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## Characterization of the Anionic Species Formed in the Hydrolysis of Some Trivalent and Pentavalent Trifluoromethylphosphorus Compounds

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Aqueous and alkaline hydrolysis of some pentavalent trifluoromethylphosphoryl and -thiophosphoryl compounds and some trifluoromethylphosphines produced the ions  $(\text{CF}_3)_2\text{PS}_2^-$ ,  $(\text{CF}_3)_2\text{PSO}^-$ ,  $(\text{CF}_3)_2\text{PO}_2^-$ ,  $\text{CF}_3\text{PS}_2\text{O}^{2-}$ ,  $\text{CF}_3\text{PSO}_2^{2-}$ ,  $\text{CF}_3\text{PO}_3^{2-}$ ,  $\text{CF}_3\text{PS}_2\text{OH}^-$ ,  $\text{CF}_3\text{PSO}_2\text{H}^-$ , and  $\text{CF}_3\text{P}(\text{H})\text{O}_2^-$  in solution. The previously unknown sulfur-containing ions have been identified and characterized by their  $^{19}\text{F}$  nmr spectra in aqueous solution. The  $^{19}\text{F}$  nmr solution spectra of the wholly oxygenated anions which were initially characterized elsewhere are also reported. The ions  $\text{CF}_3\text{PS}_2\text{OH}^-$  and  $\text{CF}_3\text{PSO}_2\text{H}^-$  have been isolated as the tetraphenylarsonium salts and characterized by analysis and infrared spectroscopy.

### Introduction

Our recent synthesis and characterization<sup>1</sup> of the mixed-valence trifluoromethylthiophosphorus compound  $(\text{CF}_3)_2\text{P}(\text{S})\text{SP}(\text{CF}_3)_2$  and the related thiophosphoryl disulfide  $[(\text{CF}_3)_2\text{P}(\text{S})]_2\text{S}_2$  have required further knowledge of the identity of the trifluoromethylphosphorus anions which remain in the hydrolysate of these and related systems.<sup>2,3</sup> The quantitative nature of the alkaline hydrolysis and the relationship of the yield of fluorofrom to the valence and structure of the trifluoromethylphosphorus compound has been so well established<sup>4-7</sup> that the alkaline hydrolysis reaction is generally used as an analytical procedure in this field. The trifluoromethylphosphorus oxy anions which remain in solution have been characterized<sup>5-7</sup> but none of the thiophosphorus anions have been characterized to date. It was therefore of interest to determine the identity of the species in solution since the apparent resistance of the  $\text{P}=\text{S}$  bond to hydrolysis has been noted<sup>2,3,8</sup> and it seemed likely that a variety of oxythiophosphorus anions would exist. In the course of the study complete  $^{19}\text{F}$  nmr data of the new oxythiophosphorus anions and the previously characterized<sup>4-7</sup> oxyphosphorus anions have been obtained.

### Results and Discussion

**(A) Neutral Hydrolysis.**—Both bis(trifluoromethyl)dithiophosphinic acid,<sup>2,3</sup>  $(\text{CF}_3)_2\text{PS}_2\text{H}$ , and bis(trifluoromethyl)thiophosphinic acid,<sup>9</sup>  $(\text{CF}_3)_2\text{P}(\text{S})\text{OH}$ , dissolve in water to provide stable aqueous solutions of their respective anions,  $(\text{CF}_3)_2\text{PS}_2^-$  and  $(\text{CF}_3)_2\text{PSO}^-$ . Alkali metal and ammonium salts of these acids behave similarly yielding the same anions which appear to be resistant to  $\text{CF}_3-\text{P}$  as well as  $\text{P}-\text{S}$  bond cleavage in moderately acidic or neutral solution. The  $(\text{CF}_3)_2\text{PSO}^-$  ion is formed by neutral hydrolysis of  $(\text{CF}_3)_3\text{PS}^8$  which also yields 1 mol of  $\text{CF}_3\text{H}$ , and the same ion is also formed when  $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}^{2,8}$  is dissolved in water further demonstrating the stability of  $(\text{CF}_3)_2\text{PS}_{2-x}\text{O}_x^-$

( $x = 0, 1$ ) ions in neutral or moderately acidic solution. Similarly the  $(\text{CF}_3)_2\text{PO}_2^-$  (*i.e.*,  $x = 2$ ) ion was obtained upon neutral hydrolysis of  $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}^{9-11}$  as would be expected in view of the previous demonstration of the stability of this ion in neutral and acidic solutions.<sup>5</sup>

The  $\text{CF}_3\text{P}(\text{H})\text{O}_2^-$  ion<sup>4-7</sup> was obtained from the neutral hydrolyses of some bis(trifluoromethyl)phosphines and was accompanied by the liberation of 1 mol of fluorofrom. In the case of  $(\text{CF}_3)_2\text{PSH}^{12}$  1 mol of hydrogen sulfide was also obtained, demonstrating the facile nucleophilic attack which occurs at trivalent phosphorus in these systems. The frequently proposed hydrolysis intermediate  $(\text{CF}_3)_2\text{POH}^{6,10}$  was also shown separately to react further with water to yield fluorofrom and the expected<sup>5,6</sup> anionic product  $\text{CF}_3\text{P}(\text{H})\text{O}_2^-$  which was readily characterized by the large  $\text{P}-\text{H}$  coupling observed in its nmr spectrum.

The more complex neutral hydrolysis of bis(trifluoromethyl)thiophosphoryl- $\mu$ -thio-bis(trifluoromethyl)phosphine gave  $(\text{CF}_3)_2\text{PS}_2^-$  and  $\text{CF}_3\text{P}(\text{H})\text{O}_2^-$  ions in solution clearly suggesting initial attack at the  $\text{P}^{\text{III}}-\text{S}$  bond to give  $(\text{CF}_3)_2\text{PS}_2^-$  and  $(\text{CF}_3)_2\text{POH}$  followed by hydrolysis of the latter to yield the observed<sup>1</sup> 1 mol of fluorofrom and the  $\text{CF}_3\text{P}(\text{H})\text{O}_2^-$  ion. The formation of the latter species provides clear evidence for the presence of tervalent phosphorus. Neutral hydrolysis of bis(bis(trifluoromethyl)thiophosphoryl) disulfide<sup>1</sup> gave a mixture of  $(\text{CF}_3)_2\text{PS}_2^-$ ,  $(\text{CF}_3)_2\text{PSO}^-$ , and  $(\text{CF}_3)_2\text{PO}_2^-$  ions in solution. The dominant anionic products  $(\text{CF}_3)_2\text{PS}_2^-$  and  $(\text{CF}_3)_2\text{PSO}^-$  can be interpreted as the result of the cleavage of the disulfide bridge to form both  $(\text{CF}_3)_2\text{PS}_2\text{H}$  (which would form the stable  $(\text{CF}_3)_2\text{PS}_2^-$  ion in aqueous solution) and a sulfonyl intermediate  $(\text{CF}_3)_2\text{P}(\text{S})\text{SOH}$  which would be expected to be unstable to decomposition or further reaction.

The behavior contrasts with that of inorganic disulfane diphosphates which appear to hydrolyze through nucleophilic displacement at phosphorus with subsequent loss of sulfur.<sup>13</sup>

The minor but significant quantities of  $(\text{CF}_3)_2\text{PO}_2^-$  may arise from the reaction of the sulfonyl intermediate with water to form OH radicals which then remove sulfur to form the fully oxygenated anionic product. Separate experiments have demonstrated that sulfur-con-

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taining anionic species are desulfurized by peroxide in neutral solution as expected from related studies.<sup>14</sup>

(B) **Alkaline Hydrolysis.**—Pentavalent phosphoryl compounds such as  $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}$  generate the previously reported<sup>4-6</sup>  $\text{CF}_3\text{PO}_3^{2-}$  ion on alkaline hydrolysis with the liberation of 1 mol of fluoroform. In a similar fashion the alkaline hydrolysis of pentavalent monothio phosphoryl compounds such as  $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}$ ,<sup>3</sup> and  $(\text{CF}_3)_2\text{P}(\text{S})\text{OH}$ <sup>9</sup> liberates 1 mol of fluoroform and forms the analogous monothio anion,  $\text{CF}_3\text{PSO}_2^{2-}$ . Tris(trifluoromethyl)phosphine sulfide<sup>8</sup> yielded the same anion and 2 mol of fluoroform. The alkaline hydrolysis of  $\text{CF}_3\text{P}(\text{S})\text{Cl}_2$ <sup>2</sup> also yielded the  $\text{CF}_3\text{PSO}_2^{2-}$  ion as the result of the loss of only the chlorine substituents upon alkaline hydrolysis. All of these reactions indicate clearly the resistance of the monothio phosphoryl function to hydrolysis in these systems and the absence of  $\text{S}^{2-}$  ions in solution was clearly demonstrated in all cases by means of the sodium nitroprusside test<sup>15</sup> on the hydrolysate. Bis(trifluoromethyl)dithiophosphinic acid gave 1 mol of fluoroform and formed the  $\text{CF}_3\text{PS}_2\text{O}^{2-}$  ion in the solution. The absence of  $\text{S}^{2-}$  was demonstrated as above.<sup>15</sup>

Alkaline hydrolyses of a series of methyl esters of bis(trifluoromethyl)phosphinic acids were also considered because the possibility of several competing reactions existed. In all three cases more than 1 mol of fluoroform was obtained in agreement with previous observations.<sup>9</sup> The monothio ester  $(\text{CF}_3)_2\text{P}(\text{S})\text{OCH}_3$ <sup>9</sup> gave only the  $\text{CF}_3\text{PSO}_2^{2-}$  ion and no sulfide. The dithio ester  $(\text{CF}_3)_2\text{P}(\text{S})\text{SCH}_3$ <sup>9</sup> gave sulfide ion and the  $\text{CF}_3\text{PSO}_2^{2-}$  ion as the only detectable trifluoromethylphosphorus species indicating that hydrolysis of the ester involves attack of the P-S bond which results in eventual formation of  $\text{S}^{2-}$  in the solution. Loss of  $\text{CF}_3\text{H}$  from a species such as  $(\text{CF}_3)_2\text{PSO}^-$  in subsequent steps to produce the observed products is to be expected in view of the pattern established above. The phosphoryl thio ester  $(\text{CF}_3)_2\text{P}(\text{O})\text{SCH}_3$  likewise underwent cleavage at the P-S bond rather than the S-C bond giving only the  $\text{CF}_3\text{PO}_3^{2-}$  ion in the hydrolysate. Again the  $\text{S}^{2-}$  ion was detected and  $\text{CF}_3\text{H}$  was liberated. The liberation of fluoroform in excess of the expected quantity may be due to a difference in the hydrolysis reaction mechanism in cases where the reaction may involve  $\text{SCH}_3$ -containing intermediates since it has been shown elsewhere<sup>16</sup> that the alkaline hydrolysis of the methyl ester of bis(trifluoromethyl)phosphinic acid,  $(\text{CF}_3)_2\text{P}(\text{O})\text{OCH}_3$ , gave exactly 1 mol of fluoroform. Any nonfluorinated phosphorus ions formed from further reaction of the trifluoromethylphosphorus anions are not of course detectable by <sup>19</sup>F nmr spectroscopy.

Alkaline hydrolysis of  $(\text{CF}_3)_2\text{P}(\text{S})\text{SP}(\text{CF}_3)_2$ <sup>1</sup> gave  $\text{CF}_3\text{PS}_2\text{O}^{2-}$  ions as a result of cleavage at the  $\text{P}^{\text{III}}\text{-S}$  bond followed by the complete hydrolysis of  $(\text{CF}_3)_2\text{-POH}$  to a nonfluorinated phosphorus ion and the hydrolysis of  $(\text{CF}_3)_2\text{PS}_2^-$  to  $\text{CF}_3\text{PS}_2\text{O}^{2-}$ . The tetrasulfide<sup>1</sup>  $[(\text{CF}_3)_2\text{PS}]_2\text{S}_2$  appears to undergo principally cleavage of the S-S bond and eventual formation of the  $\text{CF}_3\text{-PS}_2\text{O}^{2-}$  ion as the major product. Some  $\text{CF}_3\text{PSO}_2^{2-}$  ion was also formed however indicating that the compound may also undergo cleavage at the P-S bond.

Only the expected 2 mol of fluoroform per mole of tetrasulfide was obtained.

(C) **Behavior of Thiophosphorus Anions in Solution.**—The new oxythio anions  $\text{CF}_3\text{PS}_2\text{O}^{2-}$  and  $\text{CF}_3\text{PSO}_2^{2-}$  did not precipitate from alkaline solution upon the addition of large cations such as the tetraphenylarsonium ion. Neutralization of the solutions with concentrated hydrochloric acid yielded salts of the protonated anions  $\text{CF}_3\text{PS}_2\text{OH}^-$  and  $\text{CF}_3\text{PSO}_2\text{H}^-$  whose constitution is fully supported by the analytical results. Dissolution of the tetraphenylarsonium salts in 10% NaOH solution reconstituted the parent dianions. The marked but consistent variations of <sup>19</sup>F coupling constants and chemical shifts with the pH of the solutions clearly indicates that the species in alkaline solution are not identical with the species which exist in the neutral solution. The monoanionic products which precipitated from neutral solution are presumed to reflect the major species present in these solutions. The behavior of the system is entirely consistent with the proposal that the species  $\text{CF}_3\text{PS}_2\text{OH}^-$  and  $\text{CF}_3\text{PSO}_2\text{H}^-$  are weak acids formed by protonation of the dianions. The parent dibasic acid is presumably a strong acid. Titration curves of alkaline hydrolysates of  $\text{CF}_3\text{P}(\text{S})\text{Cl}_2$ <sup>2</sup> and  $(\text{CF}_3)_2\text{PS}_2\text{H}_2$ ,<sup>3</sup> with HCl and of the neutral hydrolysate of  $\text{CF}_3\text{P}(\text{S})\text{-Cl}_2$ <sup>2</sup> with NaOH were plotted and showed typical weak acid behavior. The pH at the half-neutralization point gave the approximate  $K_a$  values of  $6 \times 10^{-4}$  for the  $\text{CF}_3\text{PSO}_2\text{H}^-$  species and  $8 \times 10^{-4}$  for the  $\text{CF}_3\text{PS}_2\text{OH}^-$  species.

The parts of the curves relevant to the parent dibasic acids were in agreement with the hypothesis that both were strong acids, but there were no distinguishable breaks in the curves corresponding to the first end points (*cf.*  $\text{CF}_3\text{P}(\text{O})(\text{OH})_2$ <sup>3</sup>).

Infrared spectra of mulls of the protonated salts did not show OH or SH stretching bands although a weak band in the  $\text{CF}_3\text{PSO}_2\text{H}^-$  salt at  $2250\text{ cm}^{-1}$  could be due to hydrogen-bonded OH stretch similar to that observed<sup>5</sup> for  $\text{CF}_3\text{PO}_3\text{H}^-$ . Bending modes could be assigned to the bands at  $882$  and  $918\text{ cm}^{-1}$  and both are probably due to OH bending although SH bending motions cannot be ruled out.

The <sup>19</sup>F nmr spectra of the ions were obtained in aqueous solution. All of the coupling constant and chemical shift values quoted in Table I are the limiting

TABLE I  
NMR DATA FOR IONS IN AQUEOUS SOLUTION

Ion	$\phi,^a$ ppm	$^2J_{\text{FP}},$ Hz	Original prepn of anion
$(\text{CF}_3)_2\text{PS}_2^-$	72.9	92.0	Ref 2
$(\text{CF}_3)_2\text{PSO}^-$	73.1	97.0	Ref 9
$(\text{CF}_3)_2\text{PO}_3^-$	72.8	103.6	Ref 4
$\text{CF}_3\text{PS}_2\text{O}^{2-}$	76.1	86.6	This work
$\text{CF}_3\text{PSO}_2^{2-}$	74.6	89.9	This work
$\text{CF}_3\text{PO}_3^{2-}$	72.0	93.0	Ref 4-6
$\text{CF}_3\text{PS}_2\text{OH}^-$	77.1	99.0	This work
$\text{CF}_3\text{PSO}_2\text{H}^-$	75.8	103.0	This work
$\text{CF}_3\text{P}(\text{H})\text{O}_2^-$	77.8	100.9 <sup>b</sup>	Ref 4-7

<sup>a</sup> Relative to external  $\text{CCl}_3\text{F}$  (in capillary). Positive values to high field of standard. <sup>b</sup>  $\tau$  2.7 (relative to TMS,  $\tau$  10.0);  $^1J_{\text{HF}} = 589\text{ Hz}$ ;  $^3J_{\text{HF}} = 4.1\text{ Hz}$ .

values obtained in either acid or strongly alkaline media since intermediate values suggesting rapid (on the nmr time scale) exchange processes are observed for solutions of intermediate pH which appear to con-

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tain comparable quantities of the dianions and their singly protonated derivatives. It is interesting to note that the limiting coupling constants ( $^2J_{\text{FP}}$ ) within each series of isostructural anions are found to increase with increasing numbers of oxygen atoms replacing sulfur atoms (*i.e.*, with increasing total electronegativity of substituents) in accord with other observations.<sup>17</sup>

The  $^{19}\text{F}$  and  $^1\text{H}$  nmr spectra of the  $\text{CF}_3\text{P}(\text{H})\text{O}_2^-$  ion confirm its previously deduced structure<sup>5</sup> (see Table I).

The bis(trifluoromethyl)thiophosphorus anions  $(\text{CF}_3)_2\text{PS}_2^-$  and  $(\text{CF}_3)_2\text{P}(\text{S})\text{O}^-$  have been characterized elsewhere.<sup>3,9</sup> Silver ion in aqueous solution resulted in a rapid desulfurization of the anions precluding the use of silver salts as a source of the acids.

### Conclusions

The characterization of the anionic trifluoromethylphosphorus hydrolysis products by  $^{19}\text{F}$  nmr permits rapid, positive identification of the species produced in these hydrolysis reactions. A fuller understanding of the hydrolysis pathways can now be obtained since the products in solution can be rapidly characterized. The exceptions are the few systems known to produce fluoride and carbonate<sup>6,18</sup> on hydrolysis which we have not investigated here. In addition, it is possible to deduce more reliably the structures of the parent compounds from their hydrolysis behavior. The present results clearly indicate that sulfur attached to trivalent phosphorus is readily and completely removed by both neutral and alkaline hydrolysis, presumably as a result of the susceptibility of the system to nucleophilic attack at P(III). Terminal P=S groups on pentavalent phosphorus appear to be generally resistant to alkaline and neutral hydrolysis and the resultant anions contain the initial number of sulfur atoms even though trifluoromethyl groups are hydrolyzed by alkali so that the hydrolysate contains only the monotrifluoromethyl species. The reason for the liberation of fractionally more than 1 mol of  $\text{CF}_3\text{H}$  from the pentavalent esters containing P-S- $\text{CH}_3$  functions is not clear at this time and this behavior may be indicative of a very complex hydrolysis mechanism which may yield a variety of products other than those identifiable by  $^{19}\text{F}$  nmr spectroscopy. Further study of the hydrolysis of these thio esters is clearly warranted. Under neutral conditions the P=S group is hydrolyzed by hydrogen peroxide and is reduced by silver ions.

### Experimental Section

Materials were handled by standard vacuum techniques in a Pyrex-glass system with stopcocks lubricated with Apiezon N grease. Infrared spectra (Table II) were recorded on a Perkin-Elmer 337 instrument. Fluorine and proton nmr spectra were recorded on a Varian A-56/60A spectrometer operating at 56.4 and 60.0 MHz or a Varian HA-100 spectrometer operating at 94.1 and 100 MHz; chemical shifts were measured relative to external  $\text{CFCl}_3$  and TMS, respectively. All ions in solution were identified by nmr unless otherwise stated. Trifluoromethylodiphosphorus compounds were prepared from  $\text{CF}_3\text{I}$  and red phosphorus<sup>18</sup> and the specific compounds required were prepared by indicated literature methods. Reagent grade chemicals were used as supplied. All reactions were carried out in sealed Pyrex-glass tubes. Aqueous hydrolysates were handled in the air after the reaction had been completed.

**Neutral Hydrolyses in Aqueous Solution.**—All reactions were

TABLE II  
INFRARED SPECTRA OF THE PROTONATED  
OXYTHIOPHOSPHORYL SALTS<sup>a</sup>

$\text{CF}_3\text{PS}_2\text{OH}^-$	$\text{CF}_3\text{PSO}_2\text{H}^-$	Assignment
1188 s	2250 w, b	OH (hydrogen bonded)
1118 s	1212 m	$\nu(\text{P}-\text{O})$
	1135 s	}
	1105 s	
1107 s	1090 m	
882 s	918 s	$\delta(\text{OH})$
741 s	743 s	$\nu(\text{P}=\text{S})$
732 m	732 m	$\delta_{\text{sym}}(\text{CF}_3)$
695 s	654 s	P—O bend
574 m	506 m	$\delta_{\text{asym}}(\text{CF})$
423 m	421 m	$\nu(\text{P}-\text{CF})$

<sup>a</sup> All values are in  $\text{cm}^{-1}$  and were obtained from Nujol mulls of the tetraphenylarsonium salts by subtracting the spectrum of tetraphenylarsonium chloride from the observed spectra. Abbreviations:  $\nu$ , stretching;  $\delta$ , deformation; s, strong; m, medium; w, weak; b, broad.

carried out by condensing the compound onto 1.0 ml of degassed, distilled water and then allowing the reaction to proceed for 2 days at room temperature. Fluoroform was weighed after vacuum fractionation and identified by infrared spectroscopy.

(1) **Phosphines.**—(a)  $(\text{CF}_3)_2\text{PCl}^{19}$  (0.0738 g, 0.36 mmol) yielded  $\text{CF}_3\text{H}$  (0.0256 g, 0.37 mmol) and  $\text{CF}_3\text{P}(\text{H})\text{O}_2^-$  which remained in solution. (b)  $(\text{CF}_3)_2\text{PSH}^{12}$  (0.0613 g, 0.30 mmol) yielded  $\text{CF}_3\text{H}$  (0.0210 g, 0.30 mmol) and  $\text{H}_2\text{S}$  (0.0107 g, 0.32 mmol) the two compounds being obtained as a mixture and the amount of  $\text{H}_2\text{S}$  obtained by difference after absorbing with lead acetate solution.  $\text{CF}_3\text{P}(\text{H})\text{O}_2^-$  remained in the original solution. (c)  $(\text{CF}_3)_2\text{POH}^{10}$  (0.0619 g, 0.33 mmol) yielded  $\text{CF}_3\text{H}$  (0.0234 g, 0.33 mmol) and  $\text{CF}_3\text{P}(\text{H})\text{O}_2^-$  which remained in solution.

(2) **Phosphoryl and Thiophosphoryl Compounds.**—No fluorocarbon-containing volatiles were obtained from any of the following reactions except reaction (g). (a)  $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}^{9-11}$  (0.1007 g, 0.46 mmol) yielded the  $(\text{CF}_3)_2\text{PO}_2^-$  ion in solution. (b)  $(\text{CF}_3)_2\text{P}(\text{S})\text{OH}^9$  (0.0556 g, 0.26 mmol) yielded the  $(\text{CF}_3)_2\text{P}-\text{SO}^-$  ion in solution. (c)  $\text{CF}_3\text{P}(\text{S})\text{Cl}_2^3$  (0.0399 g, 0.20 mmol) yielded the  $\text{CF}_3\text{PSO}_2\text{H}^-$  ion in solution. (d)  $(\text{CF}_3)_2\text{P}(\text{S})-\text{Cl}^{2,9}$  (0.0987 g, 0.42 mmol) yielded the  $(\text{CF}_3)_2\text{PSO}^-$  ion in solution. Addition of excess silver carbonate precipitated silver sulfide as well as the chloride ion leaving the  $(\text{CF}_3)_2\text{PO}_2^-$  ion in solution. (e) A sample<sup>2</sup> of  $(\text{CH}_3)_3\text{NH}^+(\text{CF}_3)_2\text{PS}_2^-$  yielded a stable aqueous solution. (f)  $(\text{CF}_3)_2\text{PS}_2\text{H}^{2,3}$  (0.1079 g, 0.60 mmol) yielded the  $(\text{CF}_3)_2\text{PS}_2^-$  ion in solution. Treatment of the aqueous solution with excess silver carbonate precipitated silver sulfide and gave a filtrate containing the  $(\text{CF}_3)_2\text{PO}_2^-$  ion. (g) Slightly impure  $(\text{CF}_3)_2\text{P}=\text{S}^8$  (0.1157 g, 0.43 mmol) gave  $\text{CF}_3\text{H}$  (0.0285 g, 0.41 mmol) and the aqueous solution contained  $(\text{CF}_3)_2\text{PSO}^-$  ions.

(3) **Diphosphorus Compounds.**—(a)  $(\text{CF}_3)_2\text{P}(\text{S})\text{SP}(\text{CF}_3)_2^4$  (0.0565 g, 0.14 mmol) gave  $\text{CF}_3\text{H}$  (0.0096 g, 0.14 mmol). The ions  $(\text{CF}_3)_2\text{PS}_2^-$  and  $\text{CF}_3\text{P}(\text{H})\text{O}_2^-$  were formed in solution. (b)  $(\text{CF}_3)_2\text{P}(\text{S})\text{OP}(\text{S})(\text{CF}_3)_2^9$  (0.0753 g, 0.18 mmol) produced no fluorocarbon-containing volatiles but yielded  $(\text{CF}_3)_2\text{PSO}^-$  which remained in solution. (c)  $(\text{CF}_3)_2\text{P}(\text{S})\text{SSP}(\text{S})(\text{CF}_3)_2^4$  (0.0473 g, 0.10 mmol) yielded no fluorocarbon-containing volatiles. A small amount of elemental sulfur was obtained, and the remaining solution contained the  $(\text{CF}_3)_2\text{PS}_2^-$ ,  $(\text{CF}_3)_2\text{PSO}^-$ , and  $(\text{CF}_3)_2\text{PO}_2^-$  ions in the ratio 7.0:3.0:1.0.

**Alkaline Hydrolyses in Aqueous Solution.**—All reactions were carried out by condensing the compound onto 4.0 ml of degassed 10% NaOH solution and allowing the reaction to proceed for 2 days at room temperature. The products were treated as above. The presence or absence of sulfide ion was demonstrated with sodium nitroprusside where applicable.<sup>15</sup>

(1) **Phosphoryl and Thiophosphoryl Compounds.**—(a)  $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}^{9-11}$  (0.1081 g, 0.49 mmol) gave  $\text{CF}_3\text{H}$  (0.0345 g, 0.49 mmol) and the  $\text{CF}_3\text{PO}_3^{2-}$  ion which remained in solution. (b)  $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}^{2,3}$  (0.0888 g, 0.38 mmol) yielded  $\text{CF}_3\text{H}$  (0.0264 g, 0.38 mmol). The resultant solution contained the  $\text{CF}_3\text{PSO}_2\text{H}^-$  ion but no sulfide ion. (c)  $(\text{CF}_3)_2\text{P}(\text{S})\text{OH}^9$  (0.0632 g, 0.29 mmol) produced  $\text{CF}_3\text{H}$  (0.0204 g, 0.29 mmol) and the  $\text{CF}_3\text{PSO}_2\text{H}^-$  ion which remained in solution. Sulfide ion was again not pres-

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ent in the solution. (d)  $\text{CF}_3\text{P}(\text{S})\text{Cl}_2$  (0.0490 g, 0.24 mmol) yielded no fluorocarbon-containing volatiles, but the solution contained the  $\text{CF}_3\text{PSO}_2^-$  ion. (e)  $(\text{CF}_3)_2\text{PS}_2\text{H}^{2,3}$  (0.0791 g, 0.34 mmol) yielded  $\text{CF}_3\text{H}$  (0.0237 g, 0.34 mmol) and the  $\text{CF}_3\text{PS}_2\text{O}^{2-}$  ion in solution. The solution gave a negative test for the sulfide ion. (f)  $(\text{CF}_3)_2\text{P}(\text{O})\text{SCH}_3$  (0.0320 g, 0.14 mmol) yielded  $\text{CF}_3\text{H}$  (0.0113 g, 0.16 mmol) and both sulfide and  $\text{CF}_3\text{PO}_3^{2-}$  ions remained in the hydrolysate. (g)  $(\text{CF}_3)_2\text{P}(\text{S})\text{OCH}_3$  (0.0870 g, 0.38 mmol) yielded  $\text{CF}_3\text{H}$  (0.0290 g, 0.41 mmol) and the aqueous solution contained  $\text{CF}_3\text{PSO}_2^{2-}$  but no sulfide ion. (h)  $(\text{CF}_3)_2\text{P}(\text{S})\text{SCH}_3$  (0.0847 g, 0.34 mmol) produced  $\text{CF}_3\text{H}$  (0.0278 g, 0.40 mmol) and the hydrolysate contained  $\text{CF}_3\text{PSO}_2^{2-}$  and sulfide ions. (i) Slightly impure  $(\text{CF}_3)_3\text{P}=\text{S}$  (0.1189 g, 0.44 mmol) yielded  $\text{CF}_3\text{H}$  (0.0588 g, 0.84 mmol) and an aqueous solution which contained the  $\text{CF}_3\text{PSO}_2^{2-}$  ion.

(2) **Diphosphorus Compounds.**—(a)  $(\text{CF}_3)_2\text{P}(\text{S})\text{SP}(\text{CF}_3)_2$  (0.0533 g, 0.13 mmol) gave  $\text{CF}_3\text{H}$  (0.0279 g, 0.39 mmol) and  $\text{CF}_3\text{PS}_2\text{O}^{2-}$  remained in solution. (b)  $(\text{CF}_3)_2\text{P}(\text{S})\text{SSP}(\text{S})(\text{CF}_3)_2$  (0.0558 g, 0.12 mmol) produced  $\text{CF}_3\text{H}$  (0.0175 g, 0.25 mmol). The aqueous solution contained the  $\text{CF}_3\text{PS}_2\text{O}^{2-}$  and  $\text{CF}_3\text{PSO}_2^{2-}$  ions in the ratio 3:1. A little elemental sulfur was also obtained, but no sulfide ion was present in the solution. (c)  $(\text{CF}_3)_2\text{P}(\text{S})\text{OP}(\text{S})(\text{CF}_3)_2$  (0.0636 g, 0.15 mmol) yielded  $\text{CF}_3\text{H}$  (0.0207 g, 0.30 mmol) and  $\text{CF}_3\text{PSO}_2^{2-}$  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%  $\text{H}_2\text{O}_2$  solution and allowing the reaction to continue at room temperature for 4 days. (a)  $(\text{CF}_3)_2\text{PS}_2\text{H}^{2,3}$  (0.30 mmol) began to react as soon as the tube reached room temperature with appearance of elemental sulfur. The solution contained the  $(\text{CF}_3)_2\text{PO}_3^-$  ion and another unidentified  $\text{CF}_3\text{P}$ -containing species. (b)  $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}_2$  (0.30 mmol) reacted as above to yield the same species in solution and elemental sulfur.

**Preparation of Tetraphenylarsonium Salts.** (1)  $(\text{C}_6\text{H}_5)_4\text{As}^+\text{CF}_3\text{PSO}_2\text{H}^-$ .—Trifluoromethylthiophosphoryl dichloride<sup>2</sup> (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  $\text{C}_{25}\text{H}_{21}\text{AsPF}_3\text{SO}_2$ : 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  $\text{CF}_3\text{PSO}_2^{2-}$  ions according to the nmr spectrum.

(2)  $(\text{C}_6\text{H}_5)_4\text{As}^+\text{CF}_3\text{PS}_2\text{OH}^-$ .—Bis(trifluoromethyl)dithiophosphinic acid<sup>2,3</sup> (0.2158 g, 0.92 mmol) was hydrolyzed as above and after removal of  $\text{CF}_3\text{H}$  (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  $\text{C}_{25}\text{H}_{21}\text{AsPF}_3\text{S}_2\text{O}$ : 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  $\text{CF}_3\text{PS}_2\text{O}^{2-}$  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  $\text{CF}_3\text{P}(\text{S})\text{Cl}_2$  (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)  $(\text{CF}_3)_2\text{PS}_2\text{H}^{2,3}$  (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  $\text{CF}_3\text{P}(\text{S})\text{Cl}_2$  (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.<sup>1</sup> Aryloxy-Substituted Fluorophosphoranes

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The silyl ethers  $\text{C}_6\text{H}_5\text{OSi}(\text{CH}_3)_3$  and  $\text{C}_6\text{F}_5\text{OSi}(\text{CH}_3)_3$  undergo silicon-oxygen bond cleavage reactions with fluorophosphoranes,  $\text{R}_n\text{PF}_{5-n}$  ( $n = 0, 1, 2$ ; R =  $\text{CH}_3$ ,  $\text{C}_6\text{H}_5$ ,  $(\text{CH}_3)_2\text{N}$  in the case of  $\text{C}_6\text{H}_5\text{OSi}(\text{CH}_3)_3$ ;  $n = 0, 1, 2$ ; R =  $\text{CH}_3$ ,  $\text{C}_6\text{H}_5$  in the case of  $\text{C}_6\text{F}_5\text{OSi}(\text{CH}_3)_3$ ), to give a series of thermally stable compounds of the types  $(\text{C}_6\text{H}_5\text{O})_{3-n}\text{PR}_n\text{F}_2$  and  $(\text{C}_6\text{F}_5\text{O})_{3-n}\text{PR}_n\text{F}_2$  ( $n = 0, 1, 2$ ). The intermediate  $(\text{RO})_2\text{PF}_3$ , assumed in the reactions of  $\text{PF}_5$  with  $\text{ArOSi}(\text{CH}_3)_3$ , was isolated only in the form of the isomeric stable phosphonium salt  $[(\text{RO})_2\text{P}][\text{PF}_6]$ . The <sup>31</sup>P and <sup>19</sup>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.

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While the species  $\text{C}_2\text{H}_5\text{OPRF}_3$ <sup>4</sup> and  $\text{CH}_3\text{OPF}_4$ <sup>5</sup> have been characterized by nmr spectroscopy at low temper-

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