

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 ($^1J_{\text{FP}} = 925$, $^4J_{\text{FH}} = 1.25$ Hz) and the ^1H spectrum a doublet of doublets ($^3J_{\text{HP}} = 10.75$, $^4J_{\text{HF}} = 1.25$ 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 $\text{Me}_2\text{NH}_2^+\text{F}_2\text{PEE}'^-$ salts as in eq 10, but further reaction then takes place by attack of the other product, $\text{Me}_3\text{SiNMe}_2$, on P-F bonds in the anions $\text{F}_2\text{PEE}'^-$. This was confirmed in one case ($\text{E} = \text{E}' = \text{S}$) by allowing $\text{Me}_3\text{SiNMe}_2$ to react with the sodium and dimethylammonium salts of difluorodithiophosphinic acid. Me_3SiF was produced quantitatively, and the oil formed by reaction of the di-

methylammonium salt had ^1H and ^{19}F nmr spectra identical with those of $\text{Me}_2\text{NH}_2^+\text{F}(\text{Me}_2\text{N})\text{PS}_2^-$ produced directly from $\text{F}_2\text{P}(\text{S})\text{SSiMe}_3$ and dimethylamine.

Biermann and Glemser⁴ reported that $\text{F}_2\text{P}(\text{O})\text{OSiMe}_3$ (I) reacted with Me_2NH or Et_2NH to form $\text{Me}_3\text{SiNMe}_2$ (60%) or $\text{Me}_3\text{SiNEt}_2$ (75%) and the dialkylammonium salts of difluorophosphinic acid, whereas our results indicate further reaction of $\text{Me}_3\text{SiNMe}_2$ 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 Glemser⁴ 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

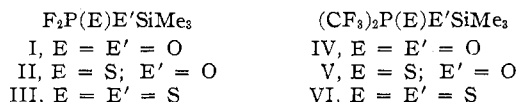
By R. G. CAVELL,* R. D. LEARY, AND A. J. TOMLINSON

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The reactions of the phosphoryl and thiophosphoryl compounds $\text{R}_2\text{P}(\text{E})\text{X}$ ($\text{R} = \text{F}, \text{CF}_3$; $\text{E} = \text{O}, \text{S}$; $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{CF}_3$) with hexamethyldisiloxane and hexamethyldisilthiane ($(\text{Me}_3\text{Si})_2\text{E}'$, $\text{E}' = \text{O}, \text{S}$) have been investigated. The esters $\text{R}_2\text{P}(\text{E})\text{E}'\text{SiMe}_3$ or $\text{R}_2\text{P}(\text{E}')\text{ESiMe}_3$ 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, $(\text{CF}_3)_3\text{P}(\text{OSiMe}_3)_2$, 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 $(\text{CF}_3)_2\text{P}(\text{O})\text{Br}$.

Introduction

Hexaalkyldisiloxanes have been found² 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 $\text{Cl}_2\text{P}(\text{O})\text{OSiMe}_3$, and its difluoro analog,⁴ $\text{F}_2\text{P}(\text{O})\text{OSiMe}_3$ (I), by the reaction of $(\text{Me}_3\text{Si})_2\text{O}$ 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



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

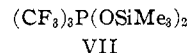
(2) E. A. Chernyshev and E. F. Bugerenko, *Organometal. Chem. Rev., Sect. A*, **3**, 469 (1968).

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

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

also obtained by several other methods; details of these methods and the physical and chemical properties of the esters are given elsewhere.¹

In one case studied,⁵ the reaction proceeded differently at room temperature. The reaction of $(\text{CF}_3)_3\text{PO}$ with $(\text{Me}_3\text{Si})_2\text{O}$ afforded the phosphorane VII, which decomposed to ester IV at 100°.



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

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

TABLE I
 REACTIONS OF PHOSPHORYL AND THIOPHOSPHORYL COMPOUNDS WITH (Me₃Si)₂O

Conditions, deg (days)	Starting reactant, mmol	Amt of (Me ₃ Si) ₂ O, mmol	Ester or other product, mmol (%)	Me ₃ SiX, mmol (%)	Recovered reactant, mmol (%)
25 (10) ^a	F ₃ PO, 4.32	4.32	F ₂ P(O)OSiMe ₃ , 4.18 (97)	Me ₃ SiF ^a	
25 (15)	F ₂ P(O)Br, 1.60	1.34	F ₂ P(O)OSiMe ₃ , ^b 1.27 (95)	Me ₃ SiBr ^a	
25 (22)	(CF ₃) ₂ PO, 2.06	1.81	(CF ₃) ₂ P(OSiMe ₃) ₂ , 1.73 (96)		(Me ₃ Si) ₂ O, 0.08 (4)
25 (13) ^a	(CF ₃) ₂ P(O)Cl, 1.52	1.53	(CF ₃) ₂ P(O)OSiMe ₃ , 1.40 (92)	Me ₃ SiCl, 1.46 (96)	
150 (2)	F ₃ PS, 0.98	1.01			F ₃ PS, 0.97 (99)
150 (3)	F ₂ P(S)Cl, 1.61	1.60			F ₂ P(S)Cl, ^b 1.42 (88)
160 (12)	F ₂ P(S)Br, 0.25	0.25	F ₂ P(S)OSiMe ₃ , ^b 0.12 (48)	Me ₃ SiBr ^a	F ₂ P(S)Br, ^b 0.06 (24)
150 (1)	(CF ₃) ₃ PS, 1.54	1.84			(CF ₃) ₃ PS, 1.54 (100)
160 (30)	(CF ₃) ₂ P(S)Cl, 0.47	0.46			(CF ₃) ₂ P(S)Cl ^a
160 (6)	(CF ₃) ₂ P(S)Br, 0.29	0.27	(CF ₃) ₂ P(S)OSiMe ₃ , 0.015 (6)	Me ₃ SiBr ^a	(CF ₃) ₂ P(S)Br, 0.275 (94)

^a Quantity not measured. ^b Quantity estimated from nmr spectrum of mixture. ^c Reaction details described in part I of this series (ref 1).

pentavalent ester (R₂P(E)E'SiMe₃, R = F, CF₃; E and E' = O or S) products, the complete characterization of which is given in more detail elsewhere.¹ Because of the close similarity of the ¹H nmr spectra, it was not always possible (Tables I and II) to measure the relative amounts of Me₃SiX compounds present in mixtures, but determination of the fluoro- or trifluoromethylphosphorus compounds was achieved in all cases using the ¹⁹F nmr spectra.

Mass spectra were recorded on an AEI MS-9 spectrometer, infrared spectra on Perkin-Elmer 337 and 457 instruments, and nmr spectra on Varian A56/60 and HA 100 instruments. The latter were recorded using 10–20% solutions in CFCl₃ (liquids) and H₂O or CD₃CN as solvents for ionic products. ¹H chemical shifts were measured relative to external TMS, ¹⁹F shifts relative to internal or external CFCl₃, and ³¹P shifts relative to external P₄O₆.

Commercial samples of (Me₃Si)₂O, Me₂NH, HCl, and F₃PO were vacuum fractionated and used without further purification. Literature methods were employed to synthesize (CF₃)₃PO,^{6a} (CF₃)₂P(O)Cl,^{6a} (CF₃)₃PS,^{6b} (CF₃)₂P(S)Cl,⁷ (CF₃)₂P(S)Br,⁷ F₂P(O)Cl,⁸ F₂P(O)Br,⁸ F₃PS,⁸ F₂P(S)Cl,⁹ and F₂P(S)Br.⁹ (Me₃Si)₂S was prepared¹⁰ from Me₃SiCl and sodium sulfide and freed from (Me₃Si)₂O by fractional condensation at –15° *in vacuo*.

(CF₃)₂P(O)Br was prepared from the reaction of (CF₃)₂P(O)NMe₂ with 2 mol of HBr and analyzed by alkaline hydrolysis (0.241 mmol yielded 0.252 mmol of CF₃H and the ion CF₃PO₃²⁻, identified¹¹ by nmr spectroscopy, in solution). (CF₃)₂P(O)Br showed a doublet (²J_{FP} = 125 Hz) in its ¹⁹F nmr spectrum at +70.7 ppm relative to CFCl₃, and the mass spectrum showed a parent ion peak at 263.8773 amu (calcd for (CF₃)₂P(O)⁷⁹Br, 263.8774). The infrared spectrum (Table III) showed some variations from that recorded by Griffiths and Burg,¹² who prepared their sample from (CF₃)₂P(O)-*t*-Bu. Notably, the C–F stretching region contained a very strong doublet at 1200 and 1188 cm⁻¹, whereas these peaks were much more widely spaced (1202 vs, 1162 s) in the previous report,¹² which also lists three other weak or medium intensity peaks (1250 w, 1047 w, 753 m) not present in our spectrum.

Tris(trifluoromethyl)bis(trimethylsiloxy)phosphorane (VII). (a) Preparation and Characterization.—Tris(trifluoromethyl)phosphine oxide^{6a} (0.525 g, 2.06 mmol) and hexamethyldisiloxane (0.292 g, 1.81 mmol) were allowed to react at room temperature for 22 days. The volatile products were transferred to a micro-reflux column,¹³ and the more volatile constituents (0.084 g, of a mixture of (CF₃)₃PO, (CF₃)₃P, and (Me₃Si)₂O) were removed *in vacuo* with the jacket maintained at –10 to –15°. The least volatile fraction obtained was VII (0.719 g, 1.73 mmol, 96%) containing a little (Me₃Si)₂O (0.013 g, 0.08 mmol, estimated from the nmr spectrum). Pure VII, which decomposes very slowly at room temperature, was obtained by redistillation.

Nmr spectrum (room temperature): ¹H τ 9.52, singlet; ¹⁹F 69.7 ppm, doublet (¹J_{FP} = 108.5 Hz); ³¹P 205.0 ppm, decet (²J_{FP} = 108 Hz). Infrared spectrum (cm⁻¹): 2967 m, 2902 w (ν_{C–H}), 1264 m (δ_{Si–CH₃}), 1208 s, 1185 vs, 1168 m, sh, 1120 s (ν_{C–F}), 1070 m (ν_{as, Si–O–P}), 1011 w, 853 s, 764 w (δ_{HCSi, ν_{Si–C}}), 599 s, 588 w. Partial mass spectrum: *m/e* 351.0223 (calcd 351.0236 for (CF₃)₂PF(OSiMe₃)(OSiMe₂)); *m/e* 347.0481 (calcd 347.0487 for (CF₃)₂P(OSiMe₃)₂).

(b) Neutral Hydrolysis.—The phosphorane VII (0.126 g, 0.30 mmol) was allowed to react with 1 ml of degassed H₂O for 1 day at room temperature. Vacuum fractionation of the volatile products gave CF₃H (0.021 g, 0.30 mmol), trapped at –196°, and (Me₃Si)₂O (0.052 g, 0.31 mmol), trapped at –84°, while the resulting solution was shown by nmr spectroscopy to contain the (CF₃)₂PO₃²⁻ ion.¹¹

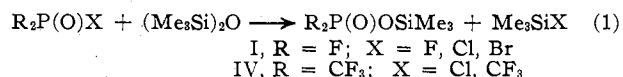
(c) Alkaline Hydrolysis.—Reaction of VII (0.106 g, 0.25 mmol) with excess degassed aqueous 10% NaOH solution for 7 days at room temperature gave as volatile products CF₃H (0.034 g, 0.49 mmol) and (Me₃Si)₂O and the solution contained the CF₃PO₃²⁻ ion.¹¹

(d) Reaction with Dimethylamine.—The phosphorane VII (0.137 g, 0.33 mmol) was allowed to react with Me₂NH (0.060 g, 1.33 mmol) for 7 days at room temperature. The volatile products were fractionated, giving CF₃H (0.024 g, 0.34 mmol), unreacted Me₂NH (0.014 g, 0.31 mmol), and Me₃SiNMe₂ (0.076 g, 0.65 mmol) while the remaining white solid was identified¹¹ as Me₂NH₂⁺(CF₃)₂PO₃²⁻.

(e) Thermal Decomposition.—The phosphorane VII (0.121 g, 0.29 mmol) was heated to 100° for 4.5 days in an evacuated sealed tube. Vacuum fractionation then gave complex mixtures of products, shown by ir and nmr spectroscopy to contain residual VII, (CF₃)₂P(O)OSiMe₃ (IV), (CF₃)₃PO, (CF₃)₃P, (Me₃Si)₂O, Me₃SiF, COF₂, and at least two additional unidentified compounds.

Results and Discussion

Reactions of Phosphoryl Compounds with Hexamethyldisiloxane.—Biermann and Glemser⁴ prepared trimethylsilyl difluorophosphinate, F₂P(O)OSiMe₃ (I), in 40–80% yield by treating hexamethyldisiloxane with either F₃PO or F₂P(O)Cl under pressure at 90–110°.



We find that I can be prepared in better than 95% yield from reaction of (Me₃Si)₂O with either F₃PO or F₂P(O)Br at room temperature in sealed glass tubes. Similarly (CF₃)₂P(O)Cl reacted with (Me₃Si)₂O at room temperature giving (CF₃)₂P(O)OSiMe₃ (IV) in 92% yield. Detailed results of these reactions are given in Table I.

Synthesis and Characterization of the Phosphorane (CF₃)₃P[OSi(CH₃)₃]₂.—In contrast to the general reaction (eq 1) described above, (CF₃)₃PO reacted with

- (6) (a) A. B. Burg and A. J. Sarkis, *J. Amer. Chem. Soc.*, **87**, 238 (1965); (b) R. G. Cavell and H. J. Emelús, *J. Chem. Soc.*, 5896 (1964).
(7) (a) R. C. Dobbie, L. F. Doty, and R. G. Cavell, *J. Amer. Chem. Soc.*, **90**, 2015 (1968); (b) K. Gosling and A. B. Burg, *ibid.*, **90**, 2011 (1968).
(8) R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 31 (1965).
(9) R. G. Cavell, *Can. J. Chem.*, **46**, 613 (1968).
(10) E. W. Abel, *J. Chem. Soc.*, 4933 (1961).
(11) A. A. Pinkerton and R. G. Cavell, *Inorg. Chem.*, **10**, 2720 (1971).
(12) J. E. Griffiths and A. B. Burg, *J. Amer. Chem. Soc.*, **84**, 3442 (1962).
(13) J. R. Spielman and A. B. Burg, *Inorg. Chem.*, **2**, 1140 (1963).

TABLE II
 REACTIONS OF PHOSPHORYL AND THIOPHOSPHORYL COMPOUNDS WITH (Me₃Si)₃S

Conditions, deg (days)	Starting reactant, mmol	Amt of (Me ₃ Si) ₃ S, mmol	Ester, ^a mmol (%)	Me ₃ SiF, ^a mmol (%)	Recovered reactant ^a mmol (%)	Other products, ^a mmol (%)
110 (19) ^e	F ₃ PO, 1.52	1.23	F ₂ P(S)OSiMe ₃ , 0.74 (60)	Me ₃ SiF, 1.29 (105)	F ₃ PO, 0.26 (17)	F ₃ PS, 0.42 (34)
110 (6)	F ₂ P(O)Cl, 1.07	1.00	F ₂ P(S)OSiMe ₃ , 0.22 (22)	Me ₃ SiCl, 0.35 (35)	F ₂ P(O)Cl, 0.75 (70)	F ₂ P(S)Cl, trace
25 (13)	F ₂ P(O)Br, 0.91	0.97	F ₂ P(S)OSiMe ₃ , 0.78 (86)	Me ₃ SiBr, 0.88 (97)	F ₂ P(O)Br, 0.05 (5)	F ₂ P(S)Br, 0.05 (5)
110 (15)	(CF ₃) ₂ PO, 1.41	1.52	(CF ₃) ₂ P(S)OSiMe ₃ , 0.28 (20)	Me ₃ SiF, 0.44 (31)	(Me ₃ Si) ₃ S, 0.42 (29)	(CF ₃) ₂ P(O)OSiMe ₃ , 0.44 (31)
110 (9)	(CF ₃) ₂ P(O)Cl, 2.10	2.14	(CF ₃) ₂ P(S)OSiMe ₃ , 0.80 (38)	Me ₃ SiCl ^c , 0.80 (38)	(CF ₃) ₂ P(O)Cl, 0.32 (15)	(CF ₃) ₂ P(S)Cl, 0.34 (16)
25 (12)	(CF ₃) ₂ P(O)Br, 1.17	0.86	(CF ₃) ₂ P(S)OSiMe ₃ , 0.43 (50)	Me ₃ SiBr, 0.76 (88)	(CF ₃) ₂ P(O)Br, 0.14 (12)	(CF ₃) ₂ P(S)Br, 0.08 (9)
110 (2)	F ₃ PS, 2.48	2.22		Me ₃ SiBr, ^d 0.55 (104)	F ₃ PS, 2.38 (96)	Me ₃ SiF, ^d 0.97 (91)
110 (15)	F ₂ P(S)Br, 1.13	0.80		Me ₃ SiBr, ^e 0.17 (68)	F ₂ P(S)Br, ^d 0.59 (99)	(CF ₃) ₂ P(S)Br, ^d 0.08 (9)
150 (1.5)	(CF ₃) ₂ PS, 0.89	0.84			(CF ₃) ₂ PS, 0.82 (92)	
150 (6)	(CF ₃) ₂ P(S)Br, 0.25	0.26			(CF ₃) ₂ P(S)Br, ^d 0.17 (68)	

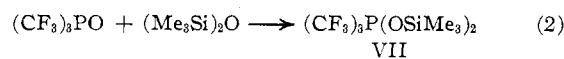
^a All quantities estimated from nmr spectrum of mixture. ^b Unidentified compound (singlet in ¹⁹F nmr at ϕ 68.2 ppm vs. CCl₃F), probably arising from decomposition of Me₃SiCF₃. Moles calculated assuming one CF₂ group per mole. ^c Quantity not measured. ^d Percentages based on eq 14 in text. ^e Reaction details described in part I of this series (ref 1).

 TABLE III
 INFRARED SPECTRA OF (CF₃)₂P(O)Br^a

This work	Ref 12	Assignment	
1320 s	1312 s	$\nu_{P=O}$	
	1250 w	C	
1200 vs	1202 vs	}	
1188 vs	1162 s		ν_{C-F}
	1047 w (?)	}	
785 vw	753 m		δ_{sym,CF_3}
580 m	ni		δ_{as,CF_3}
		OR	
558 mw	ni	ν_{P-Br}	
502 m	ni	$\delta_{P=O}$	

^a All values in cm⁻¹. Key: c = combination or overtone, sym = symmetric, as = asymmetric, ni = not investigated.

[(CH₃)₃Si]₂O at room temperature to form the phosphorane (CF₃)₃P[OSi(CH₃)₃]₂ (VII) according to eq 2 and only at 100° did this addition compound decom-



pose (*vide infra*) to yield IV and several other products.

The phosphorane VII, which decomposes very slowly at room temperature, was isolated in 96% yield from the reaction at room temperature and is a liquid of low volatility. Its infrared spectrum shows, in addition to bands typical of Me₃Si and (CF₃)₃P groupings, a band at 1070 cm⁻¹ assigned to the asymmetric stretching mode of the P-O-Si bridge unit. Also, the spectrum in both liquid and vapor phases is completely clear in the 1300-1500-cm⁻¹ region, in which peaks arising from P=O stretching vibrations are normally found, indicating the absence of such a group in the molecule. The mass spectrum showed no parent ion peak, a result which is typical of pentacoordinate phosphorus(V) compounds,¹⁴ but strong peaks at 351 and 347 amu were identified by mass measurement as arising from the ions (CF₃)₂PF(OSiMe₃)(OSiMe₂)⁺ and (CF₃)₂P(OSiMe₃)₂⁺ produced by loss of the fragments of CF₂CH₃ and CF₃, respectively, from the parent phosphorane.

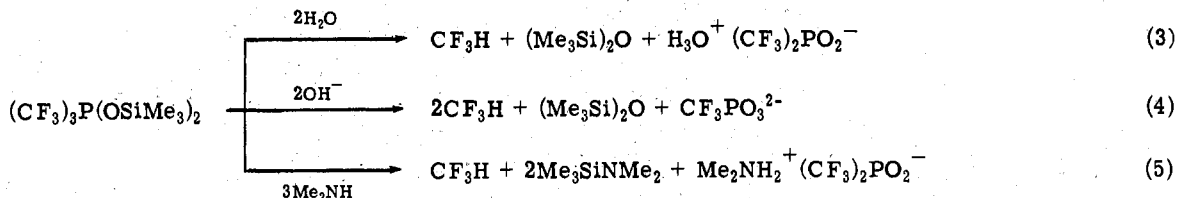
Chemical confirmation of the phosphorane structure VII was achieved by hydrolysis under neutral and alkaline conditions and by reaction with dimethylamine. A satisfactory mass balance was obtained in each case, and all products were identified by either ir or nmr spectroscopy. Neutral hydrolysis (eq 3) gave 1 mol each of fluoroform and (Me₃Si)₂O, and the (CF₃)₂PO₃⁻ ion in solution, while alkaline hydrolysis (eq 4) gave 2 mol of fluoroform, 1 mol of (Me₃Si)₂O, and the CF₃PO₃²⁻ ion in solution. Dimethylamine reacted with VII at room temperature in a 3:1 molar ratio according to eq 5.

The phosphorane underwent thermal decomposition at 100° to yield at least eight products, of which six could be unambiguously identified. (CF₃)₃PO and (Me₃Si)₂O presumably arise by thermal reversal of reaction 2, indicating that this may be an equilibrium process. (CF₃)₂P(O)OSiMe₃ (IV) could be formed *via* reaction 6 (*cf.* eq 1), and this ester was in fact produced when (CF₃)₃PO and (Me₃Si)₂O were allowed to react directly at 100°. The other expected product of this reaction, Me₃SiCF₃, has not been reported. It would be expected to be unstable under these conditions and,

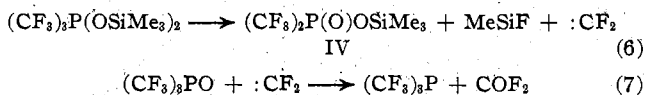
TABLE IV
 NMR SPECTRA OF $(\text{CF}_3)_3\text{P}(\text{OSiMe}_3)_2$ (VII) FROM 40 TO -140°C

Temp, °C	τ_{H}	δ_{P}	δ_{F} (eq)	δ_{F} (ax)	${}^2J_{\text{FP}}$	${}^2J_{\text{FP}}$ (eq)	${}^2J_{\text{FP}}$ (ax)	${}^4J_{\text{FP}}$
40	9.52	69.7	205.0		108.5			
0	9.52							
-40	9.52			63.8 ^b	72.9 ^b	113	103	
-70	9.52			63.8 ^c	<i>h</i>	115		13.5
-100	9.52			63.6 ^e	<i>d</i>	115		13.5
-120	9.52			63.6 ^e	66.5-74.7 ^f	115		
-140	9.52			63.6 ^e	66.5-74.7 ^f	115		16.5 (q) 7.0 (t)

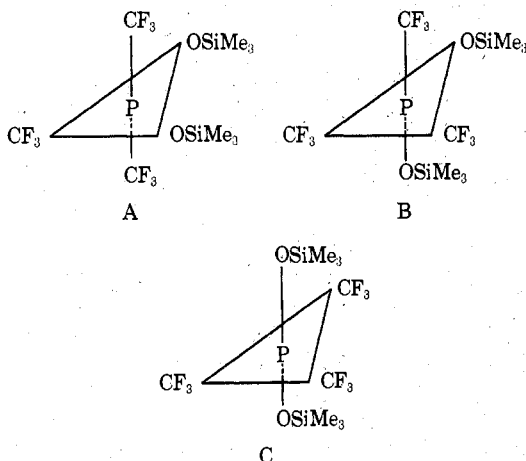
^a Chemical shifts in ppm from CFCl_3 or P_4O_{10} , coupling constants in Hz. ^b Broad. ^c Doublet of septets. ^d Broad multiplets appearing. ^e Further fine structure appearing. ^f Nine complex multiplets in this region. ^g Doublet of quintuplets of triplets. ^h Signals broadened and collapsed.



like Me_3SnCF_3 ,¹⁵ would probably decompose to Me_3SiF (an observed product) by elimination of difluorocarbene. The latter could then react further with $(\text{CF}_3)_3\text{PO}$ to yield the other identified products, $(\text{CF}_3)_3\text{P}$ and COF_2 (eq 7).



Structure of the Phosphorane.—Further information on the structure of the phosphorane is provided by the behavior of its nmr spectra at various temperatures (Table IV). Considering only the trigonal-bipyramidal framework (which is the most likely five-coordinate structure for this molecule¹⁶), it is apparent that there are three possible configurations A, B, and C. The room-temperature ¹H nmr spectrum shows a



moderately broad singlet at τ 9.52 ppm indicating that the OSiMe_3 groups do not show observable proton coupling to phosphorus. The ¹⁹F spectrum consists of a doublet (${}^2J_{\text{FP}} = 108.5$ Hz) and the ³¹P spectrum an octet of intensity distribution in agreement with that expected for the central eight lines of a ten-line pattern

arising from coupling of phosphorus to nine equivalent fluorine atoms. All observed peaks are distinctly separated from those of the starting materials with the most definitive evidence for the phosphorane structure being provided by the very high ³¹P chemical shift value.¹⁷ These observations are consistent with equivalence of the three CF_3 groups and of the two OSiMe_3 groups at room temperature, probably due to a "pseudorotation" type of process.

Several interesting features appear in the spectra on cooling (Figure 1). The doublet pattern in the ¹⁹F spectrum collapses completely at 0° and gives rise to two chemically shifted regions, of relative intensity 6:3, which appear as clear features at distinctly different temperatures between -40 and -100° . At -70° the low-field component (intensity 3) is clearly resolved into a doublet of septets at 63.8 ppm (${}^2J_{\text{FP}} = 115$ Hz, ${}^4J_{\text{FF}} = 13.5$ Hz) arising from coupling between inequivalent CF_3 groups. The high-field component (intensity 6) at 72.9 ppm is complex and resolves only partially into a doublet (${}^2J_{\text{FP}} = 103$ Hz). It is clear that the CF_3 groups exist in two different environments at temperatures between -40 and -100° , clearly excluding from the three possible configurations the structure C in which all the CF_3 groups occupy the equatorial plane. The fact that the ¹H spectrum arising from the OSiMe_3 groups is a single line at all temperatures investigated down to -140° suggests that the structure B, which has OSiMe_3 groups in two different environments, can be eliminated. Thus structure A is the most probable of the three alternatives which is in agreement with the proposal¹⁸ that the most electronegative groups, in this case CF_3 , generally occupy the axial positions in a trigonal-bipyramidal molecular structure.

On cooling to -140° the low-field doublet of septets in the ¹⁹F spectrum shows additional splitting (Figure 1), and the high-field component splits further into two regions, the higher field region (intensity 4) being a triplet of complex multiplets and the low-field region (intensity 2) having six widely spread complex mul-

(15) H. C. Clark and C. J. Willis, *J. Amer. Chem. Soc.*, **82**, 1888 (1960).

(16) R. Schmutzler, *Angew. Chem., Int. Ed. Engl.*, **4**, 496 (1965), and references therein.

(17) (a) K. J. Packer, *J. Chem. Soc.*, 960 (1963); (b) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **45**, 2926 (1966).

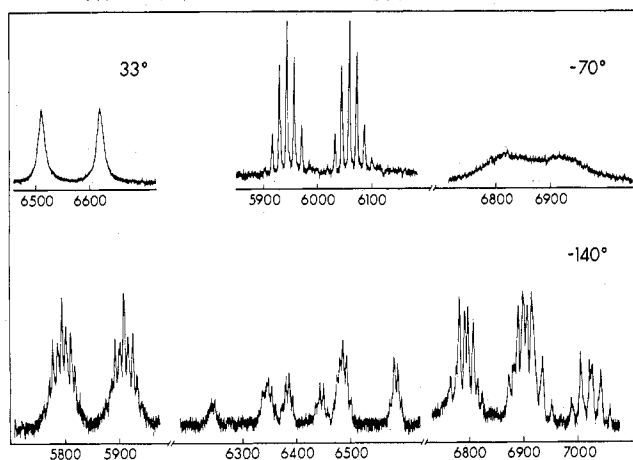
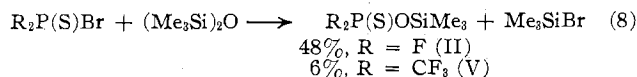


Figure 1.— ^{19}F nmr spectra of the phosphorane $(\text{CF}_3)_3\text{P}(\text{OSi}(\text{CH}_3)_2)_2$ obtained at 94.1 MHz using 15–20% solutions of the compound in CFCl_3 (33, -70°) and an approximate 50:50 mixture of $\text{CFCl}_3/\text{CF}_2\text{Cl}_2$ (-140°). The scale divisions are in hertz from CFCl_3 as standard, all values occurring to high field. Increased spectral amplitudes were used for the low-temperature spectra. Chemical shift and coupling constant values are given in Table IV.

tiplets. These features were understandable on the basis of restricted rotation of the two axial CF_3 groups (possibly as a result of the stabilization of a particular conformation of OSiMe_3 groups relative to the axial CF_3 groups) which causes two of the fluorine atoms in each group to be in a different environment from the third. The rotation of the equatorial CF_3 group does not appear to be affected, and its spectrum is in good agreement with that expected for a doublet ($^2J_{\text{PF}} = 115$ Hz) of quintets ($^4J_{\text{FF}} = 16.5$ Hz) of triplets ($^4J_{\text{FF}} = 7.0$ Hz). The axial CF_3 region, however, is extremely complex, and analysis of this part of the spectrum is currently proceeding.

Reactions of Thiophosphoryl Compounds with Hexamethyldisiloxane.—In contrast with the facile reactions of phosphoryl compounds with $(\text{Me}_3\text{Si})_2\text{O}$ at room temperature, the thiophosphoryl compounds were fairly inert toward this reagent even at elevated temperatures. The reaction conditions and products are summarized in Table I. Thus F_3PS , $\text{F}_2\text{P}(\text{S})\text{Cl}$, $(\text{CF}_3)_3\text{PS}$, and $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}$ were all recovered almost quantitatively after heating to 150° with $(\text{Me}_3\text{Si})_2\text{O}$. The thiophosphoryl bromides $\text{R}_2\text{P}(\text{S})\text{Br}$ ($\text{R} = \text{CF}_3, \text{F}$) gave the expected products $\text{R}_2\text{P}(\text{S})\text{OSiMe}_3$ in 6 and 48% yields, respectively, on heating to 160° for prolonged periods (eq 8). The greater reactivity of the bromides may

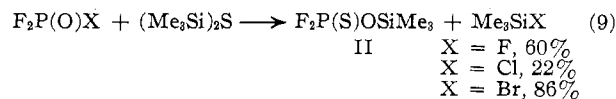


be a result of more facile cleavage of the relatively weak P–Br bonds.

Biermann and Glemser⁴ reported that F_3PS reacted with $(\text{Me}_3\text{Si})_2\text{O}$ in a nickel autoclave, producing $\text{F}_2\text{P}(\text{O})\text{OSiMe}_3$ (I), Me_3SiF , and NiS . When these reactants were heated in a sealed glass tube at 160° in the presence of excess nickel powder, we found the only products to be PF_3 and NiS , the $(\text{Me}_3\text{Si})_2\text{O}$ being recovered unchanged. Thus it appears that the initiating reaction in the autoclave may be removal of sulfur from F_3PS by nickel, and the production of ester I observed⁴ may be a result of catalytic action at the nickel surface,

under the much higher concentrations and pressures used compared with those of our experiments.

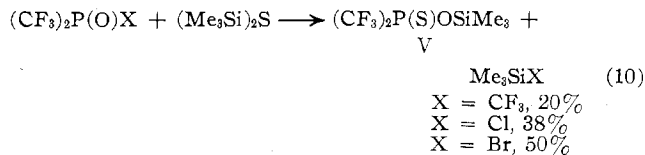
Reactions of Phosphoryl Compounds with Hexamethyldisilthiane.—The phosphoryl compounds reacted less readily with $(\text{Me}_3\text{Si})_2\text{S}$ than with $(\text{Me}_3\text{Si})_2\text{O}$, but in most cases products could be obtained in moderate or good yields on heating to 110° . The details are summarized in Table II. F_3PO and $\text{F}_2\text{P}(\text{O})\text{Cl}$ gave $\text{F}_2\text{P}(\text{S})\text{OSiMe}_3$ (II) after prolonged periods at 110° and $\text{F}_2\text{P}(\text{O})\text{Br}$ reacted similarly at room temperature (eq 9). Varying amounts of the thiophosphoryl ha-



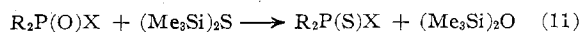
lides $\text{F}_2\text{P}(\text{S})\text{X}$ were also formed as side products in these reactions ($\text{X} = \text{F}$, 34%; $\text{X} = \text{Cl}$, trace; $\text{X} = \text{Br}$, 5%) and possible mechanisms for their formation are discussed below.

The ester II proved identical with that obtained from the alternative reaction between $\text{F}_2\text{P}(\text{S})\text{Br}$ and $(\text{Me}_3\text{Si})_2\text{O}$ (eq 8) and was shown¹ to possess the thiophosphoryl rather than the phosphoryl structure. The indicated greater stability of this structure rather than that of its isomer $\text{F}_2\text{P}(\text{O})\text{SSiMe}_3$ is in agreement with previous observations² that the few known compounds of this type exist as the thiophosphoryl isomer. However, alkyl esters of the acid $(\text{CF}_3)_2\text{P}(\text{S})\text{OH}$ have been found¹⁸ to be stable in both the isomeric forms $(\text{CF}_3)_2\text{P}(\text{S})\text{OR}$ and $(\text{CF}_3)_2\text{P}(\text{O})\text{SR}$, the latter being the more stable of the two in certain cases. It is tempting to associate this difference in behavior with π contributions to and stabilization of the P–O–Si bridge.

Similarly, $(\text{Me}_3\text{Si})_2\text{S}$ reacted with $(\text{CF}_3)_3\text{PO}$ and $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}$ at 110° and $(\text{CF}_3)_2\text{P}(\text{O})\text{Br}$ at room temperature, forming the ester V, which was again found¹ to exist as the thiophosphoryl rather than the phosphoryl isomer (eq 10). These reactions were consid-



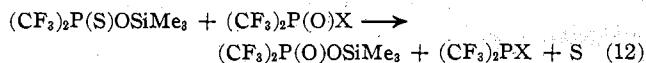
erably more complex, however, than those of the difluoro compounds. The thiophosphoryl halides $(\text{CF}_3)_2\text{P}(\text{S})\text{X}$ were again produced as by-products ($\text{X} = \text{CF}_3$, 33%; $\text{X} = \text{Cl}$, 16%; $\text{X} = \text{Br}$, 9%) and the ester $(\text{CF}_3)_2\text{P}(\text{O})\text{OSiMe}_3$ (IV) was also formed in each case. The thiophosphoryl halides could arise *via* the exchange reaction 11, and the other product of this reaction,



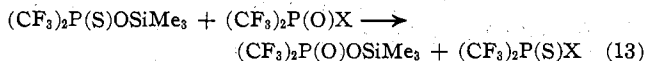
$(\text{Me}_3\text{Si})_2\text{O}$, could then react rapidly with unused phosphoryl compounds to yield ester IV. However, the absence of $\text{F}_2\text{P}(\text{O})\text{OSiMe}_3$ among the products of the reaction of F_3PO with $(\text{Me}_3\text{Si})_2\text{S}$, even though F_3PS was formed in 34% yield, indicates that in this case reaction 11 is probably not the route to the thiophosphoryl halide and also indicates doubt of its applicability in the reactions of $(\text{CF}_3)_2\text{P}(\text{O})\text{X}$ with $(\text{Me}_3\text{Si})_2\text{S}$.

A second possible method of formation of IV (eq 12)

(18) R. G. Cavell, A. A. Pinkerton, and W. Sim, unpublished results.

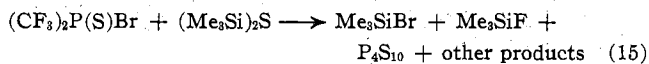
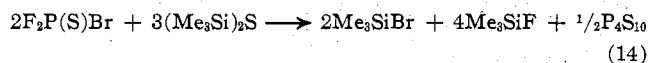


was suggested by the formation of small amounts of yellow residues in all the reactions, but this route cannot be generally valid since the other expected product, $(\text{CF}_3)_2\text{PX}$, was observed in one case only ($\text{X} = \text{CF}_3$ gave 22% $(\text{CF}_3)_3\text{P}$, but this could also arise from abstraction of oxygen from $(\text{CF}_3)_3\text{PO}$ by the CF_2 species formed by decomposition of Me_3SiCF_3 , which would itself be produced in reaction 10). A further possible method of formation of IV (eq 13), which would also



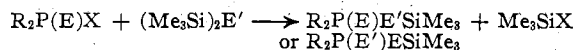
explain the formation of the thiophosphoryl halides, cannot be ruled out on the data available. Two further by-products, the siloxy and silylthio phosphines $(\text{CF}_3)_2\text{POSiMe}_3$ ^{19,20} (31%) and $(\text{CF}_3)_2\text{PSSiMe}_3$ ¹⁹ (1%), were also identified in the reaction of $(\text{CF}_3)_2\text{P}(\text{O})\text{Br}$ with $(\text{Me}_3\text{Si})_2\text{S}$. However, the sensitivity of these reactions to relatively minor substituent effects is demonstrated by lack of formation in detectable amounts of either $\text{F}_2\text{POSiMe}_3$ ¹⁹ or $\text{F}_2\text{PSSiMe}_3$ in the analogous reaction of $\text{F}_2\text{P}(\text{O})\text{Br}$ with $(\text{Me}_3\text{Si})_2\text{S}$ and renders attempts to explain the reduction of P(V) to P(III) somewhat tenuous.

Reactions of Thiophosphoryl Compounds with Hexamethyldisilthiane.—It has been shown that the sulfur-containing compounds $\text{R}_2\text{P}(\text{S})\text{X}$ and $(\text{Me}_3\text{Si})_2\text{S}$ are less reactive than their oxygen analogs $\text{R}_2\text{P}(\text{O})\text{X}$ and $(\text{Me}_3\text{Si})_2\text{O}$ in the general reaction being considered.¹ Further examples of this behavior are summarized in Table II. In accord with the general trend, F_3PS and $(\text{CF}_3)_3\text{PS}$ did not react with $(\text{Me}_3\text{Si})_2\text{S}$ even at 110–150°. The bromides $\text{F}_2\text{P}(\text{S})\text{Br}$ and $(\text{CF}_3)_2\text{P}(\text{S})\text{Br}$ gave some evidence of reaction, but the expected thioester products $\text{F}_2\text{P}(\text{S})\text{SSiMe}_3$ (III) and $(\text{CF}_3)_2\text{P}(\text{S})\text{SSiMe}_3$ (VI) were not isolated and have been shown¹ to decompose at the temperatures required to initiate reaction. The observed products could be rationalized on the basis of the stoichiometries required by eq 14 and 15, and the yields listed in Table II are calculated on this basis.



A Proposed Reaction Mechanism

We have demonstrated that phosphoryl and thiophosphoryl compounds $\text{R}_2\text{P}(\text{E})\text{X}$ undergo the general reaction with $(\text{Me}_3\text{Si})_2\text{E}'$ ($\text{E}, \text{E}' = \text{O}, \text{S}$).

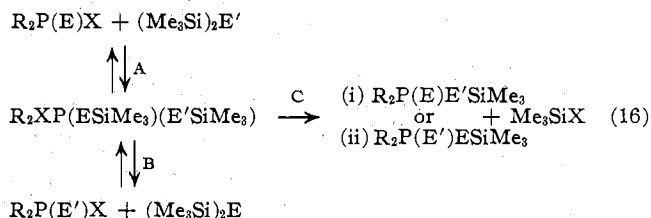


(19) R. G. Cavell, R. D. Leary, A. R. Sanger, and A. J. Tomlinson, unpublished results.

(20) A. B. Burg and J. S. Basi, *J. Amer. Chem. Soc.*, **90**, 3361 (1968).

The reactions occur very readily when $\text{E} = \text{E}' = \text{O}$, less readily when $\text{E}' = \text{S}$ and especially $\text{E} = \text{S}$, and with difficulty when $\text{E} = \text{E}' = \text{S}$. The comparative inertness of the $\text{P}=\text{S}$ group compounds compared with those of $\text{P}=\text{O}$ is notable as is the existence of the oxythioesters as the isomer $\text{R}_2\text{P}(\text{S})\text{OSiMe}_3$ rather than $\text{R}_2\text{P}(\text{O})\text{SSiMe}_3$. Also notable is the occurrence of rearrangement reactions leading to the production of thiophosphoryl siloxy esters from phosphoryl halides.

A consistent explanation of all reactions is provided by the proposal that the reactions proceed *via* addition to the $\text{P}=\text{E}$ bond, yielding a pentacoordinate phosphorane intermediate which is in general unstable under the conditions used. Decomposition may then occur by one or more of several ways to yield the observed products (eq 16).



The production of the esters $\text{R}_2\text{P}(\text{S})\text{OSiMe}_3$ from $\text{R}_2\text{P}(\text{O})\text{X}$ and $(\text{Me}_3\text{Si})_2\text{S}$ is thus simply rationalized in terms of the formation of the intermediate phosphorane followed by decomposition according to pathway C, and the need to invoke mechanisms requiring the rearrangement of the initially formed isomers (*e.g.*, $\text{R}_2\text{P}(\text{O})\text{SSiMe}_3$) is unnecessary. Further the product formed *via* route C can be taken to indicate which of the isomeric bonding situations is the more stable. Direct decomposition to the most stable ester *via* route C is not, however, essential since the "scrambling" of the E atoms can be achieved by means of the alternative dissociation of the phosphorane intermediate by means of pathway B and the subsequent metathetical reaction of the species so produced to form the observed esters. A process of this latter kind also readily explains the formation of IV from $(\text{CF}_3)_2\text{P}(\text{O})\text{X}$ and $(\text{Me}_3\text{Si})_2\text{S}$. Good evidence for the sequence involving the formation of the phosphorane intermediate and its subsequent decomposition to the most stable ester has been obtained in one case by the isolation of the phosphorane $(\text{CF}_3)_3\text{P}(\text{OSiMe}_3)_2$ (VII) which decomposes at 100° by routes A (=B when $\text{E} = \text{E}'$) and C. VII is also the first phosphorane to be synthesized directly from a phosphine oxide. The sacrifice of the very strong $\text{P}=\text{O}$ bond as well as the $\text{Si}-\text{O}-\text{Si}$ bridge in favor of two $\text{P}-\text{O}-\text{Si}$ bridges clearly suggests that the $\text{P}-\text{O}-\text{Si}$ bridge provides a very favorable bonding situation.²⁰

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