ent in the solution. (d) $CF_3P(S)Cl_2$[2] (0.0490 g, 0.24 mmol) yielded no fluorocarbon-containing volatiles, but the solution contained the $CF_3PSO_2^{2-}$ ion. (e) $(CF_3)_2PS_2H$[2,3] (0.0791 g, 0.34 mmol) yielded CF_3H (0.0237 g, 0.34 mmol) and the $CF_3PS_2O^{2-}$ ion in solution. The solution gave a negative test for the sulfide ion. (f) $(CF_3)_2P(O)SCH_3$[9] (0.0320 g, 0.14 mmol) yielded CF_3H (0.0113 g, 0.16 mmol) and both sulfide and $CF_3PO_3^{2-}$ ions remained in the hydrolysate. (g) $(CF_3)_2P(S)OCH_3$[9] (0.0870 g, 0.38 mmol) yielded CF_3H (0.0290 g, 0.41 mmol) and the aqueous solution contained $CF_3PSO_2^{2-}$ but no sulfide ion. (h) $(CF_3)_2P(S)SCH_3$[2] (0.0847 g, 0.34 mmol) produced CF_3H (0.0278 g, 0.40 mmol) and the hydrolysate contained $CF_3PSO_2^{2-}$ and sulfide ions. (i) Slightly impure $(CF_3)_3P{=}S$ (0.1189 g, 0.44 mmol) yielded CF_3H (0.0588 g, 0.84 mmol) and an aqueous solution which contained the $CF_3PSO_2^{2-}$ ion.

(2) **Diphosphorus Compounds.**—(a) $(CF_3)_2P(S)SP(CF_3)_2$[1] (0.0533 g, 0.13 mmol) gave CF_3H (0.0279 g, 0.39 mmol) and $CF_3PS_2O^{2-}$ remained in solution. (b) $(CF_3)_2P(S)SSP(S)(CF_3)_2$[1] (0.0558 g, 0.12 mmol) produced CF_3H (0.0175 g, 0.25 mmol). The aqueous solution contained the $CF_3PS_2O^{2-}$ and $CF_3PSO_2^{2-}$ ions in the ratio 3:1. A little elemental sulfur was also obtained, but no sulfide ion was present in the solution. (c) $(CF_3)_2P(S)OP(S)(CF_3)_2$[9] (0.0636 g, 0.15 mmol) yielded CF_3H (0.0207 g, 0.30 mmol) and $CF_3PSO_2^{2-}$ remained in solution. The absence of sulfide ion in the solution was demonstrated.

Reactions with Hydrogen Peroxide.—Reactions were carried out by condensing the reactants onto 1.0 ml of 5% H_2O_2 solution and allowing the reaction to continue at room temperature for 4 days. (a) $(CF_3)_2PS_2H$[2,3] (0.30 mmol) began to react as soon as the tube reached room temperature with appearance of elemental sulfur. The solution contained the $(CF_3)_2PO_2^-$ ion and another unidentified CF_3P-containing species. (b) $(CF_3)_2P(S)Cl$[2,3] (0.30 mmol) reacted as above to yield the same species in solution and elemental sulfur.

Preparation of Tetraphenylarsonium Salts. (1) $(C_6H_5)_4As^+CF_3PSO_2H^-$.—Trifluoromethylthiophosphoryl dichloride[2] (0.1257 g, 0.62 mmol) was hydrolyzed with 5.0 ml of 10% NaOH solution for 6 days. The tube was then opened and tetraphenylarsonium chloride (1.0 g, 2.4 mmol) dissolved in the minimum amount of water was added. The salt was precipitated by acidifying with concentrated hydrochloric acid dropwise using phenolphthalein indicator. The white solid was filtered off and dried under vacuum at room temperature. The yield of salt was 0.281 g (0.512 mmol). *Anal.* Calcd for $C_{25}H_{21}AsPF_3SO_2$: C, 54.75; H, 3.86; S, 5.68. Found: C, 53.88; H, 3.70; S, 5.79. Acidification of the initial solution without addition of the arsonium salt gave a solution whose nmr was consistent with a protonated anion. The salt could be redissolved in 10% NaOH solution to regenerate $CF_3PSO_2^{2-}$ ions according to the nmr spectrum.

(2) $(C_6H_5)_4As^+CF_3PS_2OH^-$.—Bis(trifluoromethyl)dithiophosphinic acid[2,8] (0.2158 g, 0.92 mmol) was hydrolyzed as above and after removal of CF_3H (0.0646 g, 0.92 mmol) treated with tetraphenylarsonium chloride (1.5 g, 3.6 mmol) and hydrochloric acid. The pale yellow solid was filtered off and dried under vacuum at room temperature. The yield of salt was 0.455 g (0.81 mmol). *Anal.* Calcd for $C_{25}H_{21}AsPF_3S_2O$: C, 53.20; H, 3.75; S, 11.36. Found: C, 53.00; H, 3.67; S, 11.25.

Acidification of a sample of the initial solution in the absence of the arsonium salt produced a solution whose nmr spectrum was consistent with the anion postulated. The tetraphenylarsonium salt was soluble in 10% NaOH solution to give $CF_3PS_2O^{2-}$ ions according to the nmr spectrum.

Titrimetric Determinations.—(A) Alkaline hydrolysates obtained by reaction of known amounts of trifluoromethylphosphorus compounds with 4.0 ml of 10% NaOH solution (carbonate free) for 2 days were diluted to ~90 ml after removal of volatile fluorocarbon products and titrated with 1.00 *N* HCl under a nitrogen atmosphere, and the curve after the first end point was compared with that of the starting NaOH solution.

(a) The alkaline hydrolysate of $CF_3P(S)Cl_2$[2] (0.0891 g, 0.44 mmol) gave an end point at 8.75 ml corresponding to the neutralization of excess base remaining in the solution. The pH after addition of 8.97 ml was 3.2 (*cf.* 2.7 for the addition of 0.22 ml of acid to the neutralized parent alkali solution). A further addition of 0.44 ml of acid yielded a pH of 2.5 (*cf.* 2.3 in the case of the parent alkali), but there was no pronounced break in the curve.

(b) $(CF_3)_2PS_2H$[2,3] (0.1093 g, 0.47 mmol) produced a titration curve with the first end point due to neutralization of unconsumed alkali at 9.56 ml. The pH after the addition of 9.79 ml was 3.1 (*cf.* 2.7 for a further addition of 0.23 ml of acid to the neutralized starting alkali). After addition of 10.25 ml of acid, the pH was 2.5 (*cf.* 2.3 in the case of the parent solution).

(B) An acid solution was obtained from the hydrolysis of $CF_3P(S)Cl_2$[2] (0.0870 g, 0.43 mmol) with 10 ml of water for 24 hr. After dilution to ~90 ml, the solution was titrated with 0.100 *N* NaOH solution under an atmosphere of nitrogen to give a curve with an end point at 17.11 ml corresponding to 4 mol of base consumed per mole of starting material. There was however only one distinct break in the curve. The pH values at the $^1/_8$, $^3/_8$, $^5/_8$, and $^7/_8$ neutralization points (corresponding to the half-neutralization point for each proton) were 2.15, 2.25, 2.50, and 3.25.

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Phosphorus–Fluorine Chemistry. XXVII.[1] Aryloxy-Substituted Fluorophosphoranes

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The silyl ethers $C_6H_5OSi(CH_3)_3$ and $C_6F_5OSi(CH_3)_3$ undergo silicon–oxygen bond cleavage reactions with fluorophosphoranes, R_nPF_{5-n} ($n = 0, 1, 2$; R = CH_3, C_6H_5, $(CH_3)_2N$ in the case of $C_6H_5OSi(CH_3)_3$; $n = 0, 1, 2$; R = CH_3, C_6H_5 in the case of $C_6F_5OSi(CH_3)_3$), to give a series of thermally stable compounds of the types $(C_6H_5O)_{3-n}PR_nF_2$ and $(C_6F_5O)_{3-n}PR_nF_2$ (n = 0, 1, 2). The intermediate $(RO)_2PF_3$, assumed in the reactions of PF_5 with $ArOSi(CH_3)_3$, was isolated only in the form of the isomeric stable phosphonium salt $[(RO)_4P][PF_6]$. The ^{31}P and ^{19}F nmr spectra of the new compounds are reported and discussed in terms of the structures of the molecules.

Several attempts have recently been made to prepare fluorophosphoranes substituted by alkoxy groups. While the species $C_2H_5OPRF_3$[4] and CH_3OPF_4[5] have been characterized by nmr spectroscopy at low temper-

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TABLE I

PHENOXYFLUOROPHOSPHORANES, PERFLUOROPHENOXYFLUOROPHOSPHORANES, AND HEXAFLUOROPHOSPHATES FROM CLEAVAGE OF ARYL TRIMETHYLSILYL ETHERS BY FLUOROPHOSPHORANES

Compd	Reactants (mol)	Reaction conditions, hr (temp, °C)	Yield, %	Bp, °C (mm) or mp, °C	Analysis, %							
					C		H		F		P	
					Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$(C_6H_5O)_3PF_2$	PF_5 (0.018) $C_6H_5OSi(CH_3)_3$ (0.074)	48 (20)	27	*a*	61.2	61.9	4.4	4.1	10.9	10.4	8.9	8.5
$(C_6H_5O)_2CH_3PF_2$	CH_3PF_4 (0.0125) $C_6H_5OSi(CH_3)_3$ (0.0250)	48 (20)	59	*a*	58.0	58.1	4.9	5.0	14.1	14.3	...	...
$(C_6H_5O)_2C_6H_5PF_2$	$C_6H_5PF_4$ (0.025) $C_6H_5OSi(CH_3)_3$ (0.050)	10 (55)	33	68–70	65.0	64.3	4.5	4.4	11.4	11.6	...	...
$(C_6H_5O)(CH_3)_2PF_2$	$(CH_3)_2PF_3$ (0.050) $C_6H_5OSi(CH_3)_3$ (0.050)	6 (reflux)	75	72–74 (0.2)	50.0	49.8	5.8	5.8	19.8	19.0	...	...
$(C_6H_5O)(C_6H_5)_2PF_2$	$(C_6H_5)_2PF_3$ (0.050) $C_6H_5OSi(CH_3)_3$ (0.050)	24 (140)	54	*a*	68.4	67.8	4.8	4.6	12.0	11.5	9.8	9.9
$(C_6F_5O)_3PF_2$[b]	PF_5 (0.40) $C_6F_5OSi(CH_3)_3$ (0.04)	48 (20)	84	*a* 138–140	35.0	35.2	...	...	52.3	52.5	5.0	5.0
$(C_6F_5O)_2CH_3PF_2$[b]	CH_3PF_4 (0.05) $C_6F_5OSi(CH_3)_3$ (0.05)	36 (100)	93	127–130	34.7	34.7	0.6	0.6	50.6	50.4	6.9	6.8
$(C_6F_5O)_2C_6H_5PF_2$[b]	$C_6H_5PF_4$ (0.033) $C_6F_5OSi(CH_3)_3$ (0.033)	5 (150)	88	127–129	42.2	42.1	1.0	1.0	44.5	44.4	6.1	6.2
$(C_6F_5O)(CH_3)_2PF_2$	$(CH_3)_2PF_3$ (0.05) $C_6F_5OSi(CH_3)_3$ (0.05)	30 (100)	93	*a*	34.1	34.3	2.1	2.1	46.6	46.3	11.0	10.8
$(C_6F_5O)(C_6H_5)_2PF_2$[b]	$(C_6H_5)_2PF_3$ (0.038) $C_6F_5OSi(CH_3)_3$ (0.038)	5 (150)	92	100–102	53.3	53.3	2.5	2.6	32.7	32.3	7.6	7.8
$[(C_6H_5O)_4P]^+[PF_6]^-$	PF_5 (0.040) $C_6H_5OSi(CH_3)_3$ (0.080) NaF (0.5 g)	2 (20)	54	*a*	52.5	53.6	3.7	4.0	20.8	20.2	...	...
$[(C_6H_5O)_2((CH_3)_2N)_2P]^+[PF_6]^-$	$(CH_3)_2NPF_4$ (0.050) $C_6H_5OSi(CH_3)_3$ (0.050)	72 (80) and 3 weeks (25)	17	*a*				*c*				
$[(C_6H_5O)_2((CH_3)_2N)_2P]^+[PF_6]^-$	$(CH_3)_2NPF_4$ (0.050) $C_6H_5OSi(CH_3)_3$ (0.050) NaF (0.1 g)	72 (80)	78	*a*	42.7	42.6	4.9	4.7	25.4	25.1	...	...

[a] Crystalline solid. [b] Mass spectra (MS 9 instrument; 70 eV) were recorded for all compounds so marked. A weak molecular peak was observed in all cases, confirming the composition of the compounds. The characteristic feature of all the spectra was that the strongest peak corresponded to loss of a C_6F_5O group from the parent molecule. [c] Analysis given with the next entry.

atures, all attempts to prepare and characterize such compounds at room temperature have resulted only in the formation of decomposition products of the otherwise uncharacterized alkoxyfluorophosphoranes,[4-7] except for compounds of the type $R_f(RO)_3PF$ (R_f = perfluoroalkenyl group).[8] Alkoxyfluorophosphoranes are, therefore, assumed to be thermally unstable compounds at room temperature. The products of the decomposition of these species are generally found to be a phosphoryl species and the corresponding alkyl fluoride,[7,9] *viz.*, $ROPR'_nF_{4-n} \rightarrow P(:O)R'_nF_{3-n} + RF$ (n = 1 or 2). In contradiction to this general observation, Mitsch reported the compounds $(CH_3O)_3PF_2$ and $(C_6H_5O)_3PF_2$ to be thermally stable species.[10] His report of the compound $(C_6H_5O)_3PF_2$ is, however, cast into doubt by the present work.

The compounds we report are thought to be the first known examples of aryloxyfluorophosphoranes.[11] Unlike the alkoxyfluorophosphoranes, the new compounds are thermally stable with respect to decomposition at room temperature, and they may be prepared in high yields by the reaction of fluorophosphoranes with aryl trimethylsilyl ethers.

Results and Discussion

Fluorophosphoranes react with aryl trimethylsilyl ethers to give aryloxydifluorophosphoranes in almost every case investigated

$$(3-n)C_6H_5OSi(CH_3)_3 + R_nPF_{5-n} \longrightarrow (C_6H_5O)_{3-n}PR_nF_2 + (3-n)FSi(CH_3)_3 \quad (n = 0, 1, 2;\ R = CH_3, C_6H_5)$$

$$(3-n)C_6F_5OSi(CH_3)_3 + R_nPF_{5-n} \longrightarrow (C_6F_5O)_{3-n}PR_nF_2 + (3-n)FSi(CH_3)_3 \quad (n = 0, 1, 2;\ R = CH_3, C_6H_5)$$

In two cases, however, ionic phosphorus compounds have been isolated from this type of reaction

$$2(CH_3)_2NPF_4 + 2C_6H_5OSi(CH_3)_3 \longrightarrow [(C_6H_5O)_2((CH_3)_2N)_2P]^+[PF_6]^- + 2FSi(CH_3)_3$$

$$PF_5 + C_6H_5OSi(CH_3)_3 \longrightarrow x(C_6H_5O)_3PF_2 + y[(C_6H_5O)_4P]^+[PF_6]^- + zFSi(CH_3)_3$$

Table I lists the compounds we have prepared by cleavage reactions of aryl trimethylsilyl ethers with fluorophosphoranes. In every reaction which yields an aryloxyfluorophosphorane, substitution of fluorine atoms in the starting fluorophosphorane occurs to such an extent as to give a difluoro derivative. This contrasts with reactions of fluorophosphoranes with alkoxy-,[4-7] organothio-,[11,12] and diorganoaminotrimethylsilanes,[6,13] which give monosubstitution products in preference to multisubstitution products.

There was evidence that the reaction of phenoxytrimethylsilane with phenyltetrafluorophosphorane proceeds *via* a trifluorophosphorane intermediate. A ^{19}F nmr spectrum was obtained on a sample of the reaction mixture after it had been kept for 2 hr at 100°. It showed the expected difluorophosphorane, together with a broad-line doublet. On cooling the sample to

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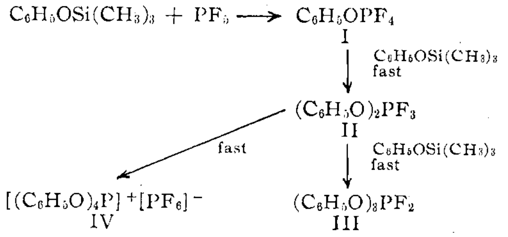
−50° this doublet disappeared and a typical spectrum of a trigonal-bipyramidal trifluorophosphorane species appeared, *i.e.*, a doublet of doublets for two axial fluorine atoms and, at higher field, a doublet of triplets for the single equatorial fluorine atom. The presence of the single sharp doublet, due to the difluorophosphorane, indicates that the trifluorophosphorane is highly reactive toward the silyl ether; its intermediacy in the reaction is clearly established (*cf.* Table IV). It is assumed, therefore, that reactions of the fluorophosphoranes, PF_5 and RPF_4, with silyl ethers proceed *via* tetra- and trifluorophosphorane intermediates, respectively.

While the fluorophosphoranes, RPF_4 and R_2PF_3, react with aryl trimethylsilyl ethers to give aryloxyfluorophosphoranes as the only phosphorus-containing products, the reaction of PF_5 with $C_6H_5OSi(CH_3)_3$ gives two phosphorus-containing products, $(C_6H_5O)_3PF_2$ and $[(C_6H_5O)_4P]^+[PF_6]^-$, under normal conditions. $(C_6H_5O)_3PF_2$ was previously reported by Mitsch as a product of the reaction of difluorodiazirine with triphenyl phosphite.[10] This product was characterized only by ^{19}F nmr spectroscopy. The ^{19}F nmr parameters quoted by Mitsch[10] are markedly different from those of the product characterized by us as $(C_6H_5O)_3PF_2$, using ^{19}F and ^{31}P nmr spectroscopy and elemental analysis. The parameters for our $(C_6H_5O)_3PF_2$, J_{P-F} and δ_F, are well in line with previously observed values for R_3PF_2, as is the highly positive δ_P value.[13] Mitsch has not obtained ^{31}P nmr spectra for any of his difluorophosphoranes.[14] It appears to us that an oxidation reaction has occurred between triphenyl phosphite and difluorodiazirine with subsequent cleavage of the P–O bonds and formation of hexafluorophosphate, PF_6^-. The near identity of both δ_F and J_{P-F} for the compounds $(CH_3O)_3PF_2$, $(C_6H_5O)_3PF_2$, and $(C_4H_9S)_3PF_2$, as reported by Mitsch,[10] and their proximity to the known parameters of the PF_6^- ion suggest that the latter species, rather than a difluorophosphorane, may have been present in these cases too.

We propose that the reaction of PF_5 with $C_6H_5OSi(CH_3)_3$ proceeds as in



As mentioned previously we have no experimental evidence in support of the formation of I or II which we assume to be highly reactive toward $C_6H_5OSi(CH_3)_3$. A competition is thought to occur between the reaction of II with more of the silyl ether to give III and the rearrangement of II to give its ionic isomer IV.

By the use of specific conditions it is possible to prepare one of the compounds, $(C_6H_5O)_3PF_2$ or $[(C_6H_5O)_4P]^+[PF_6]^-$, almost to the exclusion of the other. When a 1 molar excess of silyl ether over the quantity calculated for formation of the difluorophosphorane is present in the reaction mixture, the difluorophosphorane is formed as the only phosphorus-containing product, *viz.*

$$4C_6H_5OSi(CH_3)_3 + PF_5 \longrightarrow C_6H_5OSi(CH_3)_3 + (C_6H_5O)_3PF_2 + 3FSi(CH_3)_3$$

$C_6H_5OSi(CH_3)_3$ and $FSi(CH_3)_3$ are easily removed from the fluorophosphorane product by fractional distillation. Greater yields of $[(C_6H_5O)_4P]^+[PF_6]^-$ may be obtained by addition of traces of sodium fluoride to the reaction mixture, using the calculated molar ratio of reactants for its formation, *viz.*

$$4C_6H_5OSi(CH_3)_3 + 2PF_5 \xrightarrow{\text{NaF}} [(C_6H_5O)_4P]^+[PF_6]^- + 4FSi(CH_3)_3$$

Kolditz, *et al.*,[15] have suggested that the proposed rearrangement of $(C_6H_5O)_2PF_3$ is reversible

$$2(C_6H_5O)_2PF_3 \rightleftharpoons [(C_6H_5O)_4P]^+[PF_6]^-$$

and that such a species is covalent in the solid state, while it is ionic in solution in certain polar solvents. The present work suggests that such an equilibrium must lie well to the right under the conditions of our experiments involving sodium fluoride, such that the reactive covalent species rearranges completely to the ionic isomer.

A similar rearrangement of a covalent aryloxyfluorophosphorane to give an ionic isomer is observed during the reaction of $(CH_3)_2NPF_4$ with $C_6H_5OSi(CH_3)_3$.[16] In this case the unisolated trifluorophosphorane, $((CH_3)_2N)(C_6H_5O)PF_3$, appears to rearrange before it is able to react with further silyl ether. No trace of a difluorophosphorane product is observed, and the only product to be isolated is the ionic isomer of the trifluorophosphorane, $[(C_6H_5O)_2((CH_3)_2N)_2P]^+[PF_6]^-$.[16]

Both rearrangements of trifluorophosphoranes which we report appear to be catalyzed by sodium fluoride. We have found no evidence in this work to suggest that an equilibrium exists between the covalent and ionic forms of these trifluorophosphoranes.

The analogous reaction between pentafluorophenoxytrimethylsilane and phosphorus pentafluoride produced, apart from trimethylfluorosilane, exclusively tris(pentafluorophenoxy)difluorophosphorane. No evidence for the formation of any ionic species was obtained, the reaction proceeding, therefore, according to the equation

$$PF_5 + 3C_6F_5OSi(CH_3)_3 \longrightarrow (C_6H_5O)_3PF_2 + 3(CH_3)_3SiF$$

Properties of Aryloxyfluorophosphoranes.—The covalent aryloxyfluorophosphoranes are colorless, crystalline solids; $(CH_3)_2(C_6H_5O)PF_2$ is a mobile, colorless liquid. All the compounds are highly sensitive to moisture, making handling difficult. No apparent thermal decomposition of any of the compounds was observed at temperatures up to 100°. This is in contrast to the behavior of the analogous phenylthiodiphenyldifluorophosphorane $C_6H_5SP(C_6H_5)_2F_2$[12] which rapidly decomposes at 100°. Definite melting points were, however, difficult to obtain for the phenoxy-substituted compounds, presumably as a consequence of their very deliquescent character.

The hexafluorophosphate products are less sensitive to moisture than the covalent (pentacoordinate) compounds. Both $[((CH_3)_2N)_2(C_6H_5O)_2P]^+[PF_6]^-$ and $[(C_6H_5O)_4P]^+[PF_6]^-$ are thermally stable, colorless solids.

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^{19}F and ^{31}P Nuclear Magnetic Resonance Spectra.—The ^{19}F and ^{31}P nmr spectral data for the phenoxy- and pentafluorophenoxydifluorophosphoranes $(C_6H_5O)_{3-n}PR_nF_2$ (n = 0, 1, 2; R = CH_3, C_6H_5) and $(C_6F_5O)_{3-n}PR_nF_2$ (n = 0, 1, 2; R = CH_3, C_6H_5) are listed in Table II. The nmr data suggest that the molecules are trigonal bipyramidal in every case, with two axial fluorine atoms. The P–F coupling constants (in the range 736–900 Hz) and the comparatively low fluorine chemical shifts (in the range +4.2 to +50.3 ppm, relative to internal CCl_3F) are characteristic of axial fluorine atoms in difluorophosphoranes.[13] The strongly positive ^{31}P chemical shifts (+11.7 to +88.4 ppm, relative to external H_3PO_4) are typical of pentacoordinate phosphorus compounds.[13] The ^{19}F, ^{31}P, and ^1H nmr data for the ionic compounds $[(C_6H_5O)_4P]^+[PF_6]^-$ and $[(C_6H_5O)_2((CH_3)_2N)_2P]^+[PF_6]^-$ are also indicative of their composition; they are listed in Table III. Nmr data for the trifluorophosphorane intermediate species $C_6H_5OPF_3C_6H_5$ are give in Table IV.

TABLE II
NMR DATA FOR PHENOXY- AND PENTAFLUOROPHENOXYPHOSPHORANES

Compd^f	J_{P-F}, Hz	δ_F,^{a} ppm	δ_P,^{b} ppm
$(C_6H_5O)_3PF_2$	768	+44.8	+88.4
$(C_6H_5O)_2CH_3PF_2$	825	+18.1	c
$(C_6H_5O)_2C_6H_5PF_2$	829	+35.0	+69.0
$(C_6H_5O)(CH_3)_2PF_2$^{d}	736	+4.2	+11.7
$(C_6H_5O)(C_6H_5)_2PF_2$	797	+33.3	+34.4
$(C_6F_5O)_3PF_2$^{e}	809	+50.3	+84.0
$(C_6F_5O)_2CH_3PF_2$^{e}	870	+21.9	+54.9
$(C_6F_5O)_2C_6H_5PF_2$^{e}	817	+38.2	+60.7
$(C_6F_5O)(CH_3)_2PF_2$	747	+5.3	+3.9
$(C_6F_5O)(C_6H_5)_2PF_2$	812	+35.1	+45.5

^{a} Measured relative to an internal CCl_3F standard. ^{b} Measured relative to an external 85% H_3PO_4 standard. ^{c} The ^{31}P spectrum was not measured. ^{d} Both the ^{19}F and ^{31}P spectra were measured on a neat sample of the liquid. ^{e} The ^{31}P nmr spectra were measured on solutions in tetrahydrofuran. ^{f} Spectra of phenoxy compounds were measured on benzene solutions and those of pentafluorophenoxy compounds on acetonitrile solutions except where otherwise stated.

TABLE III^a
NMR DATA FOR IONIC SPECIES

	^1H		^{19}F		^{31}P
Compd	δ_H^{b}	J_{H-P}	δ_F^{c}	J_{F-P}	δ_P^{d}
$[((CH_3)_2N)_2(C_6H_5O)_2P]^+[PF_6]^-$	−3.1 (NCH_3) Complex aromatic region	10.2 (NCH_3–P)	+73.0	715	−19.8 (singlet) +146.0 (septet)
$[(C_6H_5O)_4P]^+[PF_6]^-$	Complex aromatic region		+72.8	720	+28.0 (singlet) +148.0 (septet)

^{a} All the spectra were measured in acetonitrile solution. ^{b} Measured relative to an internal $(CH_3)_4Si$ standard. ^{c} Measured relative to an internal CCl_3F standard. ^{d} Measured relative to an external 85% H_3PO_4 standard.

TABLE IV^a
NMR DATA FOR THE TRIFLUOROPHOSPHORANE INTERMEDIATE SPECIES $C_6H_5OPF_3C_6H_5$ AT −50°

Axial region	Equatorial region
δ_{F_a} = +38.3 ppm^b	δ_{F_e} = +65.4 ppm^b
J_{F_a-P} = 864 Hz	J_{F_e-P} = 986 Hz
$J_{F_a-F_e}$ = 72 Hz	$J_{F_e-F_a}$ = 72 Hz

^{a} Measurements made on liquid samples of reaction mixture. ^{b} Measured relative to an internal CCl_3F standard. F_a denotes an axial fluorine atom; F_e denotes an equatorial fluorine atom.

It is interesting to note that, while the fluorophosphoranes $(C_6H_5O)_nPF_{5-n}$ (n = 2 or 3) exhibit nmr evidence for covalency in the solid state ($(C_6H_5O)_2PF_3$)[15] or in acetonitrile solution ($(C_6H_5O)_3PF_2$), the phenoxyphosphorus(V) halides $(C_6H_5O)_nPX_{5-n}$ (where X = Cl, Br, or I) have all been shown to exist in ionic forms.[17]

It has been observed that organothio-substituted fluorophosphoranes of types $RSPF_4$, RPF_3SR', and R_2PF_2SR' exhibit rather marked changes in their low-temperature ^{19}F nmr spectra[13,18] which may be related to the slowing down of the P–S bond rotation, relative to the nmr time scale. Also, in the case of $RSPF_4$, the intramolecular exchange of fluorine seems to be affected upon changing the temperature during the nmr experiment. Similar studies were carried out on the oxygen-containing compound $C_6H_5O(C_6H_5)_2PF_2$, but no significant change in the room-temperature spectrum was observed on cooling a solution of the compound in toluene down to −80°.

Experimental Section

Experiments were carried out in previously dried apparatus flushed with dry nitrogen. Drying tubes were used to protect reactions from atmospheric moisture and all recrystallizations were carried out using solvents dried by standard procedures.

Room-temperature and low-temperature ^1H, ^{19}F, and ^{31}P nmr spectra were obtained on Perkin-Elmer R-10 and Varian HA-60 spectrometers.

Phenyl trimethylsilyl ether, $C_6H_5OSi(CH_3)_3$, was prepared by the method of Speier.[19] Pentafluorophenyl trimethylsilyl ether, $C_6F_5OSi(CH_3)_3$, was synthesized by the reaction of pentafluorophenol with trimethylchlorosilane in ether in the presence of triethylamine. After separation from amine hydrochloride, the filtrate gave pure pentafluorophenyl trimethylsilyl ether on fractional distillation, bp 63° (20 mm), as a colorless liquid in high yield. *Anal.* Calcd for $C_9H_9F_5OSi$: C, 42.2; H, 3.5. Found: C, 42.0; H, 3.5. Fluorophosphorane starting materials were prepared by the known methods.[13]

Preparation of Aryloxyfluorophosphoranes.—The following examples of the syntheses of aryloxy-, di(aryloxy)-, and tri(aryloxy)fluorophosphoranes illustrate the procedures used.

Triphenoxydifluorophosphorane.—Phosphorus pentafluoride (2.3 g, 0.018 mol) was condensed onto phenyl trimethylsilyl ether (11.9 g, 0.074 mol) at liquid nitrogen temperature in a glass reaction tube. The evacuated tube was sealed and warmed to room temperature. After 2 days at room temperature the product was a colorless, homogeneous liquid. The tube was opened under dry nitrogen after cooling to liquid nitrogen temperature. A gas-phase infrared spectrum of the most volatile component showed only fluorotrimethylsilane; this was subsequently removed under vacuum. Distillation of the colorless liquid residue *in vacuo* yielded unreacted phenyl trimethylsilyl ether (0.9 g, 0.006 mol), bp 38–40° (0.1 mm), and left a colorless crystalline residue which was washed with benzene and recrystallized from acetonitrile to give pure triphenoxydifluorophosphorane (1.6 g, 27%) as colorless crystals.

Diphenoxyphenyldifluorophosphorane.—Phenyltetrafluorophosphorane (4.60 g, 0.025 mol) was added dropwise with stirring to phenyl trimethylsilyl ether (8.30 g, 0.050 mol) in a two-necked flask, fitted with a dropping funnel and reflux condenser attached to a −78° trap. The stirred mixture was heated to 55° for 10 hr and fluorotrimethylsilane (4.6 g, 98%) was collected in

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the cold trap. The flask contents solidified on cooling. Three recrystallizations of the solid from benzene yielded diphenoxyphenyldifluorophosphorane (2.1 g, 33%) as a colorless crystalline solid, mp 68–70°.

Phenoxydimethyldifluorophosphorane.—Dimethyltrifluorophosphorane (5.90 g, 0.050 mol) was added with stirring to phenyl trimethylsilyl ether (8.30 g, 0.050 mol) in an apparatus similar to that used in the previous experiment. The mixture was stirred under reflux for 6 hr and fluorotrimethylsilane (3.90 g, 81%) was collected in the cold trap. Distillation of the residue *in vacuo* yielded phenoxydimethyldifluorophosphorane (7.2 g, 75%), bp 72–74° (0.2 mm), as a colorless mobile liquid. A gray viscous residue (2.6 g) was left in the flask.

Aryloxyphosphonium Hexafluorophosphates.—The following experiments illustrate the use of sodium fluoride in obtaining aryloxyphosphonium hexafluorophosphates in high yields from certain of the reactions we report.

Tetraphenoxyphosphonium Hexafluorophosphate.—Phosphorus pentafluoride (5.0 g, 0.040 mol) was condensed onto a mixture of phenyl trimethylsilyl ether (13.2 g, 0.080 mol) and sodium fluoride (0.5 g) at liquid nitrogen temperature in a glass reaction tube. On warming the sealed tube to room temperature two immiscible liquid layers formed. Removal of fluorotrimethylsilane left a crystalline solid which was recrystallized from acetonitrile to give tetraphenoxyphosphonium hexafluorophosphate (6.0 g, 54% of purified product) as a colorless, crystalline solid.

Bis(dimethylamino)bis(phenoxy)phosphonium Hexafluorophosphate.—Dimethylaminotetrafluorophosphorane (7.6 g, 0.050 mol) was added to phenyl trimethylsilyl ether (8.3 g, 0.050 mol) in a two-necked flask fitted with a dropping funnel and reflux condenser attached to a cold trap at −78°. The reaction mixture was heated at 80° for 3 days. Fluorotrimethylsilane (2.9 g, 63%) collected in the cold trap. The flask contained two immiscible liquids. The upper layer (9.2 g) was shown by ^{19}F nmr to be mainly unreacted dimethylaminotetrafluorophosphorane. The lower layer was shown by ^{19}F and ^{31}P nmr to be a mixture of hexafluorophosphate and a monosubstituted derivative of PF_6^-, either $(CH_3)_2NPF_5^-$ or $C_6H_5OPF_5^-$. After the viscous liquid stood for 3 weeks, colorless crystals appeared; these were shown by ^{19}F and ^{31}P nmr and analysis to be bis(dimethylamino)bis(diphenoxy)phosphonium hexafluorophosphate (2.0 g, 17% of crude product).

Preparation of Bis(dimethylamino)bis(phenoxy)phosphonium Hexafluorophosphate in the Presence of Sodium Fluoride.—The reaction was carried out in a manner exactly analogous to the preceding experiment. Sodium fluoride (0.1 g) was added to the reaction mixture before heating commenced. Fluorotrimethylsilane (5.0 g, ~100%) collected in the cold trap. The contents of the flask solidified on cooling. Recrystallization of this solid from acetonitrile yielded bis(dimethylamino)bis(phenoxy)phosphonium hexafluorophosphate (8.6 g, 78%) as a colorless crystalline solid.

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A Nuclear Magnetic Resonance Study of the Interaction of Cobalt(II) and Nickel(II) Ions with Thiamine Pyrophosphate

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Measurements of the ^{1}H and ^{31}P nmr of thiamine pyrophosphate (TPP) have been made in the presence of Co(II) and Ni(II) ions. Line widths and chemical shifts, $\Delta\omega_m$, were measured as a function of temperature for the phosphorus and hydrogen nuclei. The results indicate that TPP is bound to a metal ion through the pyrophosphate group and through the pyrimidine moiety. The similarity of the observed shifts and line widths with those of the ATP complex suggests the interaction may be similar in the two complexes. Proton nmr studies of the reaction of pyruvate, $CH_3C(O)COO^-$, with TPP indicate that the metal–TPP complex aids in decarboxylation, although no intermediates (*i.e.*, metal–TPP–pyruvate adduct) could be detected. These preliminary studies suggest that the metal–TPP complex acts as a more efficient catalyst toward the decarboxylation of pyruvate than TPP alone.

Introduction

In 1911, Neuberg and Karczaz[1] showed that yeast cells converted pyruvic acid, $CH_3C(O)C(O)OH$, to acetaldehyde and CO_2. The enzyme responsible for this reaction is named pyruvate decarboxylase, and several workers[2] have since shown that this enzyme decarboxylates a variety of other α-keto acids. The activity of the yeast can be destroyed, however, if it is washed with a phosphate buffer at pH 7.8.[3] Activity can be restored if magnesium ions plus an organic cofactor are added to the yeast. This cofactor, named cocarboxylase, was isolated and shown to be the pyrophosphate ester of thiamine (Figure 1).[4]

Other divalent metal ions can be used instead of magnesium to restore activity to the enzyme; those found successful in this respect include Mn(II), Co(II), Cd(II), Ca(II), Zn(II), and Fe(II).[2b,5]

Thiamine pyrophosphate (hereafter referred to as TPP) and divalent metal ions have been found to be necessary for enzyme activity in the carboxylase from

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