
		Pyridine	3.0	5.0	+48.6
		γ-Collidine	3.0	5.0	+49.0
		THF	3.0	5.0	+48.9

[a] The ^{31}P nmr shifts are given in parts per million *vs.* H_3PO_4 = 0. They were determined at 25° *immediately* after the oxyphosphorane (0.7–0.8 mmol) was dissolved in the pure solvent or in the mixture of solvent + reagent, in the volumes required to give the molarities and the reagent/oxyphosphorane mole ratios indicated. [b] The values of the ^{31}P nmr shifts in boldface are those of the pure P(5) structure. [c] δ(^{31}P) +31.5 ppm after 7.5 hr at 25°. [d] δ(^{31}P) +31.0 ppm after 7 days at 25°. [e] δ(^{31}P) +82.0 ppm after 6 hr at 25°; +81.3 ppm after 8 days at 40°. [f] δ(^{31}P) +31.8 ppm after 14 days at 25°.

change of alkoxy ligands which occurs, in the absence of base, when two different pentaoxyphosphoranes are allowed to react in nonpolar solvents.

This paper describes the behavior of pentaoxyphosphoranes toward aliphatic and heterocyclic tertiary amines and ethers. Spiropentaoxyphosphoranes[23] with two five-membered rings were emphasized in this study since this type of P(5) structure displays a relatively high degree of stability.[24] The catechol bidentate ligand in particular leads to extraordinarily stable P(5) compounds.[25-29]



(1)

Results

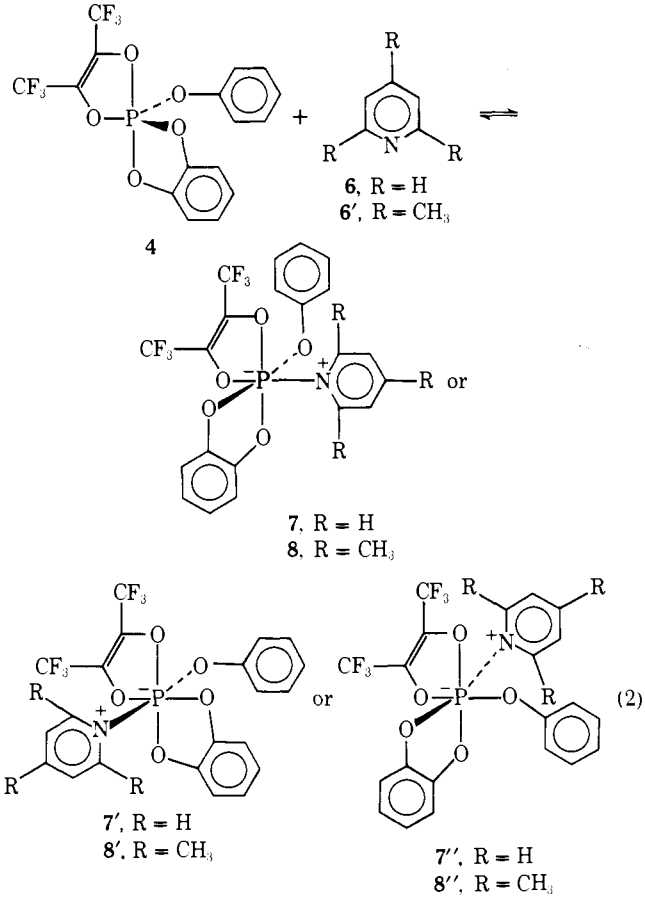
The reaction of hexafluorobiacetyl[30-32] (**1**) with phenyl *o*-phenylene phosphite[33] (**2**) and with methyl *o*-phenylene phosphite[33] (**3**) provides the corresponding spiropentaoxyphosphoranes **4** and **5** (eq 1). This synthesis of P(5) derivatives of the 1,3,2-dioxaphospholene ring system with the catechol bidentate ligand is made possible by the extraordinary reactivity of HFB[31,32] (**1**); *e.g.*, the analogous α-diketone biacetyl fails to react with the catechol phosphites **2** and **3** under all the conditions so far investigated.

The pentacovalency of the phosphorus in the spirophosphoranes **4** and **5** follows from the positive value of their ^{31}P nmr shifts;[24] see Table I. The molecules are drawn as TBP,[2] possibly with some deviations from the ideal D_{3h} skeletal symmetry, as a result of X-ray crystallographic analysis of related pentaoxyphosphoranes.[34,35]

The spirophosphoranes **4** and **5** are relatively stable toward acids, as shown by the insensitivity of their ^{31}P nmr

shifts to hexafluoroisopropyl alcohol[36] (Table I). Likewise ethers, such as tetrahydrofuran and furan, have practically no effect on the ^{31}P shifts of these compounds.

Pyridine interacts with the HFB-phenyl *o*-phenylene phosphite adduct (**4**) as can be seen from the ^{31}P nmr data summarized in Table I: the higher the ratio of pyridine to the P(5) adduct **4**, at the same concentration in methylene chloride solution, the higher the positive value of the ^{31}P nmr shift. The maximum upfield displacement of the shift to +82 ppm is observed when the adduct **4** is dissolved in pure pyridine.[37] For reasons given below, it is assumed that this variation in the ^{31}P shift results from the establishment of a relatively rapid equilibrium between the TBP P(5) adduct **4** and an octahedral P(6) complex, for which three configurations are possible, **7**, **7′**, or **7″** (eq 2). The shift in



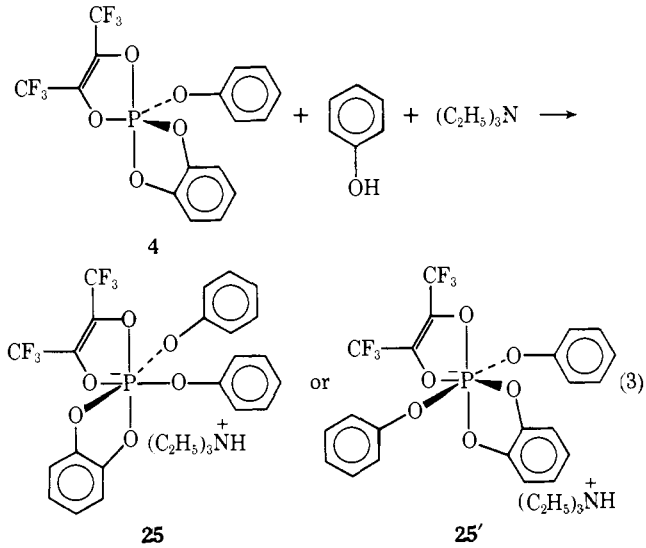
pure pyridine is that of the P(6) complex itself or very close to it. The values in methylene chloride solution correspond to weighed averages of the shifts of **4** and of **7**, **7′**, or **7″**.

The P(6) complex **7–7″** can be isolated in pure crystalline form. The elemental analysis of these crystals corresponds to the formula $C_{16}H_9O_5PF_6 \cdot C_5H_5N$. In the absence of X-ray crystallographic data, no definite assignment of configuration can be made for the P(6) complex in the crystalline state **7**, **7′**, or **7″**. The ir spectra of crystals of the P(6) complex **7–7″** and of the P(5) adduct **4** (both as Nujol mulls) show significant differences, in particular in the ratio of the bands at 1590–1680 cm^{-1}, which are due to the aromatic and the dioxaphospholene[22] C=C stretching frequencies, respectively. The crystalline P(6) complex **7–7″** undergoes decomposition on prolonged heating under vacuum to regenerate the spiropentaoxyphosphorane **4**. A related decomposition was reported by Wieber and Foroughi for the triethylammonium salt of hydridomethyl (or phenyl) bis(*o*-phenylenedioxo)phosphate.[38] A comparison of the ^1H nmr spectrum of the crystals (in $CDCl_3$) with the spectra of pyridine and of *N*-methylpyridinium dimethyl phosphate (both in $CDCl_3$) discloses that the heterocyclic protons of the P(6) complex **7–7″** have acquired the characteristics of "pyridinium ion protons"; *i.e.*, they have the shifts and multiplicity which are typical of the positively charged pyridine ring.

A freshly prepared 1.8 *M* methylene chloride solution of the P(6) complex **7–7″** gives a ^{31}P nmr shift of +60.8 ppm. A methylene chloride solution of the crystalline P(6) complex **7–7″** gives one ^{19}F nmr signal at −13.0 ppm (CF_3COOH = 0). This behavior is consistent with the existence of the relatively rapid equilibrium between the P(5) and P(6) species shown in eq 2.

As would be expected, γ-collidine (**6′**) has less effect on the ^{31}P shift of the spirophosphorane **4** than pyridine (**6**) under comparable conditions. The more hindered nucleophile results in a less favorable equilibrium with respect to the formation of the P(6) complex **8–8″**. It is interesting that triethylamine has a negligible effect on the ^{31}P shift of the spirophosphorane **4**. Probably the determining factor in this case is also the steric bulk of the attacking amine which prevents the formation of a stable P(6) complex.

The reaction of **4** with 1 mol equiv of phenol in the presence of triethylamine in ether solution gives a crystalline ether insoluble material, formulated as the P(6) complex which can have one of two structures, **25** or **25′** (eq 3). A

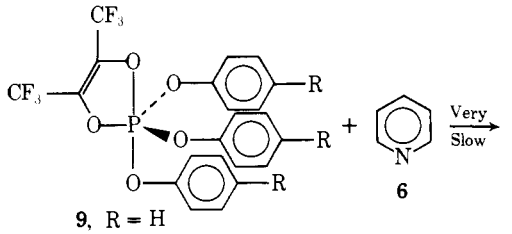


saturated solution of this substance in methylene chloride (*ca.* 1 *M*) has $\delta(^{31}P)$ = +109.5 ppm. This is the same figure observed when phenol and triethylamine were added to a methylene chloride solution of the P(5) complex **4** (Table I). The ^1H nmr spectrum of the solution has the signal due to the ethyl groups of triethylamine shifted to lower field as expected for a triethylammonium salt. The ir spectrum of this P(6) complex in methylene chloride solution has a band at 1680 cm^{-1} due to the C=C stretching; this band is also present in the precursor P(5) structure **4**.

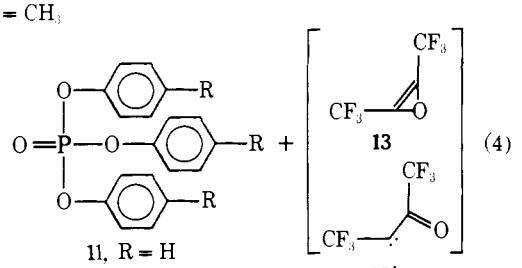
The solution of the ion pair **25** or **25′** in CH_2Cl_2 exhibits two ^{19}F nmr signals at 25°; these signals are at −13.3 and −14.1 ppm (CF_3COOH = 0) and are both quartets with J_{FF} = 10.0 Hz. The nonequivalency of the two trifluoromethyl groups is consistent with configuration **25** in which the two phenoxy ligands occupy adjacent positions (cis) on the octahedral skeleton. In configuration **25′** with colinear phenoxy ligands (trans), the two trifluoromethyl groups are structurally equivalent. It appears that the P(6) complex with six oxygen ligands and the charge distribution of an ion pair **25** is considerably more stable both in the crystalline state and in solution than the P(6) complex with five

oxygen and one nitrogen ligands and the charge distribution of a zwitterion **7–7″**.

The ability of the HFB–phenyl *o*-phenylene phosphite adduct (**4**) to form relatively stable P(6) complexes, such as **7–7″** and **25**, seems to be related to its spirophosphorane character. Pyridine has a small effect on the ^{31}P shift of the monocyclic HFB–triphenyl phosphite (**9**) and the HFB–tri-*p*-tolyl phosphite (**10**) P(5) adducts (eq 4; *cf.* Table I). On



9, R = H
10, R = CH_3



(4)

11, R = H
12, R = CH_3

prolonged contact, however, pyridine induces the decomposition of the monocyclic phosphoranes **9** and **10** to the corresponding triphenyl phosphate (**11**) and tri-*p*-tolyl phosphate (**12**). The fate of the remaining atoms originally present in the HFB (**1**) is not known, but it is evident that they constitute the elements of bis(trifluoromethyl)oxirene[39] (**13**) or of the corresponding α-keto carbene[40] **13′**. A possible mechanism for this decomposition will be advanced in the Discussion section.

uct of this reaction is *N*-methylpyridinium *o*-phenylene phosphate (**15–17**), which is presumably formed *via* the P(5) and the P(4) unstable intermediates **16** and **16′**. The stoichiometry of the reaction suggests the elimination of the elements of the oxirene **13**[39] or its α-keto carbene **13′**. An authentic sample of *N*-methylpyridinium *o*-phenylene phosphate (**15–17**) was prepared by the reaction of pyridine with methyl *o*-phenylene phosphate.[41]

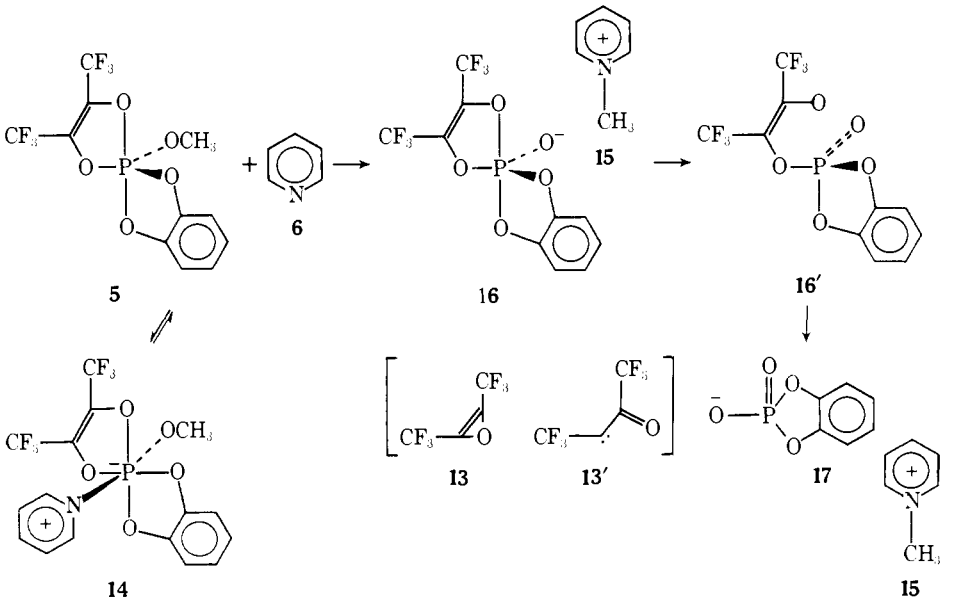
γ-Collidine interacts with the methoxyspirophosphorane **5** to a much lesser extent than pyridine. Moreover, the hindrance of the nitrogen by the two adjacent methyl groups reduces also the rate of demethylation of **5**; in fact, an equimolar mixture of the phosphorane **5** and γ-collidine in 1 *M* $CDCl_3$ solution exhibits no significant change after 3 days at 25° according to the ^1H nmr spectrum.

Triethylamine has a negligible *initial effect* on the ^{31}P nmr shift of the methoxyspirophosphorane **5**.

The HFB–trimethyl phosphite adduct (**18**) has been previously reported[32] (Scheme II). Variable-temperature ^1H nmr studies of this system reveal the occurrence of a relatively rapid permutational isomerization of the ligands among the TBP skeletal positions in the temperature range 30 to *ca.* −90°. The protons of the three methoxy groups give rise to one signal, and there is coupling between those protons and the ^{31}P nucleus, J_{HCOP} = 13.8 Hz. The fluorines of the two CF_3 groups give one nmr signal and are also coupled with the phosphorus,[42] J_{FCCOP} = 0.8 Hz. These, and other observations, indicate that the permutational isomerization of **18** occurs by an intramolecular bond-deformation process ("regular" process) and not by the rupture and re-formation of bonds ("irregular process").[43] In agreement with these conclusions, one finds that the adduct **18** is quite thermally stable; *e.g.*, it is recovered unchanged after 45 hr at 100°, in toluene solution.

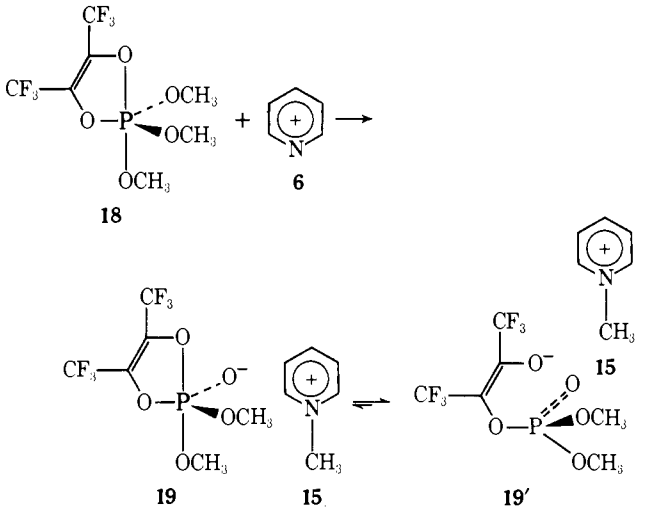
The monocyclic methoxyphosphorane **18** reacts rapidly with pyridine in methylene chloride solution at 25°. The main product of this reaction (*ca.* 90%) is a salt of the *N*-

Scheme I



Pyridine interacts rapidly with the HFB–methyl *o*-phenylene phosphite adduct (**5**); the data in Table I justify the conclusion that the initial interaction involves the establishment of an equilibrium between P(5) and P(6) structures **5** and **14** (Scheme I). In Scheme I, only one of the three possible configurations of the P(6) adduct **14** is shown. This reaction is followed by a slower demethylation of the methoxyspirophosphorane **5** by the nucleophile. The product of this reaction is *N*-methylpyridinium cation (**15**). The anion of this salt is very probably the enolate-phosphate **19′** (Scheme II), which is formed from the phosphorane **18** *via* intermediate **19**. The anion is not dimethyl phosphate, $(CH_3O)_2P(O)O^-$, as can be demonstrated by means of ^1H nmr spectrometry, after the introduction of authentic *N*-methylpyridinium dimethyl phosphate into a methylene chloride solution containing equimolar amounts of phosphorane **18** and pyridine.

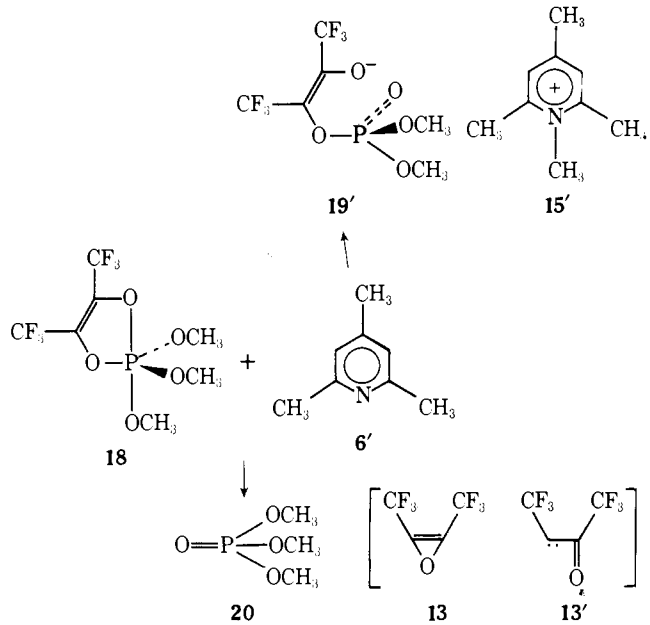
Scheme II



The enolate-phosphate salt **15–19′** decomposes mainly into *N*-methylpyridinium dimethyl phosphate on heating. Evidently the acyclic phosphate **15–19′** (Scheme II) is more stable than the five-membered cyclic phosphate **15–16′** (Scheme I), which is understandable from the properties of acyclic and five-membered cyclic phosphate esters in general.[44,45]

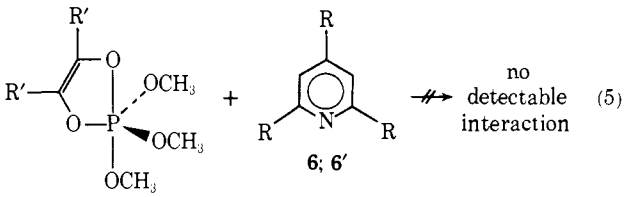
Trimethyl phosphate is not detected among the products of the reaction of the HFB–trimethyl phosphite adduct (**18**) with pyridine; this is not surprising in view of the susceptibility of adduct **18** to demethylation. The reaction of the adduct **18** with γ-collidine, however, produces trimethyl phosphate (**20**) (Scheme III). Some demethylation is still observable, as indicated by the formation of the *N*-methyl-γ-collidinium cation (**15′**). This γ-collidine induced decomposition of the monocyclic phosphorane **18** is quite slow, and its possible mechanism is discussed in the next section. The decomposition of the phosphorane **18** into trimethyl phosphate (**20**) by *catalytic* amounts of 2,6-dimethylpyridine can also be demonstrated.

Scheme III



As expected, triethylamine causes the rapid demethylation of the phosphorane **18.**

Pyridine has no detectable effect on the glyoxal–trimethyl phosphite[46] (**21**) and the biacetyl–trimethyl phosphite[47] (**22**) adducts; *e.g.*, these phosphoranes can be kept 40 hr at 40° in solution in the amine with no change (eq 5). Equimolar amounts of the biacetyl adduct **22** and γ-collidine can be kept 10 days at 25° in methylene chloride solutions without detectable change.



21, R′ = H
22, R′ = CH_3

Discussion

To our knowledge, the crystalline substance **7–7″** (eq 2) constitutes the first example of a P(6) complex derived from a pentaoxyphosphorane and having the charge distribution of a "zwitterion," rather than that of an ion pair.[3-10] The closest analog to **7–7″** would be the substance obtained by Brown and Bladon[14] from the reaction of acetylacetone with PF_5, with concomitant loss of HF.

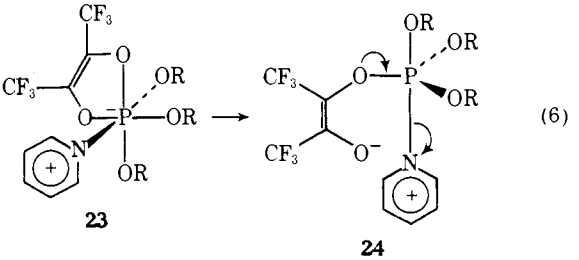
The crystalline complex **25** is also, to our knowledge, the first example of a pure isolated substance with P(6), which has two monodentate and two bidentate oxygen ligands and the charge distribution of an ion pair. Hellwinkel[5] reported ^{31}P nmr data for a related compound but did not isolate it. Several authors[4,7-9] have reported compounds analogous to **25** but with three bidentate oxygen ligands. Evidently the presence of three five-membered rings is not a prerequisite for stability of the P(6) structure.

Other findings during this investigation can be summarized as follows.

(a) The presence of the spirophosphorane structure involving two five-membered rings enhances the ability of P(5) to become P(6) upon interaction with certain nucleophiles. Compare, for instance, the differences between phosphoranes **4** and **5,** on the one hand, and **9, 10** and **18, 21, 22,** on the other hand.

(b) The ability of the nucleophile to accommodate a positive charge enhances the stability of a P(6) structure derived from certain P(5) structures; compare the differences between pyridine and γ-collidine, on the one hand, and tetrahydrofuran and furan, on the other hand.

(c) The presence of the electron-withdrawing CF_3 groups on the 1,3,2-dioxaphospholene ring enhances the ability of a given P(5) compound to interact with a suitable nucleophile to form a P(6) intermediate. This is probably due to an increase in the electrophilicity of P(5) by the CF_3 groups. Note that the HFB–trimethyl phosphite adduct (**18**) is transformed into trimethyl phosphate (**20**) under the catalytic influence of γ-collidine or of 2,6-dimethylpyridine, while the biacetyl–trimethyl phosphite (**22**) and the glyoxal–trimethyl phosphite (**21**) adducts are stable toward these nucleophiles. The formation of trimethyl phosphate can be explained by the formation of a transient P(6) complex **23** (eq 6; with R = CH_3 and the corresponding heterocycle). The rupture of a P–O bond in the P(6) complex **23** would lead to an unstable acyclic phosphorane **24.** The lat-



ter should decompose to the phosphate, the heterocycle, and the elements of bis(trifluoromethyl)oxirene,[39,40] **13** and **13'**. The same interpretation can be given for the formation of the triaryl phosphates **11** and **12**, from the reaction of the corresponding monocyclic phosphoranes **9** and **10** (eq 4) with pyridine.

(d) The presence of the CF_3 groups on the 1,3,2-dioxaphospholene ring also favors demethylation of methoxyphosphoranes by aliphatic and heterocyclic tertiary amines. This effect is probably due to a stabilization of the negatively charged leaving group and is best illustrated by contrasting the rapid demethylation of the HFB–trimethyl phosphite adduct (**18**) with the stability of the biacetyl- and the glyoxal–trimethyl phosphite adducts (**22** and **21**).

Experimental Section

Analyses by Galbraith Laboratories, Knoxville, Tenn. All reactions of oxyphosphoranes were carried out in anhydrous solvents, under N_2 or Ar. The pertinent data for the nmr measurements are as follows: proton shifts in parts per million *vs.* TMS = 10 (τ values), at 60 or 100 MHz, at 25° in $CDCl_3$; $\delta(^{31}P)$ in parts per million *vs.* H_3PO_4 = 0 at 40.5 MHz, at 25° in CH_2Cl_2 or in the solvents indicated in Table I; $\delta(^{19}F)$ in parts per million *vs.* CF_3COOH = 0 at 94.1 MHz, in CH_2Cl_2; coupling constants J in hertz.

Phenyl *o*-Phenylene Phosphite (2). The phosphite **2**, $\delta(^{31}P)$ −127.5 ppm ($CDCl_3$), was made as described in the literature.[33]

Reaction of HFB (1) with Phenyl *o*-Phenylene Phosphite (2). A solution of the diketone **1** (1.42 g, 7.3 mmol) in CH_2Cl_2 (15 ml) was added all at once to the phosphite **2** (1.3 g, 6 mmol) in CH_2Cl_2 (20 ml) at 0°. The solution was kept at 5° for 4 days. The solvent was evaporated under reduced pressure and the residue crystallized from ether–hexane to give **4**, 2.2 g, 85%, mp 85–86°. The ^{19}F nmr spectrum (CH_2Cl_2) had a signal at −12.9 ppm. *Anal.* Calcd for $C_{16}H_9O_5PF_6$: C, 45.1; H, 2.1; F, 26.7. Found: C, 45.0; H, 2.2; F, 26.8.

Reaction of the HFB–Phenyl *o*-Phenylene Phosphite Adduct (4) with Pyridine. Isolation of Crystalline P(6) Complex 7–7'. Pyridine (0.23 g, 3 mmol) was added to a solution of the adduct **4** (1.24 g, 3 mmol) dissolved in ether (10 ml). The mixture was kept at −20° for 12 hr during which time **7** slowly crystallized from the solution. The crystals were filtered, washed with a little hexane, and dried. Yield was 1.18 g (80%), mp 72–74°. The ^1H nmr spectrum ($CDCl_3$) had absorptions from the pyridinium ion protons at τ = 7.22, 7.61, and 8.60 ppm. The aromatic absorption was a complex multiplet centered at 7.0 ppm. *Anal.* Calcd for $C_{21}H_{14}O_5NPF_6$: C, 49.9; H, 2.8; F, 22.5; P, 6.1. Found: C, 49.8; H, 2.8; F, 22.3; P, 6.2.

Reaction of the HFB–Triphenyl Phosphite Adduct (9) with Pyridine. A solution of the adduct **9** and an excess of pyridine in $CDCl_3$ was kept several days at 40°. The ^{31}P nmr spectrum revealed the formation of *ca.* 20% of triphenyl phosphate, $\delta(^{31}P)$ +17.5 ppm,[48] during this time.

Reaction of HFB (1) with Tri-*p*-tolyl Phosphite. A solution of the diketone **1** (1.35 g, 7 mmol) in CH_2Cl_2 (15 ml) was added dropwise, over a 20-min period, to a stirred solution of the phosphite (2.46 g, 7 mmol) in CH_2Cl_2 (20 ml) at −78°. After 20 min at −78°, the solution was allowed to reach 25°, and was evaporated to yield essentially pure oxyphosphorane (**10**) in quantitative yield. *Anal.* Calcd for $C_{25}H_{21}O_5PF_6$: C, 54.9; H, 3.9; F, 20.8. Found: C, 54.8; H, 3.9; F, 20.6.

The ^1H nmr spectrum of the oxyphosphorane **10** had a doublet, J = 1.8 Hz at τ 7.70 ppm, which corresponds to the CH_3 group attached to the aromatic ring.

Reaction of the HFB–Tri-*p*-tolyl Phosphite Adduct (10) with Pyridine. Equimolar amounts of the oxyphosphorane **10** and pyridine were kept 6 weeks at 40°; analysis of the mixture by ^1H and ^{31}P nmr spectrometry revealed the formation of *ca.* 50% of tri-*p*-tolyl phosphate (**12**), $\delta(^{31}P)$ +16.0.[48] A sample of pure oxyphosphorane **10** which was kept 6 weeks at 40° showed the formation of only about 15% of the phosphate **12**.

Reaction of the HFB–Phenyl *o*-Phenylene Phosphite Adduct (4) with Phenol and Triethylamine. Isolation of Crystalline P(6) Complex 25. The adduct **4** (2.35 g, 5.5 mmol) was dissolved in 10 ml of dry ether. Phenol (0.50 g, 5.5 mmol) and triethylamine (0.55 g, 5.5 mmol) were added and the solution left at −20° for 2 days. During this time, **25** slowly crystallized from the solution. The crystals were filtered, washed with cold ether, and dried *in vacuo*. The yield of **25** was 2.54 g (74%), mp 119–121°. The ^1H nmr spectrum (CH_2Cl_2) had a triplet, J = 7.0 Hz, at τ 8.88 ppm; a quartet, J = 7.0 Hz, at τ 7.12 ppm; a complex multiplet centered at τ 3.16 ppm (aromatic protons); and a singlet at τ 2.00 ppm (N–H). Main infrared bands were at 1680, 1590, 1485, 1380, 1245, 1200, 990, 835, 790, and 745 cm^{-1} (Nujol mull). Crystallization from methylene chloride–hexane afforded the analytical sample. *Anal.* Calcd for $C_{28}H_{30}O_6NPF_6$: C, 54.1; H, 4.9; F, 18.3; N, 2.3. Found: C, 54.0; H, 4.8; F, 18.1; N, 2.2.

Methyl *o*-Phenylene Phosphite (3). Phosphite **3**, $\delta(^{31}P)$ −127.6 ($CDCl_3$), was made as described in the literature.[33]

Reaction of HFB (1) with Methyl *o*-Phenylene Phosphite (3). A solution of the diketone **1** (3.24 g, 17 mmol) in CH_2Cl_2 (25 ml) was added dropwise with stirring over a 45-min period to a solution of the phosphite **3** (2.6 g, 15 mmol) in CH_2Cl_2 (25 ml) at 0°. The solution was stirred 15 min at 25° and then the solvent evaporated under reduced pressure to give the oxyphosphorane **5** as an oil in quantitative yield. On standing for several hours at −20°, it solidified to colorless crystals, mp 34–35°. The ^1H nmr spectrum ($CDCl_3$) had τ (CH_3O) 6.15 ppm, J_{HCOP} = 14.5 Hz. The ^{19}F nmr spectrum (CH_2Cl_2) had a signal at −12.9 ppm. *Anal.* Calcd for $C_{11}H_7O_5PF_6$: C, 36.3; H, 1.9; F, 31.3. Found: C, 36.4; H, 2.0; F, 31.4.

Reaction of HFB–Methyl *o*-Phenylene Phosphite Adduct (5) with Pyridine. (a) A mixture of the oxyphosphorane **5** (1.17 g, 3.2 mmol) and pyridine (0.26 g, 3.2 mmol) in CH_2Cl_2 (7.5 ml) was kept 24 hr at 0°. During this time off-white crystals separated from the solution. The mixture was cooled to −20° for several hours and then filtered, and the crystalline material was washed with cold CH_2Cl_2 (5 ml). After a drying period *in vacuo* of several hours, there was obtained 0.6 g (70%) of *N*-methylpyridinium *o*-phenylene phosphate, mp 148–152°, $\delta(^{31}P)$ −13.0 ppm, τ (CH_3N) 5.68 ppm, both in d_6-DMSO.

(b) The ^{31}P nmr spectrum of a solution of the HFB–methyl *o*-phenylene phosphite adduct (**5**) in an excess of pyridine was examined after 10 min and had one detectable signal at +39.5 ppm (adduct **5** in equilibrium with complex **14**). The same solution, after 5 hr at 25°, exhibited a signal at +41 ppm (**5** and **14** in equilibrium) and another at −14 ppm [*N*-methylpyridinium (**15**) *o*-phenylene phosphate (**17**)]. A 2.5 *M* solution of adduct **5** and 1 mol equiv of pyridine in CH_2Cl_2, which had stood 90 min at 25°, had one detectable signal at +35.5 ppm (**5** and **14** in equilibrium). The pure adduct **5** in $CDCl_3$ solution had a signal at +25.5 ppm (*cf.* Table I).

Preparation of Authentic *N*-Methylpyridinium (15) *o*-Phenylene Phosphate (17). Pyridine (2 g, 25 mmol) was added to a solution of methyl *o*-phenylene phosphate (2.32 g, 13 mmol) in dioxane, and the mixture was kept 16 hr at 25°. The crystalline precipitate was filtered, washed with dioxane, and dried at 0.5 mm to give the salt **15–17**, mp 150–154°, in 90% of the theory. The ^1H nmr spectrum (d_6-DMSO) and the ir spectrum (Nujol mull) of this material were identical with those of the substance isolated from the reaction of pyridine with the oxyphosphorane **5**.

Reaction of the HFB–Methyl *o*-Phenylene Phosphite Adduct (5) with γ-Collidine. (a) The ^1H nmr spectra of the HFB–methyl *o*-phenylene phosphite adduct (**5**) in a fresh $CDCl_3$ solution and in a $CDCl_3$ solution which contained 1 mol equiv of γ-collidine and had stood 72 hr at 25° were indistinguishable.

(b) The ^{31}P nmr spectrum of a fresh solution of adduct **5** in CH_2Cl_2 with 1.0 mol equiv of γ-collidine is recorded in Table I.

Thermal Stability of the HFB–Trimethyl Phosphite Adduct (18). A solution of adduct **18** in toluene underwent no significant changes after 45 hr at 100°, according to the ^1H nmr spectrum.

Reaction of the HFB–Trimethyl Phosphite Adduct (18) with Pyridine. (a) The adduct **18** (0.39 g, 1.2 mmol) and pyridine (0.097 g, 1.2 mmol) were dissolved in CH_2Cl_2 (3 ml), and the solution was kept 20 hr at 40°. The ^1H nmr spectrum of the CH_2Cl_2 solution showed the complete disappearance of the adduct and the appearance of a substance which gave a singlet at τ 5.45 ppm and a doublet, J = 11.2 Hz, at τ 6.23 ppm (enolate salt **15–19'**). The addition of some authentic *N*-methylpyridinium dimethyl phosphate, $(C_5H_5NCH_3)^+$ $(CH_3O)_2P(O)O^-$, to this solution gave *two sets of doublets*, τ 6.50 ppm, J = 11.2 Hz, for the latter salt and τ 6.23

ppm, J = 11.2 Hz, for the enolate salt **15–19′**; the N-methylpyridinium cation gave a signal at τ 5.45 ppm.

According to the ^{1}H nmr spectrum, this reaction afforded less than 10% of by-products, in addition to the enolate salt **15–19′**.

Reaction of the HFB–Trimethyl Phosphite Adduct (18) with γ-Collidine. A solution of adduct **18** and an excess of γ-collidine in $CDCl_3$ was kept 24 hr at 40°. The ^{1}H nmr spectrum had a doublet, J = 11.2 Hz, at τ 6.27 ppm due to $(CH_3O)_3PO$ (**20**). The spectrum contained another set of signals, all singlets, at τ 5.85, 7.12, and 7.44 ppm (relative intensities as 1:2:1) due to the N-methyl-γ-collidinium cation **15′**. The estimated proportion of trimethyl phosphate to the γ-collidinium ion was *ca.* 85:15. The signals due to the CH_3O groups of the phosphate associated with the γ-collidinium cation were not detected and were presumably under the $(CH_3O)_3PO$ doublet. The formation of the latter was confirmed by addition of an authentic sample of trimethyl phosphate to the $CDCl_3$ solution and examination of the ^{1}H nmr spectrum. Trimethyl phosphate was isolated from the mixture of products by distillation.

Reaction of the HFB–Trimethyl Phosphite Adduct (18) with 2,6-Dimethylpyridine. A solution containing the adduct **18** (3.02 g, 9.5 mmol) and 2,6-dimethylpyridine (0.54 g, 5.0 mmol) in CH_2Cl_2 (3 ml) was kept 8 days at 25° under Ar. Analysis of the products by ^{1}H nmr spectrometry showed the formation of trimethyl phosphate (**20**) (*ca.* 85% of the theory) and of N-methyl-2,6-dimethylpyridinium cation (*ca.* 15% of the theory).

Reaction of the HFB–Trimethyl Phosphite Adduct (18) with Triethylamine. A solution of adduct **18** (1.2 mmol), triethylamine (1.2 mmol), and CH_2Cl_2 (0.2 ml) was kept at 25°, while ^{1}H and ^{31}P nmr spectra were being taken at various time intervals. Complete disappearance of the adduct **18** was observed after 20 hr; the formation of methyltriethylammonium ion was observed.

Attempted Reaction of the Glyoxal–Trimethyl Phosphite Adduct (21) and the Biacetyl–Trimethyl Phosphite Adduct (22) with Pyridine and γ-Collidine. The ^{1}H nmr spectra of the adducts **21** and **22** in pyridine solutions showed no changes after 40 hr at 40°.

A solution containing the biacetyl–trimethyl phosphite adduct (**22**, 2.4 mmol), γ-collidine (2.4 mmol), and CH_2Cl_2 (0.3 ml) was kept 10 days at 25°, under Ar; the ^{1}H nmr spectrum showed no detectable changes.

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References and Notes

(1) This work was supported by Public Health Service Grant No. CA-04769 from the National Cancer Institute and by the National Science Foundation Grant P040523-X00.
(2) The following abbreviations will be employed in this paper: P(4), P(5), P(6) = four-, five-, and six-coordinate phosphorus, respectively; TBP = trigonal bipyramidal or trigonal bipyramid; HFB = hexafluorobiacetyl, $CF_3COCOCF_3$.
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