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Trimethylsilyl Esters of Phosphorus Acids. I. Preparation and Properties of Esters of Difluoro- and Bis(trifluoromethyl)phosphinic, -thiophosphinic, and -dithiophosphinic Acids

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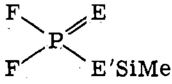
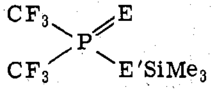
Trimethylsilyl esters of difluorophosphinic, -thiophosphinic, and -dithiophosphinic acids and their bis(trifluoromethyl) analogs have been prepared by one or more of four different synthetic routes and characterized by infrared and nmr spectroscopy. Their reactions with anhydrous hydrogen chloride and thermal behavior have been investigated, the esters containing a P–S–Si bridge unit being markedly less thermally stable than those possessing the P–O–Si bridge. Dimethylamine reacts with the bis(trifluoromethyl) esters to give Me_3SiNMe_2 and dimethylammonium salts of the phosphinic acids, but in the case of the difluoro esters the initial product Me_3SiNMe_2 then attacks P–F bonds in the anions $F_2PEE'^-$ (E, E' = O, S) yielding Me_3SiF and the anions $F(Me_2N)PEE'^-$.

Introduction

Molecules containing the bridge system P–O–Si are well known for both tervalent and pentavalent phosphorus;[1] for example, trimethylsilyl difluorophosphinate, $F_2P(O)OSiMe_3$ (I), has been prepared by Roesky[2] from $F_2P(O)OP(O)F_2$ and $(Me_3Si)_2O$, by Kreshkov, *et al.*,[3] from Me_3SiCl and $NH_4^+F_2PO_2^-$, and by Biermann and Glemser[4] from $F_2P(O)X$ (X = F, Cl) and $(Me_3Si)_2O$. In contrast the P–S–Si bridge system is less well known, the only reported examples[1] being a few derivatives of the type $R_2P(S)SSiMe_3$. Recently the synthesis of $F_2P(S)SSiMe_3$ (III) from F_2PS_2H and Me_3SiNMe_2 or Me_3SiH was reported.[5] We now describe novel preparations and the properties of I, III, the mixed oxythio analog $F_2P(S)OSiMe_3$ (II), and the related bis(trifluoromethyl) esters IV, V, and VI.



I, E = E' = O
II, E = S; E' = O
III, E = E' = S



IV, E = E' = O
V, E = S; E' = O
VI, E = E' = S

Experimental Section

Standard vacuum techniques were used throughout. Reactions were carried out on a 0.2–5 m*M* scale in evacuated sealed tubes in the absence of solvent, and the products were separated and purified by fractional condensation *in vacuo*. Infrared and nmr spectroscopy was used for routine identification of products. Infrared spectra were recorded on Perkin-Elmer 337, 457, and 421 and Beckman IR 11 spectrometers, nmr spectra on Varian A56/60 and HA 100 instruments, and mass spectra on AEI MS-2 or MS-9 instruments at ionizing voltages of 70 eV using a specially designed direct inlet system which replaced the standard direct probe sample insertion system of the MS-9 instrument.

Proton and fluorine nmr spectra were recorded using 10–20% solutions in $CFCl_3$ (liquids) and water, MeOH, or CD_3CN (salts). Proton chemical shifts were measured relative to external TMS and fluorine shifts relative to internal or external (capillary) $CFCl_3$. Phosphorus spectra were recorded (relative to a capillary of P_4O_6[6]) on neat liquid samples at 40.3 MHz using the Varian HA 100 instrument.

Commercially available samples of Me_3SiCl, $(Me_3Si)_2O$, $(Me_3Si)_2NH$, Me_2NH, HCl, and F_3PO were fractionated under vacuum and used without further purification. The compounds F_2PS_2H,[7] $(SPF_2)_2O$,[8] $(CF_3)_2P(O)Cl$,[9] $(CF_3)_2PS_2H$,[10a] $(CF_3)_2P(S)OH$,[10b] $[(CF_3)_2P(S)]_2O$,[10b] and $Me_4N^+(CF_3)_2PSO^-$ [10b] were prepared by literature methods. The disilthiane $(Me_3Si)_2S$ was prepared by the method of Abel[11] and freed from $(Me_3Si)_2O$ by fractional condensation at −15° *in vacuo*. Me_3SiNMe_2 was made from the reaction of Me_3SiCl with 2 molar equiv of Me_2NH and condensed under vacuum at −84°.

Preparations. Trimethylsilyl Difluorophosphinate (I).—Phosphoryl trifluoride (0.449 g, 4.32 mmol) and $(Me_3Si)_2O$ (0.700 g, 4.32 mmol) were allowed to react at room temperature for 10 days. Fractionation of the volatile products gave only Me_3SiF, which was trapped at −196°, and $F_2P(O)OSiMe_3$ (I) (0.728 g, 4.18 mmol, 97%), which was trapped at −84°.

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Trimethylsilyl Difluorothiophosphinate (II).—(a) Phosphoryl trifluoride (0.158 g, 1.52 mmol) and $(Me_3Si)_2S$ (0.220 g, 1.23 mmol) were heated to 110° for 19 days. Fractionation of the volatile products gave, at −196°, a mixture of F_3PO (0.027 g, 0.26 mmol, 17% recovery), F_3PS (0.050 g, 0.42 mmol, 34%), and Me_3SiF (0.119 g, 1.29 mmol, 105%) as estimated by nmr spectroscopy and $F_2P(S)OSiMe_3$ (II, 0.141 g, 0.74 mmol, 60%) which was trapped at −84°. Vapor-phase molecular weight determination gave $M = 196$ (calcd for II, $M = 190$).

(b) A mixture of $(SPF_2)_2O$ (0.362 g, 1.66 mmol) and $(Me_3Si)_2O$ (0.272 g, 1.68 mmol) was left at room temperature for 2 days and then heated to 80° for 1 day. Fractional condensation at −63° gave II (0.503 g, 2.65 mmol, 80%). Small amounts of Me_3SiF and unreacted starting materials passed this trap.

(c) Dimethylammonium difluorothiophosphinate, $Me_2NH_2^+F_2PSO^-$, was made[12] from $(SPF_2)_2O$ (0.433 g, 1.98 mmol) and Me_2NH (0.183 g, 4.07 mmol). Removal of the volatile products (mainly $F_2P(S)NMe_2$) gave $Me_2NH_2^+F_2PSO^-$ as a white solid, to which Me_3SiCl (0.288 g, 2.65 mmol) and dry diethyl ether (3 ml) were subsequently added. The tube was sealed and the contents shaken at 50° for 4 days. Fractional condensation *in vacuo* at −63° then gave a mixture (0.212 g, 1.12 mmol, 56% based on $(SPF_2)_2O$) of II and a little ether, the latter being removed only with difficulty by repeated redistillation.

Trimethylsilyl Difluorodithiophosphinate (III).—F_2PS_2H[7] (0.244 g, 1.82 mmol) and $(Me_3Si)_2NH$ (0.102 g, 0.63 mmol) reacted rapidly below room temperature to yield a white solid and a colorless liquid. After standing for 1 hr the contents was fractionated *in vacuo* and pure $F_2P(S)SSiMe_3$ (III, 0.200 g, 0.97 mmol, 80% based on eq 4) was trapped at −45°. The more volatile fraction (0.029 g) contained F_2PS_2H, $(Me_3Si)_2NH$, and Me_3SiF. The residual white solid was shown by nmr spectroscopy to contain the $F_2PS_2^-$ ion.[7a]

Trimethylsilyl Bis(trifluoromethyl)phosphinate (IV).—After 13 days of reaction at room temperature a mixture of $(CF_3)_2P(O)Cl$[9] (0.336 g, 1.52 mmol) and $(Me_3Si)_2O$ (0.248 g, 1.53 mmol) gave Me_3SiCl (0.158 g, 1.46 mmol, 96%) which was trapped at −84° and $(CF_3)_2P(O)OSiMe_3$ (IV, 0.385 g, 1.40 mmol, 92%) which was trapped at −45°.

Trimethylsilyl Bis(trifluoromethyl)thiophosphinate (V).—(a) $[(CF_3)_2P(S)]_2O$[10b] (0.613 g, 1.47 mmol) and $(Me_3Si)_2O$ (0.256 g, 1.59 mmol) were heated to 110° for 1 day. Subsequent vacuum fractionation gave $(CF_3)_2P(S)OSiMe_3$ (V, 0.822 g, 2.84 mmol, 97%) as a volatile liquid which was trapped at −45°.

(b) $(CF_3)_2P(S)OH$[10b] (0.389 g, 1.78 mmol) and $(Me_3Si)_2NH$ (0.190 g, 1.18 mmol) reacted rapidly below room temperature to yield a white solid and a colorless liquid. After 15 min the contents was fractionally condensed at −45° and a colorless liquid (0.414 g) was obtained and identified as a mixture of V and unreacted $(Me_3Si)_2NH$. The residual solid was shown by nmr spectroscopy to contain the $(CF_3)_2PSO^-$ ion.[13]

(c) $Me_4N^+(CF_3)_2PSO^-$ was prepared[10b] from $(CF_3)_2P(S)Cl$[14] (0.503 g, 2.12 mmol), methanol (0.098 g, 3.06 mmol), and trimethylamine (0.262 g, 4.44 mmol) as a white solid which was formed immediately on warming from −196° to room temperature. The volatile products (excess MeOH, Me_3N, and a little CF_3H) were removed and to the remaining solid (a mixture[10b] of Me_4N^+, Me_3NH^+, $(CF_3)_2PSO^-$, Cl^-) were added Me_3SiCl (0.247 g, 2.28 mmol) and dry diethyl ether (2 ml). The tube was sealed and warmed to 50° for 1 day. Subsequent distillation of the reaction mixture through a −45° trap yielded V (0.031 g, 0.11 mmol, 5%).

Trimethylsilyl Bis(trifluoromethyl)dithiophosphinate (VI).—$(CF_3)_2PS_2H$[10a] (0.707 g, 3.02 mmol) and $(Me_3Si)_2NH$ (0.180 g, 1.12 mmol) reacted rapidly on warming from −196°. After 15 min at room temperature the volatile products were fractionated to give $(CF_3)_2P(S)SSiMe_3$ (VI, 0.492 g, 1.61 mmol, 80% based on eq 4) trapped at −30°. The more volatile products (0.050 g) which passed this trap were shown by infrared spectroscopy to be largely unchanged $(CF_3)_2PS_2H$, and the residual solid contained the $(CF_3)_2PS_2^-$ ion, identified by nmr spectroscopy.[13]

Chemical Reactions. (a) **Neutral Hydrolysis of the Trifluoromethyl Esters.**—Ester IV (0.086 g, 0.31 mmol) was allowed to react with 1 ml of degassed water for 4 days at room temperature. The volatile products were then fractionated to give $(Me_3Si)_2O$ (0.026 g, 0.16 mmol) while the remaining solution was shown by nmr spectroscopy[13] to contain the $(CF_3)_2PO_2^-$ ion. Similarly ester V gave the ion $(CF_3)_2PSO^-$ and ester VI gave $(CF_3)_2PS_2^-$, and in each case the volatile products included $(Me_3Si)_2O$.

(b) **Alkaline Hydrolysis of the Trifluoromethyl Esters.**—Ester IV (0.091 g, 0.33 mmol) was treated with degassed 10% NaOH solution for 7 days at room temperature. The volatile products were $(Me_3Si)_2O$ (0.024 g, 0.15 mmol), collected at −132°, and CF_3H (0.024 g, 0.34 mmol), collected at −196°, and the resulting solution contained[13] the $CF_3PO_3^{2-}$ ion.

Ester V (0.224 g, 0.773 mmol), under similar conditions, gave CF_3H (0.052 g, 0.74 mmol) and $(Me_3Si)_2O$ and the solution contained the $CF_3PSO_2^{2-}$ ion, while ester VI (0.077 g, 0.25 mmol) gave CF_3H (0.018 g, 0.26 mmol), $(Me_3Si)_2O$ (0.017 g, 0.11 mmol), and the $CF_3PS_2O^{2-}$ ion in solution.[13]

(c) **Thermal Behavior.**—When a sample of I (0.223 g, 1.28 mmol) was heated to 200° for 5 days, 0.130 g (0.75 mmol, 59%) was recovered unchanged. A mixture of Me_3SiF and F_3PO (0.031 g) was also produced and an aqueous solution of the residual oil and solid mixture was shown to contain PO_4^{3-} by the ammonium molybdate test.

Ester II (0.132 g, 0.695 mmol), heated to 225° for 8 days, was largely recovered unchanged (0.118 g, 0.62 mmol, 89%). The only decomposition product identified was Me_3SiF (0.007 g, 0.075 mmol, 12%).

A sample of III (0.252 g, 1.22 mmol), heated to 110° for 2 days, gave yellow crystals and a colorless oil. Fractionation of the volatile products gave Me_3SiF (0.090 g, 0.98 mmol) trapped at −196° and an oil which trapped at −84°. The oil had infrared (broad peaks at 900 (ν_{P-F}) and 700 cm^{-1} ($\nu_{P=S}$)), ^{19}F nmr (ϕ 28.1 ppm, $^1J_{PF} = 1264$ Hz), and mass spectral properties consistent with its formulation as a polymer containing F, P, and S. The residual yellow crystals (0.035 g, 0.08 mmol) were identified as P_4S_{10} by infrared spectroscopy, melting point (275–280°, lit.[15] 286–290°), and microanalysis (% S found 70.3, 70.5; calcd 72.1).

A sample of IV (0.079 g, 0.29 mmol), heated for 15 days at 195°, was recovered almost quantitatively (0.078 g, 0.29 mmol). Similarly, V (0.192 g, 0.66 mmol), after 9 days at 200°, was recovered virtually unchanged (0.187 g, 0.645 mmol).

Heating a sample of VI (0.454 g, 1.48 mmol) to 160° for 5 days gave a yellow liquid and a mixture of yellow and white solids. The solids were shown by infrared spectroscopy and melting point determination to contain elemental sulfur, P_4S_{10}, and a component which fumed in air. The volatile products contained 0.208 g of a mixture of Me_3SiF and at least two other unidentified compounds, trapped at −196°, and a mixture (0.119 g) trapped at −84° which contained small amounts of $(CF_3)_2P(S)SP(CF_3)_2$,[10a] $(CF_3)_2PSP(CF_3)_2$,[16] and at least three other unidentified components, as indicated by nmr spectroscopy.

(d) **Reactions with Anhydrous Hydrogen Chloride.**—Reaction of anhydrous HCl with the esters I, II, IV, and V proceeded very slowly at 110°, producing in each case trace amounts of Me_3SiF, Me_3SiCl, and $(Me_3Si)_2O$ as the only identified products.

Ester III (0.093 g, 0.45 mmol) reacted completely with HCl (0.017 g, 0.465 mmol) after 11 days at room temperature to give a mixture (0.084 g) of Me_3SiCl, F_2PS_2H, and a little excess HCl.

Ester VI (0.060 g, 0.20 mmol) reacted with excess HCl during 2 days at room temperature to give a mixture (0.053 g) of Me_3SiCl and $(CF_3)_2PS_2H$.

(e) **Reactions with Dimethylamine.**—Dimethylamine (0.176 g, 3.91 mmol) reacted with I (0.329 g, 1.89 mmol) at room temperature to give a white solid which changed to an oil on standing. After 3 days the only volatile components were Me_3SiF (0.180 g, 1.95 mmol) trapped at −196° and $(Me_3Si)_2O$ (0.006 g) trapped at −84°. A methanolic solution of the residual white deliquescent solid gave an nmr spectrum (Figure 1) consistent with its formulation as $Me_2NH_2^+F(Me_2N)PO_2^-$.

Ester II (0.187 g, 0.985 mmol) reacted in a similar manner with Me_2NH (0.094 g, 2.09 mmol) to give, after 8 days at room

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[16] (a) R. G. Cavell and H. J. Emeléus, *J. Chem. Soc.*, 5825 (1964); (b) A. B. Burg and K. Gosling, *J. Amer. Chem. Soc.*, **87**, 2113 (1965).

temperature, Me_3SiF (0.090 g, 0.98 mmol) containing a trace of $(Me_3Si)_2O$. The residual oil, dissolved in methanol, gave nmr spectra assignable to $Me_2NH_2^+F(Me_2N)PSO^-$.

Ester III (0.258 g, 1.25 mmol) reacted similarly with Me_2NH (0.112 g, 2.49 mmol) to give, after 2 days at room temperature, Me_3SiF (0.1125 g, 1.22 mmol) and an oil, the nmr spectrum (solution in methanol) of which was consistent with the formulation $Me_2NH_2^+F(Me_2N)PS_2^-$.

After 9 days at room temperature IV (0.069 g, 0.25 mmol) and Me_2NH (0.036 g, 0.80 mmol) gave a mixture containing as volatile components excess Me_2NH (0.014 g, 0.31 mmol) collected at −116° and Me_3SiNMe_2 (0.028 g, 0.24 mmol) collected at −84°. The remaining white solid had an nmr spectrum in CD_3CN solution identified[13] as that of $Me_2NH_2^+(CF_3)_2PO_2^-$.

Under similar conditions V (0.073 g, 0.25 mmol) and Me_2NH (0.021 g, 0.47 mmol) gave Me_3SiNMe_2 (0.0275 g, 0.235 mmol) and a white solid identified[13] by its nmr spectrum (aqueous solution) as $Me_2NH_2^+(CF_3)_2PSO^-$.

Likewise VI (0.099 g, 0.32 mmol) and Me_2NH (0.042 g, 0.93 mmol) gave excess Me_2NH, Me_3SiNMe_2 (0.033 g, 0.28 mmol), and an oil identified[13] by its nmr spectrum as $Me_2NH_2^+(CF_3)_2PS_2^-$.

(f) **Reaction of Me_3SiNMe_2 with $F_2PS_2^-$ Salts.**—$Na^+F_2PS_2^-$ was made from F_2PS_2H (0.699 g, 5.22 mmol) and sodium methoxide (0.232 g, 4.29 mmol). The volatile products were removed and Me_3SiNMe_2 (0.574 g, 4.91 mmol) was added to the solid residue. Evolution of gas took place slowly at room temperature, and after 2 days the volatile products were fractionated to yield Me_3SiF (0.383 g, 4.16 mmol, 97% based on NaOMe) and $(Me_3Si)_2O$ (0.015 g). The residual solid rapidly decomposed in methanol solution.

$Me_2NH_2^+F_2PS_2^-$, prepared from F_2PS_2H and Me_2NH, similarly reacted with Me_3SiNMe_2 to give Me_3SiF and an oil, the nmr spectrum (in methanol) of which was identical with that produced directly from III and Me_2NH.

Results and Discussion

Preparative Methods.—Esters I, II, IV, and V could all be prepared by the reaction of appropriate phosphoryl derivatives with $(Me_3Si)_2O$ or $(Me_3Si)_2S$ (eq 1).

$$\begin{array}{c} R_2P(O)X + (Me_3Si)_2E \longrightarrow Me_3SiX + R_2P(E)OSiMe_3 \qquad (1) \\ \mathrm{I},\ R = F;\ X = F, Br;^{17}\ E = O \\ \mathrm{II},\ R = F;\ X = F, Cl,^{17} Br;^{17}\ E = S \\ \mathrm{IV},\ R = CF_3;\ X = CF_3, Cl;\ E = O \\ \mathrm{V},\ R = CF_3;\ X = CF_3,^{17} Cl, Br;^{17}\ E = S \end{array}$$

With one exception, the reactions where E = O proceeded smoothly at room temperature. $(CF_3)_3PO$ initially formed the phosphorane[17] $(CF_3)_3P(OSiMe_3)_2$ which decomposed in the expected manner at 100° yielding IV. In contrast, heating to 100° was usually necessary to effect reaction 1 in systems where E = S, and the products (esters II and V) were shown (*vide infra*) to have the "rearranged" thiophosphoryl ester structures. These esters could also be obtained *via* the "reverse" route from the thiophosphoryl derivatives and $(Me_3Si)_2O$ (eq 2),[17] but lower yields were generally obtained even at elevated temperatures.

$$\begin{array}{c} R_2P(S)X + (Me_3Si)_2O \longrightarrow R_2P(S)OSiMe_3 + Me_3SiX \qquad (2) \\ \mathrm{II},\ R = F;\ X = Br \\ \mathrm{V},\ R = CF_3;\ X = Br \end{array}$$

The thiophosphoryl compounds also reacted with $(Me_3Si)_2S$, but the temperatures required for reaction caused concomitant thermal decomposition of the products. Reactions using this preparative route were found in many cases to be more complicated than indicated by eq 1 and 2 and are discussed in more detail elsewhere.[17]

The mixed oxythio esters II and V were also formed from the reaction of $(Me_3Si)_2O$ with the thio acid anhydrides VII (eq 3). These reactions proceeded rapidly

$$\begin{array}{c} \underset{\mathrm{VII}}{R_2P(S)OP(S)R_2} + (Me_3Si)_2O \longrightarrow 2R_2P(S)OSiMe_3 \qquad (3) \\ \mathrm{II},\ R = F \\ \mathrm{V},\ R = CF_3 \end{array}$$

and virtually quantitatively at 80–100° and were found to be the best preparative routes to esters II and V, a result which is not unexpected in view of the likely increase in bond energy arising from the transformation of the P–O–P and Si–O–Si bridges into two P–O–Si bridges.[18]

The dithio esters III and VI were prepared by the rapid reaction of hexamethyldisilazane with the acids $R_2P(S)SH$ (eq 4). This method has been used else-

$$3R_2P(S)EH + (Me_3Si)_2NH \longrightarrow 2R_2P(S)ESiMe_3 + NH_4^+R_2P(S)E^- \qquad (4)$$

where to prepare $(EtO)_2P(S)SSiMe_3$[19] but is less convenient for the synthesis of V from $(CF_3)_2P(S)OH$ because of difficulties[10b] in the manipulation of volatile reagents and products in this case. Ester II could not be made by this route because of the apparent instability[20] of the starting material, $F_2P(S)OH$.

Alternatively esters II and V were synthesized by the reaction (eq 5) of Me_3SiCl in diethyl ether solution

$$R_4N^+X_2PSO^- + Me_3SiCl \longrightarrow X_2P(S)OSiMe_3 + R_4NCl \qquad (5)$$

with amine salts of the acids $R_2P(S)OH$, a technique previously used[3] to prepare ester I from $NH_4^+F_2PO_2^-$. However, yields from these reactions were moderate to low, and difficulties were encountered in the separation of products II and V from diethyl ether.

Structures and Characterization.—Two of the six esters prepared here have been previously described. Our results are in agreement with the infrared and nmr data given for $F_2P(O)OSiMe_3$ (I)[2,4] and $F_2P(S)SSiMe_3$ (III)[5] and, together with data for the other four esters, are summarized in Tables I and II. All esters showed ir bands typical of Me_3Si and F_2P or $(CF_3)_2P$ structural units.

$(CF_3)_2P(O)OSiMe_3$ (IV) had strong bands in its infrared spectrum at 1333 and 501 cm^{-1} which can be assigned to P=O stretching and bending vibrations, respectively (*cf.* I,[2] 1358 and 500 cm^{-1}; $(CF_3)_2P(O)Cl$,[9] 1332, 1327 (PR bands), and 504 cm^{-1}). A band at 1042 cm^{-1} is assigned to the asymmetric P–O–Si stretching vibration (*cf.* 1058 and 1049 cm^{-1} in $(CF_3)_2POSiMe_3$[18]).

$(CF_3)_2P(S)OSiMe_3$ (V) and $(CF_3)_2P(S)SSiMe_3$ (VI) showed medium to strong bands at 735 and 732 cm^{-1} assigned as P=S stretching modes (*cf.* III,[5] 716 cm^{-1}; $(CF_3)_2P(S)SMe$,[15] 732 cm^{-1}; $(CF_3)_2P(S)SH$,[15] 731 cm^{-1}). The former also had a band at 1050 cm^{-1} assigned to the P–O–Si stretching vibration, while the latter had a medium intensity P–S or P–S–Si stretching band at 526 cm^{-1} (*cf.* $(CF_3)_2PSSiMe_3$,[21] 527 cm^{-1}; III,[5] 525 cm^{-1}).

Confirmation of the structure of $F_2P(S)OSiMe_3$ (II) by ir spectroscopy was not so straightforward. This ester exhibited an asymmetric P–O–Si stretching band

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TABLE I

INFRARED SPECTRAL DATA FOR $R_2P(E)E'SiMe_3$ COMPOUNDS[a]

$F_2P(O)$-$OSiM_3$[b]	$F_2P(S)$-$OSiMe_3$	$F_2P(S)$-$SSiMe_3$[c]	$(CF_3)_2P(O)$-$OSiMe_3$	$(CF_3)_2P(S)$-$OSiMe_3$	$(CF_3)_2P(S)$-$SSiMe_3$	Assignment
3000 w	2980 w	2960 w	2973 w	2965 w	2931 w	
2930 w	2920 vw	2900 vw	2914 vw	2910 vw	2906 vw	ν_{CH}
			2850 vw			
			1467 vw			
1430 w	1420 vw	1416 w	1425 vw	1420 vw		δ_{as,CH_3}
1358 vs			1333 s			$\nu_{P=O}$
1270 s	1265 m	1265 m	1266 m	1267 m	1262 m	δ_{Si-CH_3}
			1234 s	1220 s	1203 vs	
			1211 s	1188 vs	1187 vs	ν_{C-F}
			1185 vs	1165 m, sh	1163 vs	
			1135 m	1135 m		
1110 vs	1085 vs		1042 s	1050 s		$\nu_{as,Si-O-P}$
940 vs	930 vs					$\nu_{as,P-F}$
		892 s				
910 vs	910 s					$\nu_{sym,P-F}$
850 vs	860 s	850 s	857 s	855 s	855 s	δ_{HCSi}
765 w	760 m[d]	765 mw		765 w		ν_{Si-C}
			767 wm		772 m	
				790 m		δ_{sym,CF_3}
	760 m[d]	716 vs		735 m	732 s	$\nu_{P=S}$
660 s	635 w	625 mw	720 vw	650 vw	632 w	
			665 vw			
605 s	565 vw		583 m	555 w	572 s	
			566 w, sh			
		525 mw			526 m	ν_{P-S-Si}
500 vs			501 m			$\delta_{P=O}$
485 vs	440 w	425 mw		500 vw	477 m	
		385 m				
		365 m		430 w	429 m	
		340 m				

[a] All values in cm^{-1}. Key: v = very, s = strong, m = medium, w = weak, sh = shoulder, sym = symmetric, as = asymmetric. [b] Taken from ref 2. [c] Taken from ref 5. [d] See text.

TABLE II

NMR SPECTRAL DATA FOR $R_2P(E)E'SiMe_3$ COMPOUNDS

Ester	τ_H	ϕ_F[a]	δ_P[b]	J_{FP}, Hz	Origin
$F_2P(O)OSiMe_3$	9.87	82.8	141.2[c]	984	Ref 2
	9.57	82.4		987	This work
$F_2P(S)OSiMe_3$	9.45	41.3		1115	This work
$F_2P(S)SSiMe_3$	9.4	12.2	24.5[c]	1200	Ref 5
		12.2		1198	This work
$(CF_3)_2P(O)OSiMe_3$	9.47	73.2	143.4	120	This work
$(CF_3)_2P(S)OSiMe_3$	9.48	73.5		116	This work
$(CF_3)_2P(S)SSiMe_3$	9.24	71.6	66.4	105	This work

[a] Ppm from internal $CFCl_3$, positive values indicating resonance to high field of the standard. [b] Ppm from external P_4O_6. [c] Measured *vs.* external H_3PO_4, converted to P_4O_6 as in ref 6.

at 1085 cm^{-1}, and the areas expected to contain the normally strong P═O and P—S stretching and P═O bending bands were completely clear. However, no peak obviously assignable as a P═S stretching vibration was apparent in either the ir or Raman spectrum. The area in which this band would be expected to occur does contain a peak at 760 cm^{-1}, assigned as a H—C—Si bending vibration, which is commonly found in Me_3Si compounds. This peak was somewhat stronger than in the other esters in comparison with the other peaks arising from the Me_3Si unit, and it seems reasonable to assume that it masks (or includes as an unresolvable component) the P═S stretching band. Although P═S stretching bands are sometimes weak in the infrared, they are usually clearly visible as strong Raman bands,[22] and hence it is somewhat surprising that neither spectrum showed this absorption. The ir and nmr spectra were clearly different from those of $F_2POSiMe_3$.[21] Confirmation of the presence of sulfur in the molecule was provided by hydrolysis at 150° in 10% HCl, when H_2S was evolved, by vapor-phase molecular weight determination (found 196, calcd 190), and by the mass spectrum, which showed a parent ion peak at 189.9840 amu (calcd for $F_2P(S)OSiMe_3$, 189.9847 amu). Thus the oxythio esters II and V have both been assigned the thiophosphoryl rather than the phosphoryl structure. The significance of this result is discussed in more detail elsewhere.[17]

All the nmr spectra (Table II) were in good agreement with the proposed structures. The trimethylsilyl protons appeared as a singlet in each case, with chemical shifts in the range τ 9.2–9.6 ppm. The ^{19}F spectra of the difluoro esters were doublets ($^1J_{FP}$ = 987–1198 Hz) and both chemical shift and coupling constant values formed series dependent on the degree of substitution of oxygen by sulfur, chemical shifts decreasing and coupling constants increasing on replacement of O by S. The bis(trifluoromethyl) esters also showed doublets ($^2J_{PF}$ = 105–120 Hz) in their ^{19}F nmr spectra, and the seven-line patterns in the ^{31}P spectra possessed intensity distributions expected for the coupling of six equivalent fluorine atoms to phosphorus.

Chemical Properties.—The esters containing the P–O–Si bridge unit were considerably more thermally stable than those containing the P–S–Si bridge. Compounds IV and V were recovered unchanged after heating to 200° for prolonged periods while II had decomposed approximately to the extent of 10% after 8 days at 225°, the only identified decomposition product being Me_3SiF. About 40% decomposition of I had occurred after 5 days at 200°, the decomposition being best represented by eq 6 and 7.

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(22) J. R. Durig and J. W. Clark, *J. Chem. Phys.*, **46**, 3057 (1967).

$$3F_2P(O)OSiMe_3 \longrightarrow 3Me_3SiF + \frac{3}{n}(FPO_2)_n \qquad (6)$$

$$\frac{3}{n}(FPO_2)_n \longrightarrow OPF_3 + P_2O_5 \qquad (7)$$

Kreshkov, *et al.*,[3] found that $F_2P(O)OSiEt_3$ decomposed by a similar route under unspecified conditions and identified Et_3SiF and P_2O_5 as products. In this case all three decomposition products were identified. The proposed "FPO_2" intermediate has been suggested as a polymeric product of the oxidation of PF_3[23] and of the fluorination of P_4O_{10}.[24]

Ester III was reported to decompose slowly at room temperature by McKennon and Lustig,[5] who observed vapor pressures of 21.8 (28.5°), 28.8 (33.4°), and 38.9 mm (39.8°) for this ester. Our samples showed vapor pressures of less than 1 mm at 27° when freshly prepared, although pressures rose considerably on standing owing to the formation of the volatile product Me_3SiF. Decomposition was rapid at 110°, forming Me_3SiF. The other products were P_4S_{10}, identified by ir spectroscopy, melting point, and microanalysis, and an oil of low volatility, the nature of which was indicated by its infrared, ^{19}F nmr, and mass spectra to be one or more polymeric species containing F, P, and S. In particular, the mass spectrum of the polymeric product showed ions assignable as $F_2PS_2H^+$, $P_nS_{2n-1}F_{n+2}{}^+$ ($n = 1, 2$), and fragments containing S_m ($m = 1$–8), F and S only, and P and S only (including a strong peak at m/e 254 assigned as $P_2S_6{}^+$).

High molecular weight polymeric ions of the types $P_nO_{2n-1}F_{n+2}{}^+$ ($n = 2$–10) have been observed[24] in the mass spectrum of the proposed intermediate polymers $(FPO_2)_n$ formed in the P_4O_{10}–F_2 reaction. Hence it can be suggested that the decomposition of III initially proceeds in an analogous manner to eq 6, forming Me_3SiF and $(FPS_2)_n$. This polymer then decomposes not by formation of SPF_3, by analogy with eq 7, but gives instead P_4S_{10} and a second polymer, the oil mentioned above, which may be a sulfur analog(s) of one or more of the products observed in the fluorination of P_4O_{10}.

Finally, ester VI also decomposed quite rapidly above 100°, the major volatile product again being Me_3SiF. Significant amounts of $(CF_3)_2PSP(CF_3)_2$[16] and $(CF_3)_2P(S)SP(CF_3)_2$[10a] were also formed, while the residue contained both P_4S_{10} and elemental sulfur. The existence of several other compounds in small quantities was indicated by nmr spectroscopy, some of them presumably arising from the fragment $CF_3P(CF_2)S_2$ (eq 8), which may undergo subsequent polymerization or reaction.

$$(CF_3)_2P(S)SSiMe_3 \longrightarrow Me_3SiF + [CF_3P(CF_2)S_2] \qquad (8)$$

The two silylthio esters, III and VI, reacted smoothly and quantitatively with anhydrous hydrogen chloride at room temperature, forming Me_3SiCl and the acids F_2PS_2H and $(CF_3)_2PS_2H$ (eq 9). In contrast, the

$$R_2P(S)SSiMe_3 + HCl \longrightarrow R_2P(S)SH + Me_3SiCl \qquad (9)$$

siloxy esters I, II, IV, and V all reacted very slowly with excess HCl even at 110°. As well as a little Me_3SiCl, traces of Me_3SiF were produced either by attack of HCl on the P–F or C–F bonds or by HCl-catalyzed thermal decomposition.

The three bis(trifluoromethyl) esters IV, V, and VI all reacted readily with excess dimethylamine, producing Me_3SiNMe_2 and white solids identified by nmr spectroscopy as the dimethylammonium salts $Me_2NH_2{}^+(CF_3)_2PEE'^-$

$$(CF_3)_2P(E)E'SiMe_3 + 2Me_2NH \longrightarrow Me_3SiNMe_2 + Me_2NH_2{}^+(CF_3)_2PEE'^- \qquad (10)$$

In contrast, when the difluoro esters I, II, and III were treated with dimethylamine, white solids which were formed immediately subsequently converted on standing into colorless involatile oils. The only volatile product was Me_3SiF, produced in almost theoretical yield in each case. The oils showed some tendency to decompose in solution, but the ^1H and ^{19}F spectra obtained (Table III) showed them to be the salts $Me_2NH_2{}^+F(Me_2N)PEE'^-$ (eq 11).

$$F_2P(E)E'SiMe_3 + 2Me_2NH \longrightarrow Me_3SiF + Me_2NH_2{}^+F(Me_2N)PEE'^- \qquad (11)$$

Typical spectra for $Me_2NH_2{}^+F(Me_2N)PO_2{}^-$ (VIII)

TABLE III

NMR SPECTRA[a] OF THE SALTS $Me_2NH_2{}^+F(Me_2N)P(E)E'^-$

	E = E′ = O (VIII)	E = S, E′ = O	E = E′ = S
$\tau_{Me_2NH_2{}^+}$	7.41 (s)	7.33 (s)	7.05 (s)
τ_{Me_2N}	7.40 (dd)	7.33 (dd)	7.05 (dd)
ϕ_F[b]	78.4 (ds)	38.9 (ds)	19.2 (ds)
$^3J_{HP}$, Hz	10.75	12.6	14.3
$^4J_{HF}$, Hz	1.25	1.5	1.6
$^1J_{FP}$, Hz	925	1024	1063

[a] All spectra run using 10–30% solutions in dry methanol; s = singlet, ds = doublet of septets, dd = doublet of doublets.

[b] Ppm from external $CFCl_3$.

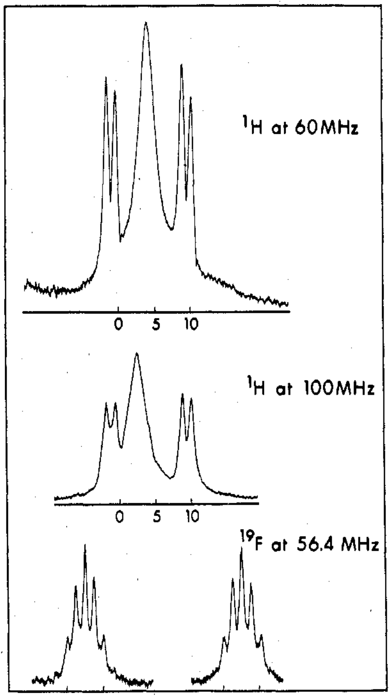

Figure 1.—Nmr spectra of $Me_2NH_2{}^+F(Me_2N)PO_2{}^-$ obtained using 20% solutions in dry methanol. Scale units are in hertz. Chemical shifts and coupling constant values are given in Table III.

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(23) U. Wannagat and J. Rademachers, *Z. Anorg. Allg. Chem.*, **289**, 66 (1957).

(24) D. W. Muenow, O. M. Uy, and J. L. Margrave, *J. Inorg. Nucl. Chem.*, **31**, 3411 (1969).

are shown in Figure 1, the thio and dithio derivatives being very similar. All chemical shifts and coupling constants show regular variations along the series, coupling constants increasing and chemical shifts decreasing as oxygen is replaced by sulfur. The ^{19}F spectrum of VIII is a doublet of septets ($^1J_{FP} = 925$, $^4J_{FH} = 1.25$ Hz) and the ^1H spectrum a doublet of doublets ($^3J_{HP} = 10.75$, $^4J_{HF} = 1.25$ Hz) surrounding a central peak caused by the methyl groups in the cation. This central peak was shown to be independent of the outer doublet of doublets by a comparison of the 60- and 100-MHz spectra (Figure 1).

It appears that the white solids first formed in these reactions may be the $Me_2NH_2^+F_2PEE'^-$ salts as in eq 10, but further reaction then takes place by attack of the other product, Me_3SiNMe_2, on P–F bonds in the anions $F_2PEE'^-$. This was confirmed in one case (E = E′ = S) by allowing Me_3SiNMe_2 to react with the sodium and dimethylammonium salts of difluorodithiophosphinic acid. Me_3SiF was produced quantitatively, and the oil formed by reaction of the dimethylammonium salt had ^1H and ^{19}F nmr spectra identical with those of $Me_2NH_2^+F(Me_2N)PS_2^-$ produced directly from $F_2P(S)SSiMe_3$ and dimethylamine.

Biermann and Glemser[4] reported that $F_2P(O)OSiMe_3$ (I) reacted with Me_2NH or Et_2NH to form Me_3SiNMe_2 (60%) or Me_3SiNEt_2 (75%) and the dialkylammonium salts of difluorophosphinic acid, whereas our results indicate further reaction of Me_3SiNMe_2 with the anion of this acid and its thio and dithio analogs. The possible reasons for this variance are twofold. First, our experiments were conducted in sealed tubes *in vacuo*, in the absence of solvent, whereas Biermann and Glemser[4] carried out the reactions in diethyl ether solution. Second, these workers used reaction times of only 12 hr, whereas several days were needed for the anion reactions to proceed to completion at room temperature.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Trimethylsilyl Esters of Phosphorus Acids. II.[1] Reactions of Fluoro- and Trifluoromethylphosphorus(V) Oxides and Sulfides with Hexamethyldisiloxane and Hexamethyldisilthiane and the Synthesis of a Novel Phosphorane

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The reactions of the phosphoryl and thiophosphoryl compounds $R_2P(E)X$ (R = F, CF_3; E = O, S; X = F, Cl, Br, CF_3) with hexamethyldisiloxane and hexamethyldisilthiane ($(Me_3Si)_2E'$, E′ = O, S) have been investigated. The esters $R_2P(E)E'SiMe_3$ or $R_2P(E')ESiMe_3$ are generally formed, the yield obtained and ease of reaction being reduced when S replaces O in either starting reactant. Evidence indicates that the reactions proceed *via* intermediates having pentacoordinate phosphorus atoms, and one such phosphorane intermediate, $(CF_3)_3P(OSiMe_3)_2$, has been isolated and characterized. This new phosphorane, the first to be directly synthesized from a phosphine oxide, exhibits temperature-dependent ^{19}F and ^1H nmr spectral behavior which can be partially interpreted in terms of a fluxional trigonal-bipyramidal model. Nmr and new infrared data are also reported for $(CF_3)_2P(O)Br$.

Introduction

Hexaalkyldisiloxanes have been found[2] to react with phosphoryl compounds by scission of a Si–O bond, with formation of trialkylsilyl esters of phosphorus(V) oxyacids. Examples of this procedure include the syntheses of trimethylsilyl dichlorophosphinate,[3] $Cl_2P(O)OSiMe_3$, and its difluoro analog,[4] $F_2P(O)OSiMe_3$ (I), by the reaction of $(Me_3Si)_2O$ with either Cl_3PO or F_3PO. We now describe the results of an investigation into the general course of this type of reaction and the effect of replacement of oxygen by sulfur in either or both of the reactants. The products, esters I–VI, were also obtained by several other methods; details of these methods and the physical and chemical properties of the esters are given elsewhere.[1]

$F_2P(E)E'SiMe_3$	$(CF_3)_2P(E)E'SiMe_3$
I, E = E′ = O	IV, E = E′ = O
II, E = S; E′ = O	V, E = S; E′ = O
III, E = E′ = S	VI, E = E′ = S

In one case studied,[5] the reaction proceeded differently at room temperature. The reaction of $(CF_3)_3PO$ with $(Me_3Si)_2O$ afforded the phosphorane VII, which decomposed to ester IV at 100°.

$(CF_3)_3P(OSiMe_3)_2$
VII

Experimental Section

The reactions were carried out in evacuated sealed tubes in the absence of solvent, and starting materials were used in 0.25–5-mmol quantities and approximately 1:1 molar ratios. Experimental details are outlined in Tables I and II. Products were separated and purified where possible by fractional condensation *in vacuo*. In cases where separation could not be achieved, the compositions of the mixtures were determined by analyses of the nmr spectra. A combination of infrared, nmr, and mass spectroscopy and vapor-phase molecular weight determinations was used for the routine identification of the

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(1) For part I see R. G. Cavell, R. D. Leary, and A. J. Tomlinson, *Inorg. Chem.*, **11**, 2573 (1972).

(2) E. A. Chernyshev and E. F. Bugerenko, *Organometal. Chem. Rev., Sect. A*, **3**, 469 (1968).

(3) M. Schmidt, H. Schmidbaur, and A. Binger, *Chem. Ber.*, **93**, 872 (1960).

(4) U. Biermann and O. Glemser, *ibid.*, **102**, 3342 (1969).

(5) For a preliminary communication, see R. G. Cavell and R. D. Leary, *Chem. Commun.*, 1520 (1970).