

Registry No. 1,7-B<sub>10</sub>C<sub>2</sub>H<sub>12</sub>, 16986-24-6; 9-Br-1,7-B<sub>10</sub>C<sub>2</sub>H<sub>11</sub>, 17819-81-7; 9,10-Br<sub>2</sub>-1,7-B<sub>10</sub>C<sub>2</sub>H<sub>10</sub>, 17032-20-1; 9,10-Cl<sub>2</sub>-1,7-B<sub>10</sub>C<sub>2</sub>H<sub>10</sub>, 17702-39-5; 1,7-(CH<sub>3</sub>)<sub>2</sub>-1,7-B<sub>10</sub>C<sub>2</sub>H<sub>10</sub>, 17499-00-2; 9,10-Br<sub>2</sub>-1,7-(CH<sub>3</sub>)<sub>2</sub>-1,7-B<sub>10</sub>C<sub>2</sub>H<sub>8</sub>, 51935-97-8; 1,7-(CH<sub>3</sub>S)<sub>2</sub>-1,7-B<sub>10</sub>C<sub>2</sub>H<sub>10</sub>, 51935-98-9; 9,10-Br<sub>2</sub>-1,7-(CH<sub>3</sub>S)<sub>2</sub>-1,7-B<sub>10</sub>C<sub>2</sub>H<sub>8</sub>, 52003-52-8; 1,2-B<sub>10</sub>C<sub>2</sub>H<sub>12</sub>, 16872-09-6; 9-Br-1,2-B<sub>10</sub>C<sub>2</sub>H<sub>11</sub>, 17141-89-8; 9,12-Br<sub>2</sub>-1,2-

B<sub>10</sub>C<sub>2</sub>H<sub>10</sub>, 17702-36-2; 8,9,12-Br<sub>3</sub>-1,2-B<sub>10</sub>C<sub>2</sub>H<sub>9</sub>, 20313-40-0; [(CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>][(1,2-B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>)<sub>2</sub>Co<sup>-</sup>], 12305-41-8; [(CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>][(9-Br-1,2-B<sub>9</sub>C<sub>2</sub>H<sub>10</sub>)<sub>2</sub>Co<sup>-</sup>], 52003-54-0; [(CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>][(9,12-Br<sub>2</sub>-1,2-B<sub>9</sub>C<sub>2</sub>H<sub>9</sub>)<sub>2</sub>Co<sup>-</sup>], 51936-00-6; 1,2-B<sub>10</sub>H<sub>10</sub>CHP, 30112-97-1; 9,12-Br<sub>2</sub>-1,2-B<sub>10</sub>H<sub>8</sub>CHP, 51936-01-7; <sup>11</sup>B, 14798-13-1; <sup>13</sup>C, 14762-74-4; P, 7723-14-0.

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## Phosphoranes. I. Tris(trifluoromethyl)bis(dimethylamino)phosphorane, (CF<sub>3</sub>)<sub>3</sub>P[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, and Related Chlorodimethylaminotrifluoromethylphosphoranes

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New trifluoromethylalkylaminophosphoranes (CF<sub>3</sub>)<sub>3</sub>P[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, (CF<sub>3</sub>)<sub>3</sub>PCl[N(CH<sub>3</sub>)<sub>2</sub>], and (CF<sub>3</sub>)<sub>2</sub>PCl<sub>2</sub>[N(CH<sub>3</sub>)<sub>2</sub>] were obtained from the trifluoromethylchlorophosphoranes and dimethylamine. The latter compound was also prepared by addition of Cl<sub>2</sub> to (CF<sub>3</sub>)<sub>2</sub>PN(CH<sub>3</sub>)<sub>2</sub>. Nmr spectroscopic behavior at low temperatures of the two tris(trifluoromethyl)phosphoranes is consistent with two and one axial CF<sub>3</sub> substituents in a trigonal-bipyramidal framework, respectively. Axial substitution of CF<sub>3</sub> groups appears to be characterized by unusually low <sup>2</sup>J<sub>PF</sub> (~50 Hz) couplings to phosphorus. The lack of temperature dependence in the <sup>19</sup>F nmr spectrum of (CF<sub>3</sub>)<sub>2</sub>PCl<sub>2</sub>[N(CH<sub>3</sub>)<sub>2</sub>] and the large <sup>2</sup>J<sub>PF</sub> coupling constant (156.9 Hz) in this compound suggest equatorial CF<sub>3</sub> substitution and the absence of positional averaging. It is suggested that the halogens occupy axial positions in preference to CF<sub>3</sub> even if the halogen has a lower formal electronegativity than CF<sub>3</sub>. Acidic reagents such as methanol, methyl mercaptan, and H<sub>2</sub>S displace CF<sub>3</sub>H from (CF<sub>3</sub>)<sub>3</sub>P[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> to form pentavalent, four-coordinate products in complicated reactions. Some reduction to phosphorus(III) occurs in the sulfur system perhaps through intermediate, unstable thiophosphoranes. Alkaline hydrolysis liberates 2 mol of CF<sub>3</sub>H quantitatively in all cases but neutral and acidic hydrolyses which also liberate CF<sub>3</sub>H are less straightforward as a result of secondary reactions in the medium. The new anion CF<sub>3</sub>PO<sub>3</sub>H<sup>-</sup> has been observed in acidic media. Nmr parameters for CF<sub>3</sub>P(E)[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and CF<sub>3</sub>P(E)Cl[N(CH<sub>3</sub>)<sub>2</sub>] (E = O, S) are reported for the first time.

### Introduction

Recent review articles demonstrate a continuing active interest in the location of substituents in the five-coordinate phosphorane framework.<sup>1,2</sup> Early studies by Muettterties and coworkers<sup>3</sup> suggested that, for a limited range of substituents, the axial position of the assumed trigonal-bipyramidal framework was preferentially occupied by the most electronegative group. Trifluoromethylfluorophosphoranes presented some ambiguities which were resolved by assigning the CF<sub>3</sub> substituent to either axial or equatorial positions<sup>3</sup> in different molecules suggesting that CF<sub>3</sub> could replace F in axial position in some cases in spite of its lower electronegativity. Recent calculations<sup>2c,4</sup> have suggested that back-bonding into the "d" orbitals of the phosphorus atom is more effective from equatorial than from axial positions and this difference may well be responsible for the observed positional preferences. Thus, on phosphorus, groups with strong back-bonding tendencies would favor location in equatorial positions and those with weak or nonexistent back-bonding requirements favor axial positioning. Each group therefore has a specific "apicophilic" character.<sup>4</sup> We have been engaged in a systematic study of the chemistry of trifluoromethylphosphoranes with the aim of providing some

insight into the substitutional preference of substituent groups on phosphorus. We report herein some studies of dimethylaminophosphoranes containing CF<sub>3</sub> substituents.

### Experimental Section

**Materials, Apparatus, and Techniques.** All manipulations were carried out using standard vacuum techniques in a system constructed with Pyrex glass with stopcocks lubricated with Apiezon N grease. Involatile materials which remained in the reaction vessels were handled in a nitrogen atmosphere while aqueous solutions were handled in the air since it had been found by experience that such products were invariably air stable.

Reactions were generally carried out in sealed Pyrex glass tubes of approximate volumes 10, 25, or 75 cm<sup>3</sup> depending on the scale of the reaction and the maximum calculated pressure expected. A reactor tube which allowed combination of reagents in gaseous form in spite of relatively low volatility (Figure 1) was used in most of the reactions.

**Materials.** Trifluoromethyliodophosphines and (CF<sub>3</sub>)<sub>3</sub>P were prepared from the reaction of CF<sub>3</sub>I (Columbia Organic Chemical Co.) with red phosphorus at 220° for 48 hr.<sup>5</sup> The remaining trifluoromethylphosphorus compounds required in this study were prepared from these phosphines according to indicated literature methods. Commercially available chemicals of "reagent" grade were used without further purification. Gaseous reagents were usually fractionated before use to remove any moisture or gross impurities.

**Instrumental Techniques.** Infrared spectra of gases were obtained using a 9-cm gas cell with potassium bromide windows. All spectra were recorded with a Perkin-Elmer 457 spectrophotometer. Mass spectra were recorded with an AEI MS-9 spectrometer operating at an ionizing voltage of 70 eV. Gaseous samples were introduced directly through a heated inlet, whereas liquids of low volatility were introduced *via* a heated capillary. Solid samples were introduced *via* the direct probe. All nmr spectra were recorded with either a Varian A56/60, a Varian HA 100, or a Bruker HFX-90 spectrometer. Proton spectra were recorded at 60.0 MHz and fluorine spectra at 56.4 MHz using the A56/60 instrument. In the case of the HA 100 instrument, proton spectra were recorded at 100 MHz and fluorine spectra

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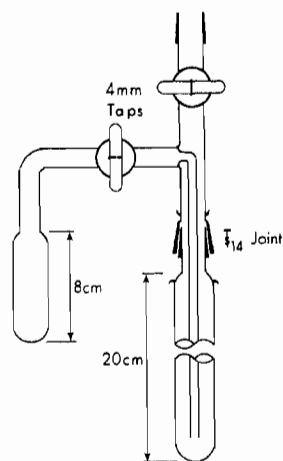


Figure 1. Reaction vessel for gas-phase reaction with low-volatile materials.

at 94.1 MHz while in the case of the Bruker instrument the proton spectra were recorded at 90 MHz and the fluorine spectra at 84.67 MHz. Proton and fluorine spectra were routinely recorded on samples containing an approximate 10% solution of the compound in  $\text{CFCl}_3$  or  $\text{CF}_2\text{Cl}_2$ . Nmr measurements for involatile products were obtained in solutions of  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CD}_3\text{CN}$ , or  $\text{H}_2\text{O}$ . Fluorine chemical shifts were measured relative to internal  $\text{CFCl}_3$  solvent. In cases where other solvents were employed an external  $\text{CCl}_3\text{F}$  (capillary) reference was used. Proton chemical shifts were measured relative to external tetramethylsilane (TMS) as a 5% solution in  $\text{CCl}_3\text{F}$  in all cases. Each instrument was equipped with a variable-temperature controller which was established as accurate to within  $\pm 5^\circ$  of the temperature indicated on the controller by calibration.

**Preparation and Characterization of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ .** Tris-(trifluoromethyl)dichlorophosphorane,  $(\text{CF}_3)_3\text{PCl}_2$ <sup>5</sup> (1.390 g, 4.50 mmol), and dimethylamine,  $(\text{CH}_3)_2\text{NH}$  (0.825 g, 18.30 mmol), were allowed to react in a sealed tube at room temperature for 72 hr. Vacuum fractionation gave  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  (1.312 g, 4.02 mmol) in 89.3% yield collected at  $-45^\circ$ . Other products were  $(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$ <sup>6,7</sup> (0.017 g, 0.08 mmol), dimethylamine (0.05 g, 1.00 mmol), and  $\text{CF}_3\text{H}$  (0.027 g, 0.39 mmol). The  $(\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-$  salt remained as an involatile white solid in the reaction tube. In another reaction, when this salt was dissolved in a solution of 25%  $\text{AgNO}_3$ , 96% of the chlorine in the original  $(\text{CF}_3)_3\text{PCl}_2$  was recovered as  $\text{AgCl}$ .

The compound is a white solid at room temperature which decomposes upon melting at  $94^\circ$ . Decomposition also occurs over long periods of time at room temperature and more rapidly at elevated temperatures.<sup>8</sup>

The mass spectrum of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  showed no parent ion, a result which is typical of pentacoordinate phosphorus compounds.<sup>9</sup> The strong ions at  $m/e$  257 and 282 were identified by mass measurements (calcd for  $(\text{CF}_3)_2\text{P}[\text{N}(\text{CH}_3)_2]_2^+$   $m/e$  257.0644, found  $m/e$  257.0640, calcd for  $(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2^+$   $m/e$  282.0095, found  $m/e$  282.0090) and have a composition which strongly suggests that they arise from the fragmentation of the unobserved parent phosphorane  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  by loss of  $\text{CF}_3$  or  $\text{N}(\text{CH}_3)_2$ , respectively. The mass spectral results are given in Table I. Infrared data are found in Table II and nmr data in Table III.

(a) **Alkaline Hydrolysis.** Hydrolysis of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  (0.118 g, 0.36 mmol) with approximately 0.8 ml of degassed 10%  $\text{NaOH}$  at room temperature for 24 hr gave  $\text{CF}_3\text{H}$  (0.052 g, 0.74 mmol). Nmr spectra of the remaining aqueous solution indicated the presence of the  $\text{CF}_3\text{PO}_3^{2-}$  ion.<sup>10</sup>

(b) **Neutral Hydrolysis.** Hydrolysis of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  (0.095 g, 0.29 mmol) with approximately 0.8 ml of degassed distilled  $\text{H}_2\text{O}$  at room temperature for 24 hr gave  $\text{CF}_3\text{H}$  (0.029 g, 0.41 mmol). Nmr spectra of the remaining aqueous solution indicated the presence of the  $(\text{CF}_3)_2\text{PO}_2^-$  and  $\text{CF}_3\text{PO}_3^{2-}$  ions in the approximate ratio 2:1.<sup>10</sup>

(c) **Acid Hydrolysis.** Hydrolysis of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  (0.180 g, 0.55 mmol) with approximately 0.8 ml of degassed distilled  $\text{H}_2\text{O}$

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Table I. Mass Spectra of Phosphoranes<sup>a</sup>

$m/e$	$(\text{CF}_3)_3\text{-P}[\text{N}(\text{C}-\text{H}_3)_2]_2^b$	$(\text{CF}_3)_3\text{-PCI}[\text{N}(\text{C}-\text{H}_3)_2]^b$	$(\text{CF}_3)_2\text{-PCI}_2\text{N}(\text{C}-\text{H}_3)_2^b$	Assignment
282	0.2 <sup>c</sup>	1.4 <sup>d</sup>		} $\text{C}_5\text{F}_9\text{H}_6\text{NP}$
275		0.1		
273		0.4		} $\text{C}_5\text{F}_9\text{ClP}$
257	0.05 <sup>c</sup>			
250		0.3	0.01	} $\text{C}_6\text{F}_6\text{N}_2\text{H}_{11}\text{P}$
248		1.1 <sup>d</sup>	0.03 <sup>e</sup>	
243			0.011	} $\text{C}_4\text{F}_6\text{ClH}_6\text{NP}$
241			0.069	
239			0.100	} $\text{C}_2\text{F}_6\text{Cl}_2\text{P}$
232		3.8		
229	0.7	1.7	4.0	} $\text{C}_4\text{F}_7\text{H}_6\text{NP}$
228			0.3	
228			0.3	} $\text{C}_4\text{F}_7\text{H}_3\text{NP}$
213	1.8			
207		0.8		} $\text{C}_4\text{F}_6\text{H}_6\text{NP}$
206			0.02	
204			0.06	} $\text{C}_2\text{F}_6\text{ClP}$
182	0.9	3.1	0.5	
178			0.5	} $\text{C}_5\text{F}_5\text{H}_2\text{NP}$
166		0.9		
160	0.9	3.8	6.9	} $\text{C}_3\text{F}_6\text{H}_3$
151			0.6	
150		1.0		} $\text{C}_3\text{F}_4\text{H}_3\text{NP}$
144	3.9			
135		1.3	0.4	} $\text{C}_2\text{F}_5\text{P}$
132	0.8	3.7	0.6	
128		0.7	0.8	} $\text{C}_3\text{F}_3\text{H}_2\text{NP}$
119	1.9	6.2	0.7	
113	1.3			} $\text{CF}_4\text{H}_2\text{NP}$
112	1.7			
110	1.0	5.5	9.9	} $\text{C}_4\text{F}_2\text{H}_{12}\text{N}$
101			0.6	
100		3.8		} $\text{C}_3\text{F}_2\text{H}_3\text{NP}$
99			0.7	
97		1.0		} $\text{CF}_3\text{HP}$
94	7.1	10.2	9.1	
91			0.6	} $\text{CF}_2\text{H}_4\text{NP}$
90		1.1	1.4	
85			3.8	} $\text{C}_2\text{FH}_6\text{NP}$
81		1.0	0.4	
76			0.6	} $\text{C}_2\text{FH}_3\text{NP}$
70	0.6			
69	29.7	12.2	11.6	} $\text{CF}_3\text{H}$ , $\text{HPF}_2$
64	0.9			
60	0.7	1.3	0.6	} $\text{CF}_3, \text{F}_2\text{P}$
57	3.0		0.6	
56	2.8			} $\text{C}_2\text{F}_2\text{H}_2$
51	17.5	3.1		
50	4.9	2.4	0.7	} $\text{CH}_3\text{NP}$
47		9.8	4.9	
44	0.6	2.4	2.0	} $\text{H}_2\text{NP}$
43	2.3	2.6	2.4	
42	3.3	7.5	8.4	} $\text{C}_2\text{H}_5\text{N}$
41	1.9		0.8	
40		1.2		} $\text{C}_2\text{H}_4\text{N}$
38		0.9		
36		3.3		} $\text{C}_2\text{H}_3\text{N}$
32		18.9		
31	9.0	5.8	1.0	} $\text{CFH}$

<sup>a</sup> Intensities are expressed relative to the total ionization defined as  $\Sigma(\text{intensity})$  for all ions with mass greater than 30 whose intensity is greater than 2% of the base peak. <sup>b</sup> The parent ion was not observed. <sup>c</sup> The identity of these peaks was established by mass measurement under high resolution and values are given in the text of the Experimental Section. <sup>d</sup> The identity of these peaks was established by mass measurement under high resolution ( $\text{C}_5\text{F}_9\text{H}_6\text{NP}^+$   $m/e$ : calcd, 282.0093; found, 282.0086.  $\text{C}_4\text{F}_6^{35}\text{ClH}_6\text{NP}^+$   $m/e$ : calcd, 247.9830; found, 247.9824). <sup>e</sup> The identity of this peak was established by mass measurement under high resolution ( $\text{C}_4\text{F}_6^{35}\text{ClH}_6\text{NP}^+$   $m/e$ : calcd, 247.9830; found, 247.9833).

adjusted to a pH  $\sim 1$  at room temperature for 24 hr gave  $\text{CF}_3\text{H}$  (0.0554 g, 0.79 mmol). Nmr spectra of the remaining aqueous solution indicated the presence of the  $(\text{CF}_3)_2\text{PO}_2^-$ <sup>10</sup> and an ion which we have identified as the  $\text{CF}_3\text{PO}_3\text{H}^-$  ion in the molar ratio 4:3. The latter ion

Table II. Infrared Spectra of Phosphoranes

(CF <sub>3</sub> ) <sub>3</sub> P[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> <sup>a,b</sup>	(CF <sub>3</sub> ) <sub>3</sub> P(Cl)-N(CH <sub>3</sub> ) <sub>2</sub> <sup>a</sup>	(CF <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> -PN(CH <sub>3</sub> ) <sub>2</sub> <sup>a</sup>	Assignment
3021 vw	3028 vw	3031 vw	ν(C-H)
2943 m	2945 w	2954 w	
2922 w, sh	2877 w	2945 w, sh	
2878 w	2828 w	2875 w	
2824 w		2832 w	
1463 m	1464 w	1467 w	δ(CH <sub>3</sub> ) + ν(C <sub>2</sub> N)
1375 w	1283 m	1328 w	
1290 m		1291 w	
1200 s	1205 s	1204 m	ν(C-F)
1150 vs	1182 s	1185 s	
1129 m, sh	1152 ms	1168 s	
1092 s	1131 s	1162 s, sh	
		1153 s, sh	
		1148 s	ν <sub>as</sub> (C <sub>2</sub> N)
987 m	988 m	990 m	
741 w	709 m	708 m	δ <sub>s</sub> (CF <sub>3</sub> )
660 m	593 m	590 m	ν <sub>as</sub> (N <sub>2</sub> -P)
		558 w	ν(P-Cl)?
562 m	578 m <sup>c</sup>	536 m	δ <sub>as</sub> (CF <sub>3</sub> )
541 w, sh			
499 w	508 m <sup>c</sup>		ν(P-CF <sub>3</sub> )
	483 m <sup>c</sup>		

<sup>a</sup> All values in cm<sup>-1</sup>. Spectra were investigated over the range 4000–300 cm<sup>-1</sup>. Abbreviations: ν, stretching; δ, deformation; s, strong; m, medium; w, weak; v, very; sh, shoulder; as, antisymmetric; s, symmetric. <sup>b</sup> To increase the intensity of the peaks the ir cell was heated to 60°. <sup>c</sup> One of these peaks is probably due to ν(P-Cl), but we are not able to make an unambiguous assignment at this time.

Table III. Summary of Nmr Parameters

Compd	Ppm			Hz				Notes
	φ <sub>F</sub> <sup>a</sup>	τ <sub>H</sub> <sup>b</sup>	σ <sub>P</sub> <sup>c</sup>	<sup>2</sup> J <sub>FP</sub>	<sup>3</sup> J <sub>HP</sub>	<sup>5</sup> J <sub>FH</sub>	<sup>4</sup> J <sub>FF</sub>	
CF <sub>3</sub> P(S)[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	67.7	7.49		93.7	12.11	0.75		<i>d, e</i>
CF <sub>3</sub> P(S)Cl[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	73.2	7.19		121.5	13.65	0.75		<i>d, f</i>
CF <sub>3</sub> P(O)[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	67.7	7.50		96.3	9.95	0.73		<i>d, g</i>
CF <sub>3</sub> P(O)Cl[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	73.7	7.32		125.5	11.8	0.72		<i>d, f</i>
CF <sub>3</sub> PO <sub>3</sub> H <sup>-</sup>	73.5			107				In H <sub>2</sub> O
(CF <sub>3</sub> ) <sub>3</sub> P[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	56.7	7.05		<i>h</i>	11.6	0.95		At 40°
	57.0		158.0 <sup>i</sup>	50.5 <sup>j</sup>			16.5	} At -30° in CF <sub>2</sub> Cl <sub>2</sub>
	55.6			108 <sup>k</sup>				
	~58.2			~71				
(CF <sub>3</sub> ) <sub>3</sub> PCl[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	59.1	7.20	156.5 <sup>l</sup>	105.5	13.9	0.68		At 40°
	59.3			130 <sup>m</sup>				} At -120° in CF <sub>2</sub> Cl <sub>2</sub>
	57.7			~53 <sup>n</sup>				
(CF <sub>3</sub> ) <sub>2</sub> PCl <sub>2</sub> [N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	67.8	7.17	143.5	156.9	12.5	1.09		

<sup>a</sup> Spectra were recorded on dilute solutions in CFCl<sub>3</sub> at normal temperatures unless otherwise stated. Chemical shifts are given in ppm upfield from CFCl<sub>3</sub> in solvents other than CFCl<sub>3</sub>; the chemical shifts were recorded relative to external CFCl<sub>3</sub>. Positive values indicate resonances to high field of standard. <sup>b</sup> Shifts are given on the τ scale (τ(CH<sub>3</sub>)<sub>4</sub>Si = 10.0) relative to an external capillary of 5% TMS. <sup>c</sup> Chemical shifts are given relative to P<sub>4</sub>O<sub>6</sub> (capillary) with positive values indicating resonance to high field of standard. The chemical shift of 85% H<sub>3</sub>-PO<sub>4</sub> is +112 vs. P<sub>4</sub>O<sub>6</sub> [A. C. Chapman, J. Homer, D. J. Mowthorpe, and K. T. Jones, *Chem. Commun.*, 121 (1965)]. <sup>d</sup> <sup>1</sup>H spectrum is a doublet of quartets. <sup>e</sup> <sup>19</sup>F spectrum consists of a doublet of 11 lines each with an intensity distribution in good agreement with that expected for the 11 inner lines of a 13-line multiplet due to coupling of 12 equivalent protons with F. <sup>f</sup> <sup>19</sup>F spectrum consists of a doublet of septets. <sup>g</sup> <sup>19</sup>F spectrum consists of a doublet of asymmetric multiplets containing at least 10 lines. <sup>h</sup> Signals are broad multiplets. <sup>i</sup> At -40°. With <sup>1</sup>H irradiation the spectrum is a quartet of septets; <sup>2</sup>J<sub>FP</sub>eq = 110 Hz, <sup>2</sup>J<sub>FP</sub>ax = 52 Hz.<sup>22</sup> <sup>j</sup> Intensity ratio 2, assigned to axial CF<sub>3</sub> groups. <sup>k</sup> Intensity ratio 1, assigned to equatorial CF<sub>3</sub> group. <sup>l</sup> With <sup>1</sup>H irradiation <sup>2</sup>J<sub>FP</sub>(av) = 106 Hz.<sup>22</sup> <sup>m</sup> Intensity ratio 2, assigned to equatorial CF<sub>3</sub> groups. <sup>n</sup> Intensity ratio 1, assigned to axial CF<sub>3</sub> group.

gave <sup>19</sup>F parameters (φ 73.5 ppm and <sup>2</sup>J<sub>FP</sub> = 107 Hz in H<sub>2</sub>O) which are comparable to those<sup>10</sup> of CF<sub>3</sub>PS<sub>2</sub>OH<sup>-</sup> and CF<sub>3</sub>PSO<sub>2</sub>H<sup>-</sup>, and adding strong base to the solution results in the formation of CF<sub>3</sub>PO<sub>3</sub><sup>2-</sup>, identified by its nmr parameters.<sup>10</sup>

**Preparation and Characterization of Bis(trifluoromethyl)dimethylaminodichlorophosphorane, (CF<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>PN(CH<sub>3</sub>)<sub>2</sub>.** Using the apparatus shown in Figure 1 (CH<sub>3</sub>)<sub>2</sub>NH (0.132 g, 2.93 mmol) was allowed to react with gaseous (CF<sub>3</sub>)<sub>2</sub>PCl<sub>2</sub><sup>11</sup> (0.274 g, 0.99 mmol) at room temperature for 30 min. Separation of the volatile products gave a mixture (0.139 g) of (CF<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>PN(CH<sub>3</sub>)<sub>2</sub> (0.133 g, 0.47 mmol) and (CF<sub>3</sub>)<sub>2</sub>PCl<sub>2</sub> (0.006 g, 0.02 mmol) which was trapped at -45°. Also obtained was unreacted (CF<sub>3</sub>)<sub>2</sub>PCl<sub>2</sub><sup>7</sup> (0.059 g, 0.21 mmol, trapped

at -96°), (CH<sub>3</sub>)<sub>2</sub>NH (0.036 g, 0.80 mmol, trapped at -116°), and CF<sub>3</sub>H (0.009 g, 0.13 mmol, trapped at -196°). Pure (CF<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>PN(CH<sub>3</sub>)<sub>2</sub> was obtained by further careful refractionation of the crude mixture collected at -45°. This procedure gave optimum yield<sup>12</sup> of (CF<sub>3</sub>)<sub>2</sub>PCl<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub> from this aminolysis route.

In an alternate synthesis developed by Dr. K. I. The, (CF<sub>3</sub>)<sub>2</sub>PN(CH<sub>3</sub>)<sub>2</sub><sup>6,7</sup> (0.696 g, 3.27 mmol) and Cl<sub>2</sub> (0.293 g, 4.13 mmol) were combined in a sealed tube at -196° and allowed to warm slowly to room temperature. Separation of the volatile products gave unreacted Cl<sub>2</sub> (0.049 g, 0.69 mmol) and (CF<sub>3</sub>)<sub>2</sub>PCl<sub>2</sub>[N(CH<sub>3</sub>)<sub>2</sub>] (0.910 g, 3.20 mmol). The reacting ratio (CF<sub>3</sub>)<sub>2</sub>PN(CH<sub>3</sub>)<sub>2</sub>:Cl<sub>2</sub> is therefore 1.02:1.08 to yield 1.0 mol (>98%) of the desired phosphorane.

The compound (CF<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>PN(CH<sub>3</sub>)<sub>2</sub> is a relatively involatile white solid at room temperature and is stable for several weeks at room temperature. The compound was characterized by the chemical reactions described below and its spectroscopic properties (mass spectroscopy Table I, ir Table II, and nmr Table III). The identity of the ion at *m/e* 248 was established by accurate mass measurements [found *m/e* 247.9833, calcd *m/e* 247.9830] to be the C<sub>4</sub>F<sub>6</sub><sup>3+</sup>CH<sub>6</sub><sup>-</sup>NP<sup>+</sup> ion. A parent ion was not observed.

**Alkaline Hydrolysis.** (CF<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>PN(CH<sub>3</sub>)<sub>2</sub> (0.160 g, 0.56 mmol) was combined with 0.8 ml of 10% NaOH solution and allowed to react for 48 hr at room temperature. The only volatile product was CF<sub>3</sub>H (0.040 g, 0.57 mmol). Nmr spectra of the remaining aqueous solution indicated the presence of the CF<sub>3</sub>PO<sub>3</sub><sup>2-</sup> ion.<sup>10</sup>

**Neutral Hydrolysis.** Hydrolysis of (CF<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>PN(CH<sub>3</sub>)<sub>2</sub> (0.105 g, 0.37 mmol) with approximately 0.8 ml of degassed distilled water at room temperature for 48 hr gave CF<sub>3</sub>H (0.001 g, 0.014 mmol). The nmr spectrum of the remaining aqueous solution indicated the presence of the (CF<sub>3</sub>)<sub>2</sub>PO<sub>2</sub><sup>-</sup> ion.<sup>10</sup>

**Reactions of Tris(trifluoromethyl)bis(dimethylamino)phosphorane. (a) With Dimethylamine.** A sample of (CF<sub>3</sub>)<sub>3</sub>P[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.092 g, 0.28 mmol) and (CH<sub>3</sub>)<sub>2</sub>NH (0.214 g, 4.76 mmol) did not react over a period of 84 hr at room temperature and un-

changed (CF<sub>3</sub>)<sub>3</sub>P[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.080 g, 0.24 mmol, identity confirmed by nmr) and (CH<sub>3</sub>)<sub>2</sub>NH (0.215 g, 4.78 mmol) were recovered.

**(b) With Hydrogen Chloride.** No reaction took place when (CF<sub>3</sub>)<sub>3</sub>P[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.100 g, 0.31 mmol) was treated with HCl (0.048 g, 1.33 mmol) for 2 days at room temperature. Excess hydrogen chloride (0.633 g, 17.3 mmol) and (CF<sub>3</sub>)<sub>3</sub>P[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.193 g, 0.59 mmol) for 48 hr in a small (~10 cm<sup>3</sup>) tube at room temperature gave (CF<sub>3</sub>)<sub>3</sub>PCl<sub>2</sub> (0.099 g, 0.32 mmol) and a mixture (0.550 g) of HCl and very small amounts of at least two as yet unidentified compounds (indicated by ir) which trapped at -196°. Nmr spectra of CD<sub>3</sub>CN solutions of the involatile white solid which remained in the reaction vessel indicated that it was principally (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup>Cl<sup>-</sup>

with very small amounts of two unidentified  $\text{CF}_3\text{P}$ -containing compounds [ $J = 114$  Hz,  $\phi_{\text{F}} 65.7$  ppm;  $J = 168$  Hz,  $\phi_{\text{F}} 64.3$  ppm].

(c) **With Methanol.** The reaction of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  (0.134 g, 0.41 mmol) with  $\text{CH}_3\text{OH}$  (0.027 g, 0.85 mmol) for 10 min at room temperature gave  $(\text{CH}_3)_2\text{NH}$  (0.006 g, 0.13 mmol) and  $\text{CF}_3\text{H}$  (0.030 g, 0.43 mmol) as the only volatile products. The clear liquid of low volatility which remained in the reaction tube was dissolved in  $\text{CD}_3\text{CN}$  and identified by nmr as principally  $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$  (*vide infra*) plus two as yet unidentified  $\text{CF}_3\text{P}$ -containing compounds ( $\phi_{\text{F}} 74.1$  ppm,  $J = 94$  Hz;  $\phi_{\text{F}} 72.7$  ppm,  $J = 97$  Hz) in small amounts.

(d) **With Methyl Mercaptan.** Reaction of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  (0.096 g, 0.30 mmol) with  $\text{CH}_3\text{SH}$  (0.028 g, 0.58 mmol) in a sealed tube at room temperature after 48 hr gave an unseparated mixture (0.084 g) trapped at  $-116^\circ$  consisting of  $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  (0.039 g, 0.21 mmol),  $(\text{CF}_3)_2\text{PSCH}_3$  (0.010 g, 0.05 mmol),  $(\text{CF}_3)_3\text{P}^{5,7}$  (0.003 g, 0.01 mmol), and  $\text{CH}_3\text{SSCH}_3$  (0.032 g, 0.34 mmol), together with a small amount of  $(\text{CH}_3)_2\text{NH}$  (as determined by nmr spectroscopy).  $\text{CF}_3\text{H}$  (0.035 g, 0.50 mmol) was collected in the  $-196^\circ$  trap.

(e) **With Hydrogen Sulfide.** The reaction of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  (0.252 g, 0.77 mmol) and  $\text{H}_2\text{S}$  (0.053 g, 1.56 mmol) proceeded rapidly and exothermally at room temperature. After 10 min the reaction subsided and subsequent vacuum fractionation afforded  $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$  (0.020 g, 0.09 mmol) (*vide infra*),  $(\text{CF}_3)_2\text{P}(\text{S})\text{N}(\text{CH}_3)_2$  (0.025 g, 0.10 mmol),  $(\text{CH}_3)_2\text{NH}$  (0.012 g, 0.27 mmol), and  $\text{CF}_3\text{H}$  (0.056 g, 0.80 mmol) which was purified by washing with a degassed solution of lead acetate to remove  $\text{H}_2\text{S}$ . The nmr spectra of the involatile liquid which remained in the reaction tube indicated the presence of the  $(\text{CF}_3)_2\text{PS}_2^-$  ion.<sup>10</sup>

**Preparation and Characterization of Tris(trifluoromethyl)chlorodimethylaminophosphorane.** Using the apparatus shown in Figure 1 tris(trifluoromethyl)dichlorophosphorane  $(\text{CF}_3)_3\text{PCl}_2$  (0.757 g, 2.45 mmol) and gaseous  $(\text{CH}_3)_2\text{NH}$  (0.227 g, 5.04 mmol) were allowed to react for only 5 min at room temperature. The volatile products collected at  $-45^\circ$  were a mixture (0.528 g) of  $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$  (0.401 g, 1.26 mmol) and  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  (0.127 g, 0.39 mmol) (analyzed by nmr spectroscopy). Pure  $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$  was obtained by further careful fractionation of this mixture.  $(\text{CF}_3)_3\text{PCl}_2$  (0.198 g, 0.64 mmol) was found in the  $-96^\circ$  trap and unreacted  $(\text{CH}_3)_2\text{NH}$  (0.456 g, 1.01 mmol) was collected at  $-196^\circ$ .

The compound  $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$  is a white solid which decomposes quite rapidly over a period of days under vacuum at room temperature. In  $\text{CCl}_3\text{F}$  solution  $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$  decomposes over 48 hr at room temperature to give a small amount of  $(\text{CF}_3)_3\text{P}$  and smaller amounts of other  $\text{CF}_3\text{P}$  species (by nmr) soluble in  $\text{CCl}_3\text{F}$  plus unidentified solid materials.

The compound was characterized by its spectroscopic properties (ir Table II, nmr Table III) by mass spectrometry (Table I) and by chemical reactions described below.

**Alkaline Hydrolysis.** Hydrolysis of  $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$  (0.069 g, 0.22 mmol) with approximately 0.8 ml of degassed 10% NaOH at room temperature for 24 hr gave  $\text{CF}_3\text{H}$  (0.029 g, 0.42 mmol). Nmr spectra of the remaining aqueous solution showed the presence of the  $\text{CF}_3\text{PO}_3^{2-}$  ion.<sup>10</sup>

**Neutral Hydrolysis.** Reaction of  $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$  (0.223 g, 0.70 mmol) with approximately 0.8 ml of degassed distilled  $\text{H}_2\text{O}$  at room temperature for 48 hr gave  $\text{CF}_3\text{H}$  (0.049 g, 0.70 mmol). Nmr spectra of the remaining aqueous solution showed the presence of the  $(\text{CF}_3)_2\text{PO}_2^-$  ion.<sup>10</sup>

**Acid Hydrolysis.** The compound  $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$  (0.124 g, 0.39 mmol) was allowed to react with 0.8 ml of degassed distilled water adjusted to a pH  $\sim 1$  by the addition of HCl. After 24 hr at room temperature vacuum fractionation afforded  $\text{CF}_3\text{H}$  (0.028 g, 0.40 mmol). Nmr spectra of the remaining aqueous solution indicated the presence of the  $(\text{CF}_3)_2\text{PO}_2^-$  ion.<sup>10</sup>

**Reaction of Tris(trifluoromethyl)chlorodimethylaminophosphorane with Dimethylamine.** The reaction of  $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$  (0.133 g, 0.42 mmol) with  $(\text{CH}_3)_2\text{NH}$  (0.107 g, 2.38 mmol) at room temperature for 24 hr gave  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  (0.130 g, 0.40 mmol). Unreacted  $(\text{CH}_3)_2\text{NH}$  (0.073 g, 1.62 mmol) was the only other vola-

Table IV. Infrared Spectra of Trifluoromethyldimethylaminophosphorus Oxides and Sulfides<sup>a</sup>

$\text{CF}_3\text{P}(\text{E})[\text{N}(\text{CH}_3)_2]_2$		$\text{CF}_3\text{P}(\text{E})\text{Cl}[\text{N}(\text{CH}_3)_2]_2$		Assignment
$\text{E} = \text{O}^d$	$\text{E} = \text{S}^{b,d}$	$\text{E} = \text{O}$	$\text{E} = \text{S}$	
3008 w	3010 w	3018 w	3012 w	} $\nu(\text{C-H})$
2942 m	2938 m	2955 m	2958 m	
2920 m	2900 m	2925 w, sh	2920 w, sh	
2868 w	2860 w	2873 w	2865 w	
2822 w	2825 w	2835 w	2825 w	
1487 w	1460 s	1483 w	1477 w	} $\delta(\text{CH}_3), \nu_s(\text{C}_2\text{N})$
1462 m	1411 w	1460 m	1460 m	
1252 s	1296 s	1295 w	1296 m	
	1275 w			
1312 s		1327 s		} $\nu(\text{P=O})$
1202 vs	1194 vs	1206 vs	1194 s, sh	} $\nu(\text{C-F})$
1167 s	1147 vs	1168 vs	1186 vs	
1125 vs, br	1127 vs	1153 vs	1166 s	
			1153 vs	
			1148 vs	
1072 w	1065 m	1072 w	1067 w	} $\nu_{\text{as}}(\text{C}_2\text{N})$
1000 vs	993 s	998 s	994 s	
985 s, sh	965 s			} $\nu(\text{P=S})$
	778 s		785 s	
759 m		752 w	747 w	
744 w	735 w			
677 m	618 w	717 m	677 s <sup>c</sup>	
552 m, sh				
		589 s	520 s	} $\nu(\text{P-Cl})$
542 m			574 w	
467 w	492 w	535 m	550 m	
450 w		510 m	452 m	

<sup>a</sup> All values in  $\text{cm}^{-1}$ . Abbreviations:  $\nu$ , stretching;  $\delta$ , deformation; s, strong; m, medium; w, weak; v, very; sh, shoulder; as, antisymmetric; s, symmetric; br, broad. <sup>b</sup> In good agreement with ref 16 except for band at  $1460 \text{ cm}^{-1}$  which was given as  $1467 \text{ cm}^{-1}$  and that at  $2900 \text{ cm}^{-1}$  given as  $2910 \text{ cm}^{-1}$ . We do not observe any band at  $540 \text{ cm}^{-1}$  reported earlier.<sup>16</sup> <sup>c</sup> This band may be due to  $\nu(\text{P-Cl})$ . <sup>d</sup> To increase the intensity of the peaks the ir cell was heated to  $60^\circ$ .

tile product. The white solid which remained in the reaction tube was identified as the  $(\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-$  salt by nmr.

**Preparation of  $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$  and  $\text{CF}_3\text{P}(\text{S})\text{Cl}[\text{N}(\text{CH}_3)_2]$ .** (a) The reaction of  $\text{CF}_3\text{P}(\text{S})\text{Cl}_2$  (0.671 g, 3.30 mmol) with excess dimethylamine (0.697 g, 15.49 mmol) occurred immediately on contact at room temperature. After 18 hr at room temperature separation gave unreacted dimethylamine (0.096 g, 2.14 mmol) and  $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$  (0.701 g, 3.18 mmol, 96.5% yield). The reacting ratio  $(\text{CH}_3)_2\text{NH}:\text{CF}_3\text{P}(\text{S})\text{Cl}_2$  is 4.04:1 in agreement with eq 10 ( $\text{E} = \text{S}$ ). Spectroscopic parameters are given in Tables III (nmr) and IV (ir). Mass measurement of the parent molecular ion confirmed the formula (found  $m/e$  220.0404, calcd for  $\text{C}_5\text{H}_{12}\text{F}_3\text{N}_2\text{P}^{32}\text{S}$   $m/e$  220.0409).

(b) Hydrogen chloride (0.0845 g, 2.32 mmol) and  $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$  (0.240 g, 1.1 mmol) were allowed to react for 5 days at  $65^\circ$ . The volatile products were  $\text{CF}_3\text{P}(\text{S})\text{Cl}[\text{N}(\text{CH}_3)_2]_2$  (0.096 g, 0.45 mmol, 41% yield) together with unreacted  $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$  (0.0495 g, 0.22 mmol, 20% yield by nmr) and  $\text{CF}_3\text{P}(\text{S})\text{Cl}_2$  (0.069 g, 0.34 mmol, 31% yield). No HCl was recovered. Spectroscopic parameters of purified  $\text{CF}_3\text{P}(\text{S})\text{Cl}[\text{N}(\text{CH}_3)_2]_2$  are given in Table III (nmr) and Table IV (ir). Mass measurement of the parent molecular ion confirmed the formula (found  $m/e$  210.9605; calcd for  $\text{C}_3\text{H}_6\text{F}_3\text{N}^{32}\text{P}^{35}\text{S}$   $m/e$  210.9599). The quantity of dimethylammonium chloride remaining in the reaction vessel (0.092 g, 1.13 mmol) was consistent with the stoichiometry.

In another experiment HCl (0.0735 g, 2.01 mmol) was treated with  $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$  (0.219 g, 1.0 mmol) for 1 day at room temperature followed by 1 day at  $65^\circ$ . Unreacted HCl was recovered (0.0117 g, 0.47 mmol) along with  $\text{CF}_3\text{P}(\text{S})\text{Cl}_2$  (0.039 g, 0.19 mmol, 19% yield),  $\text{CF}_3\text{P}(\text{S})\text{Cl}[\text{N}(\text{CH}_3)_2]_2$  (0.143 g, 0.67 mmol, 67% yield), as well as unreacted  $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$  (0.325 g, 0.15 mmol, 15% yield). Thus longer reaction times and higher temperatures (*vide supra*) result in complete consumption of HCl; however, the slow reaction of HCl with the diamino compound appears to prevent specific synthesis of the monochloro compound.

**Preparation of  $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$  and  $\text{CF}_3\text{P}(\text{O})\text{Cl}[\text{N}(\text{CH}_3)_2]$ .** (a) The reaction of  $\text{CF}_3\text{P}(\text{O})\text{Cl}_2$  (0.322 g, 1.72 mmol) and dimeth-

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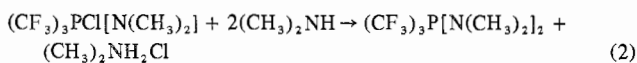
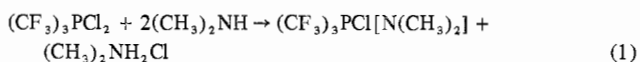
(17) R. C. Dobbie, L. F. Doty, and R. G. Cavell, *J. Amer. Chem. Soc.*, 90, 2015 (1968).

ylamine (0.414 g, 9.20 mmol) proceeded smoothly at room temperature. After 24 hr volatile products were  $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$  (0.267 g, 1.31 mmol, 76% yield) and unreacted dimethylamine (0.107 g, 2.38 mmol). Dimethylammonium chloride (0.264 g, 3.24 mmol) remained in the reaction vessel. The reacting ratio  $(\text{CH}_3)_2\text{NH}:\text{CF}_3\text{P}(\text{O})\text{Cl}_2$  was 3.97:1. The low yield of dialkylamino product is probably due to its rather low volatility and the consequent difficulty of removing it from the solid salt. Spectroscopic parameters of  $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$  are given in Tables III (nmr) and IV (ir).

(b) Hydrogen chloride (0.0402 g, 1.10 mmol) reacted with  $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$  (0.112 g, 0.55 mmol) at room temperature for 2 days to give a mixture of unreacted  $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$  (0.003 g, 0.015 mmol, 3%) and  $\text{CF}_3\text{P}(\text{O})\text{Cl}[\text{N}(\text{CH}_3)_2]$  (0.088 g, 0.44 mmol, 80%). Another fraction contained a small amount of  $\text{CF}_3\text{P}(\text{O})\text{Cl}_2$  (0.0104 g, 0.06 mmol, 10%). No HCl was recovered. The yield of dimethylammonium chloride (0.039 g, 0.48 mmol) is consistent with the stoichiometry. Spectroscopic parameters of  $\text{CF}_3\text{P}(\text{O})\text{Cl}[\text{N}(\text{CH}_3)_2]$  are given in Tables III (nmr) and IV (ir). Mass measurement of the parent molecular ion confirms the formula (found  $m/e$  195.9832, calcd for  $\text{C}_3\text{H}_6\text{F}_3\text{PON}^{35}\text{Cl}$   $m/e$  195.9827).

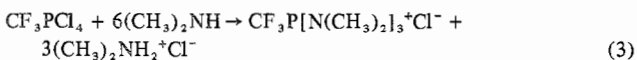
## Results and Discussion

**Synthesis and Characterization of Phosphoranes.** Aminolysis of the chlorophosphorane yields both the diamino phosphorane  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  and the monochloro intermediate  $(\text{CF}_3)_3\text{PCl}[\text{N}(\text{CH}_3)_2]$



The reaction typically produces both products and the monochlorophosphorane is readily converted to the diamino phosphorane by dimethylamine suggesting that the reaction proceeds stepwise. The use of limited quantities of dimethylamine results in incomplete reaction rather than preferential formation of the monochloro derivative, implying that the rates of (1) and (2) are competitive. For example, reaction of 2 mol of dimethylamine with  $(\text{CF}_3)_3\text{PCl}_2$  gave a 25% yield of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  and 75% yield of  $(\text{CF}_3)_3\text{PCl}[\text{N}(\text{CH}_3)_2]$  (relative to consumed dichlorophosphorane); with 4 molar equiv of dimethylamine the yield of the diamino phosphorane increased to 89% and no unconverted chlorophosphorane was detected. Small amounts of  $(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$  and  $\text{CF}_3\text{H}$  were however recovered, perhaps from a substitution reaction on a small amount of  $(\text{CF}_3)_3\text{P}$  which might have been present in the starting material or, possibly, an unknown decomposition reaction. The monochlorophosphorane  $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$  was rather less stable and consequently more difficult to characterize. It appeared to decompose with reduction since small amounts of  $(\text{CF}_3)_3\text{P}$  formed during decomposition; however all products of the decomposition have not been identified.

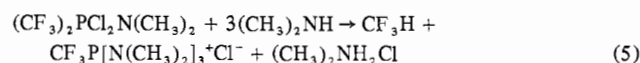
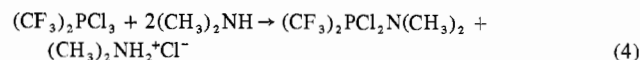
Under similar conditions  $(\text{CF}_3)_2\text{PCl}_3$  was about 50% converted to  $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$ , and  $\text{CF}_3\text{H}$  was observed in the product. Intermediate substitution products such as  $(\text{CF}_3)_2\text{PCl}[\text{N}(\text{CH}_3)_2]_2$  which might have been expected were not observed. The yield of  $\text{CF}_3\text{H}$  increases with the proportion of dimethylamine used and the solid product contains increasing proportions of  $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{Cl}^-$  which can only arise from removal of a  $\text{CF}_3$  substituent from phosphorus by dimethylamine. This new phosphonium salt can also be obtained from the reaction



and details of its characterization will be given elsewhere.<sup>12</sup> Other trifluoromethylphosphonium salts which might be expected from thermal decompositions, rearrangements,

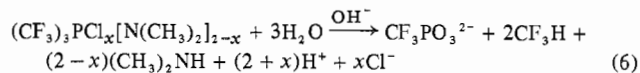
halide loss, or other processes remain unidentified at present, although further investigations are in progress.

More detailed investigation of the aminolysis of  $(\text{CF}_3)_2\text{PCl}_3$ <sup>12</sup> showed that both  $(\text{CF}_3)_2\text{PCl}_2\text{N}(\text{CH}_3)_2$  and the phosphonium salt are formed at all amine:  $(\text{CF}_3)_2\text{PCl}_3$  reaction ratios with maximum yield of  $(\text{CF}_3)_2\text{PCl}_2\text{N}(\text{CH}_3)_2$  being obtained at a reacting ratio of 3:1. Unreacted  $(\text{CF}_3)_2\text{PCl}_3$  is found in the products until the reaction ratio exceeds 5:1. The process can be described as the sum of two major reactions with comparable rates

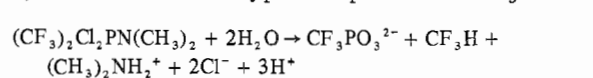


involving initially simple chloride substitution and a more complex process involving removal of Cl and  $\text{CF}_3$  to form the phosphonium salt. Equation 5 has been established by an independent experiment.<sup>12</sup>

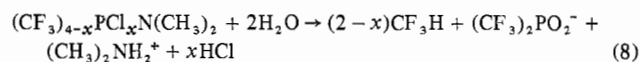
Alkaline hydrolysis of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  gave 2 molar equiv of  $\text{CF}_3\text{H}$ , 1 molar equiv of  $\text{CF}_3\text{PO}_3^{2-}$ , and 2 molar equiv of  $(\text{CH}_3)_2\text{NH}$  (eq 6,  $x = 0$ ). Similarly  $(\text{CF}_3)_3\text{PCl}[\text{N}(\text{CH}_3)_2]$  gave 2 mol of  $\text{CF}_3\text{H}$  and the  $\text{CF}_3\text{PO}_3^{2-}$  ion (eq 6,  $x = 1$ ), and  $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$  gave 1 molar equiv of  $\text{CF}_3\text{H}$  (eq 7). Such behavior is typical of pentavalent  $\text{CF}_3\text{P}$  com-



ounds,<sup>5,10</sup> and these alkaline hydrolysis reactions were used for characterization purposes.



Neutral and acid hydrolysis of  $(\text{CF}_3)_3\text{PCl}[\text{N}(\text{CH}_3)_2]$  gave 1 mol of  $\text{CF}_3\text{H}$  and neutral hydrolysis of  $(\text{CF}_3)_2\text{PCl}_2\text{N}(\text{CH}_3)_2$  gave only a trace of  $\text{CF}_3\text{H}$  forming in all cases the  $(\text{CF}_3)_2\text{PO}_2^-$  ion in solution (eq 8;  $x = 1, 2$ ).



Both the neutral and acid hydrolyses of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{C}-\text{H}_3)_2]_2$  were complex yielding 1.3 and 1.44 mol of  $\text{CF}_3\text{H}$  and forming two ions,  $(\text{CF}_3)_2\text{PO}_2^-$  and the new ion tentatively identified as  $\text{CF}_3\text{PO}_3\text{H}^-$  in the solution. This new species was characterized by comparing its nmr parameters with the known<sup>10</sup> related species  $\text{CF}_3\text{PS}_2\text{OH}^-$  and  $\text{CF}_3\text{PSO}_2\text{H}^-$  and by conversion to the known anion  $\text{CF}_3\text{PO}_3^{2-}$  in basic solution. The complexity undoubtedly arises from the liberation of dimethylamine which converts the neutral medium to a basic one which then causes further hydrolysis of  $(\text{CF}_3)_2\text{PO}_2^-$  to yield additional  $\text{CF}_3\text{H}$  and  $\text{CF}_3\text{PO}_3^{2-}$ . This does not occur with the Cl-containing compounds because HCl is also liberated which neutralizes the amine. In the strong acid solution further hydrolysis of  $(\text{CF}_3)_2\text{PO}_2^-$  also occurred leading to the new anion  $\text{CF}_3\text{PO}_3\text{H}^-$  and additional  $\text{CF}_3\text{H}$ . The non-stoichiometric results obtained from acid hydrolysis reactions are probably due to their slower reaction rates.

**Some Reactions of the Phosphoranes.** Starting materials were recovered from the reaction of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  with a large excess of  $(\text{CH}_3)_2\text{NH}$  over a period of days at room temperature although in view of the behavior of  $(\text{CF}_3)_2\text{PCl}_3$  with dimethylamine<sup>12</sup> some  $\text{CF}_3\text{H}$  formation might have been expected. Quantitative conversion of

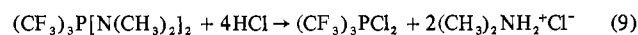
Table V. Reaction Products of  $(CF_3)_3P[N(CH_3)_2]_2$  and  $CH_3SH$ 

	Expected quantities according to				Obsd
	Eq 11	Eq 12	Eq 13	Total	
$CF_3H$	0.42	0.05		0.47	0.50
$CH_3SSCH_3$	0.21	0.05	0.01	0.27	0.34 <sup>a</sup>
$(CH_3)_2NH$		0.10	0.02	0.12	<sup>b</sup>

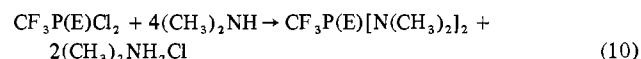
<sup>a</sup> Contained some  $(CH_3)_2NH$ . <sup>b</sup> Present in  $CH_3SSCH_3$  fraction.

$(CF_3)_3PCl[N(CH_3)_2]$  to  $(CF_3)_3P[N(CH_3)_2]_2$  was achieved with excess dimethylamine; thus, as expected, Cl is readily replaced by  $N(CH_3)_2$  but  $CF_3$  is not. The relatively unusual systems in which  $CF_3H$  can be easily eliminated from  $CF_3P$  compounds by dimethylamine (for example  $(CF_3)_3PO$ ,<sup>19</sup>  $(CF_3)_2POSi(CH_3)_3$ ,<sup>20</sup> and the aminolysis of  $(CF_3)_2PCl_3$ <sup>12</sup>) must have particular mechanistic pathways available to them. It is interesting to note (*vide infra*) that more acidic reagents such as methanol, methyl mercaptan, and  $H_2S$  can apparently liberate  $CF_3H$  from the phosphorane with different degrees of facility.

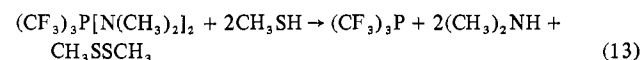
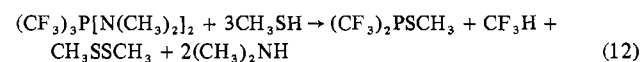
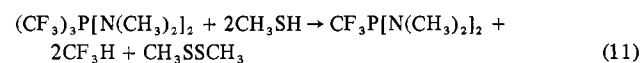
No reaction occurred between  $(CF_3)_3P[N(CH_3)_2]_2$  and anhydrous HCl at low partial pressures. However  $(CF_3)_3P-PCl_2$  was obtained in 54% yield when  $(CF_3)_3P[N(CH_3)_2]_2$  was allowed to react with excess HCl at high partial pressures according to eq 9.



The only identified phosphorus-containing product resulting from the reaction of  $(CF_3)_3P[N(CH_3)_2]_2$  and  $CH_3OH$  was  $CF_3P(O)[N(CH_3)_2]_2$  along with 1 mol of  $CF_3H$  and 0.3 mol of dimethylamine plus smaller amounts of at least two other unidentified  $CF_3P$ -containing compounds which were detected among the products by nmr spectroscopy. The phosphine oxide  $CF_3P(O)[N(CH_3)_2]_2$  was characterized by comparison of its nmr parameters with those of an authentic sample prepared from  $CF_3P(O)Cl_2$  and dimethylamine (eq 10,  $E = O$ ).



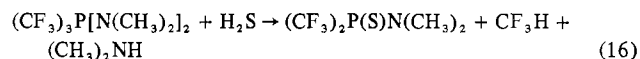
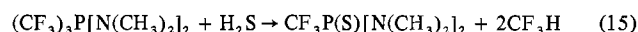
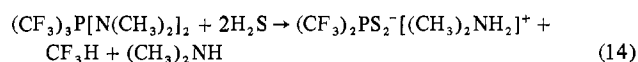
The reaction of  $(CF_3)_3P[N(CH_3)_2]_2$  with  $CH_3SH$  appeared to proceed along three pathways leading to  $CF_3P[N(CH_3)_2]_2$ ,  $(CF_3)_2PSCH_3$ , and  $(CF_3)_3P$  as the major phosphorus-containing products in 68.5, 15.5, and 4.5% yield, respectively. Simplified routes leading to these three compounds are represented in eq 11–13 although the overall reaction mechanism



is quite possibly more complicated. Other products identified were  $CF_3H$ ,  $CH_3SSCH_3$ , and  $(CH_3)_2NH$  produced in amounts consistent with the above stoichiometries (Table V). The yield of unique P compound was used to estimate the contribution of each reaction to the total.

Treatment of  $(CF_3)_3P[N(CH_3)_2]_2$  with  $H_2S$  gave 11.7 and 13.0% yields of  $CF_3P(S)[N(CH_3)_2]_2$ <sup>16</sup> and  $(CF_3)_2P(S)N-$

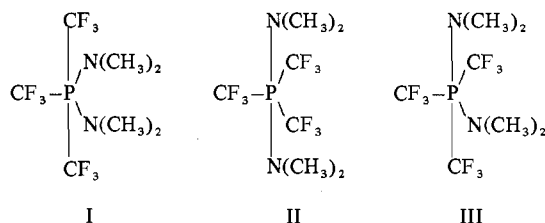
$(CH_3)_2$ ,<sup>16,17</sup> respectively, and a 67.5% yield of the  $(CF_3)_2-PS_2^-$  ion<sup>10</sup> as deduced from the amount of  $CF_3H$  evolved. These results can be summarized by eq 14–17 although again



the overall reaction mechanism may be more complicated. The yields of  $(CH_3)_2NH$  and  $CF_3H$  were again consistent with the stoichiometries described by these equations allowing for the reaction of  $(CH_3)_2NH$  with excess  $H_2S$ . The identity of  $CF_3P(S)[N(CH_3)_2]_2$ <sup>16</sup> was established by comparison of its nmr parameters with those obtained on an authentic sample prepared from  $CF_3P(S)Cl_2$ <sup>18</sup> and dimethylamine (eq 10,  $E = S$ ). Authentic nmr parameters are given in Table III.

**Nmr Spectroscopic Studies and Stereochemistry of the Phosphoranes.** Much information has been obtained on the stereochemistry of pentacoordinate phosphorus compounds from nmr studies although in the case of  $CF_3P$  phosphoranes the results have been somewhat ambiguous.<sup>3</sup> The behavior of the new aminophosphoranes however provides further information which resolves some of these ambiguities.

There are three possible combinations of locations of  $CF_3$  groups within the trigonal-bipyramidal framework<sup>1–4</sup> of the compound  $(CF_3)_3P[N(CH_3)_2]_2$ : (1) a structure with two equatorial  $N(CH_3)_2$  groups (I), (2) one with two axial  $N(CH_3)_2$  groups (II), and (3) a third alternative with one  $N(CH_3)_2$  group in the equatorial position and the other  $N(CH_3)_2$  group in the axial position (III).



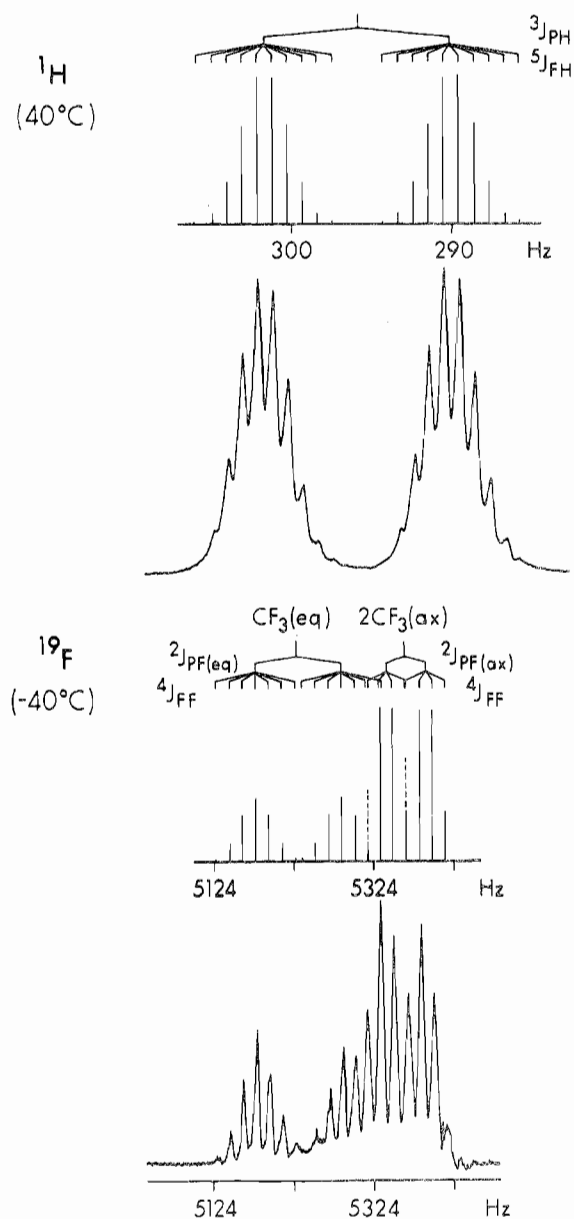
The room temperature <sup>1</sup>H nmr spectrum of  $(CF_3)_3P[N(CH_3)_2]_2$  shows an apparent doublet of either octets or decets (Figure 2) with an intensity distribution in good agreement with that expected for the central eight lines of a ten-line pattern. This spectrum arises from coupling to a phosphorus nucleus and nine equivalent fluorine atoms thus confirming the presence of three  $CF_3$  groups on phosphorus. On cooling of the sample to  $-80^\circ$  the doublet observed in the <sup>1</sup>H spectrum remained unchanged indicating that the  $N(CH_3)_2$  groups are equivalent at this temperature suggesting that structure III probably does not occur although it cannot be conclusively excluded by this evidence.

At room temperature the <sup>19</sup>F nmr spectrum was a broad multiplet (Figure 3). Upon cooling to  $-40^\circ$  the multiplets were completely resolved into two overlapping chemically shifted regions with a 2:1 intensity ratio. These consisted of a doublet of quartets and a doublet of septets, respectively (Figure 2). At  $-90^\circ$  the higher intensity peaks had lost their fine structure (Figure 3) and were replaced by further unresolved complex multiplets appearing in detail at  $-140^\circ$  (Figure 3). The lower intensity peaks lost their fine structure at  $-115^\circ$  (Figure 3) and did not resolve again within the temperature range studied. These features are understandable on the basis of structure I, the two different en-

(19) A. B. Burg and A. J. Sarkis, *J. Amer. Chem. Soc.*, **87**, 238 (1965).

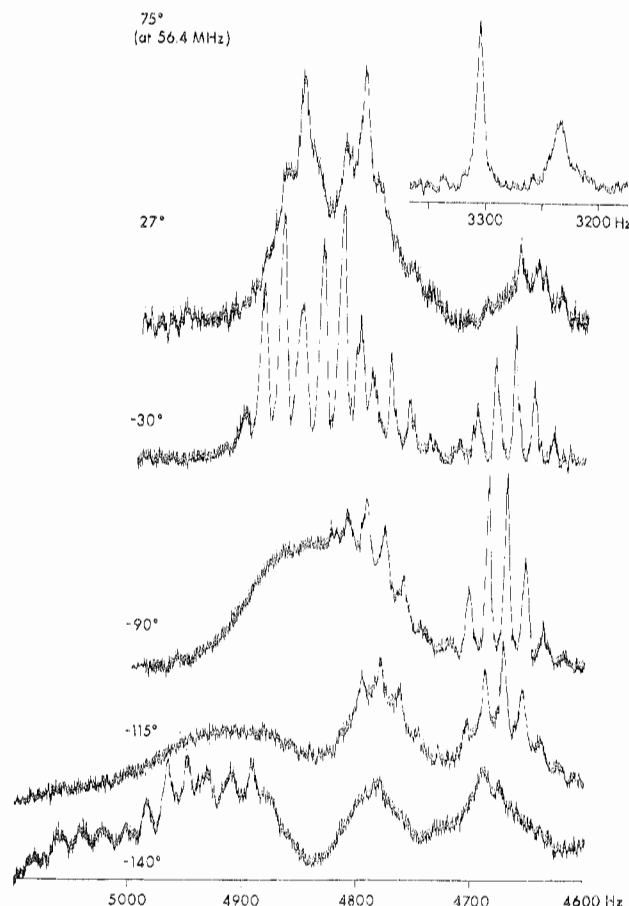
(20) R. G. Cavell, R. D. Leary, A. R. Sanger, and A. J. Tomlinson, *Inorg. Chem.*, **12**, 1374 (1973).





**Figure 2.** Nmr spectra of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ . The upper portion of the figure shows the calculated (stick diagram) and observed (lower trace) 100-MHz  $^1\text{H}$  nmr spectra of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  obtained at  $40^\circ$ . The frequency scale is measured relative to TMS with a positive sign denoting lower field. The lower portion of the figure shows the calculated (stick diagram) and observed 94.1-MHz  $^{19}\text{F}$  nmr spectra of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  at  $-40^\circ$ . The frequency scale is measured relative to  $\text{CFCl}_3$ , with a positive sign denoting high field.

vironments of  $\text{CF}_3$  groups giving rise to well-resolved multiplets observed at  $-30^\circ$ . The quartets and septets in this spectrum result from the coupling ( $^4J_{\text{FF}} = 16.5$  Hz) between the two types of  $\text{CF}_3$  groups, thus eliminating structure II which contains three equivalent  $\text{CF}_3$  groups. At temperatures below  $-90^\circ$  additional processes (most probably those involving restricted rotation around the P-N bonds) occur which destroy the equivalences within the  $\text{CF}_3$  group such that a complex second-order  $^{19}\text{F}$  nmr spectrum results because the different environments of the F atoms can then be distinguished. These features are very similar to those observed in the  $^{19}\text{F}$  nmr spectrum of  $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ <sup>21</sup> and are at present poorly understood because of the difficul-



**Figure 3.** Temperature dependence of the  $^{19}\text{F}$  nmr spectrum of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ . The spectrum obtained at  $75^\circ$  was measured at 56.4 MHz on a  $\text{C}_6\text{F}_6$  solution of the compound while those obtained at  $27^\circ$ ,  $-30^\circ$ ,  $-90^\circ$ ,  $-115^\circ$ , and  $-140^\circ$  were measured at 84.7 MHz on a  $\text{CF}_2\text{Cl}_2$  solution of the compound. The frequency scales are measured relative to  $\text{CFCl}_3$ , with a positive sign denoting resonance to high field of the standard.

ty of making unambiguous spectral assignments. Further, there is no clear method of separating the interactions of two  $\text{N}(\text{CH}_3)_2$  (or  $\text{OSi}(\text{CH}_3)_3$ ) groups with each other from the interactions of these groups with the  $\text{CF}_3$  groups. Additional studies now in progress on simpler compounds<sup>22</sup> will hopefully allow detailed elucidation of the averaging processes involved in these molecules.

The preferred structure (I) therefore is in agreement with the structure predicted by the rule proposed by Muetterties, *et al.*,<sup>3</sup> in which the most electronegative substituent (in this case  $\text{CF}_3$ )<sup>23</sup> is considered to occupy preferentially the axial position of a trigonal bipyramid. At relatively high temperatures the distinction between axial and equatorial substituents is usually obscured by environmental averaging of the substituents due to a pseudorotation type of process. The room-temperature spectrum of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  represents an intermediate state between the distinction of axial and equatorial environments observed below  $-30^\circ$  and the fast exchange which is approached upon heating to  $+75^\circ$  (see Figure 3). Increased temperatures were not investigated because the compound is thermally unstable.<sup>8</sup>

Similar studies were applied to  $(\text{CF}_3)_3\text{PCl}[\text{N}(\text{CH}_3)_2]$  in the hope of distinguishing the  $\text{CF}_3$  environments therein. The room-temperature  $^1\text{H}$  spectrum shows an apparent doublet of either octets or decets, with an intensity distribution in

(21) R. G. Cavell, R. D. Leary, and A. J. Tomlinson, *Inorg. Chem.*, **11**, 2578 (1972).

(22) R. G. Cavell and K. I. The, unpublished data.

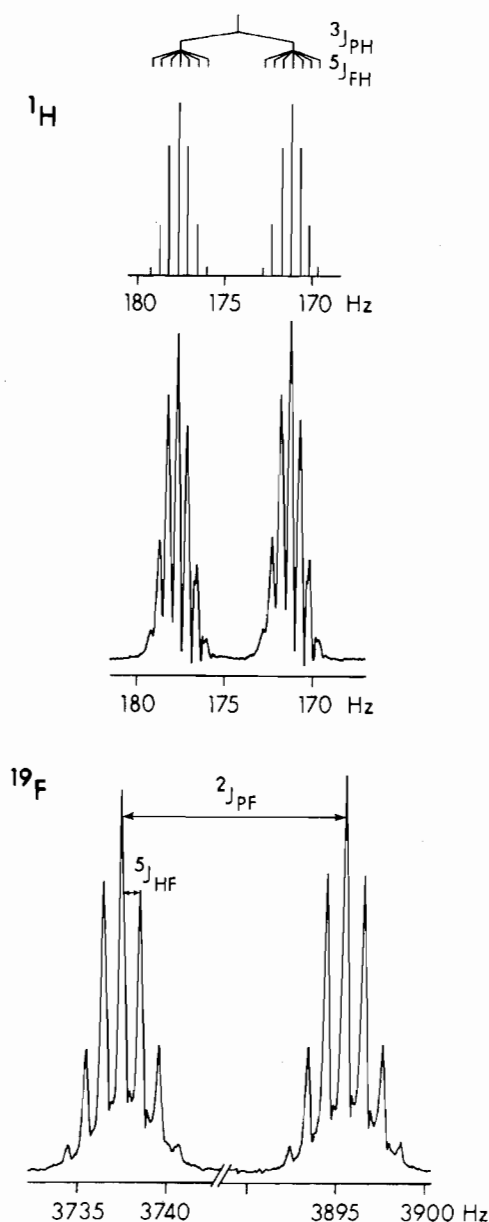
(23) J. J. Lagowski, *Quart. Rev., Chem. Soc.*, **13**, 233 (1959).

good agreement with that expected for the central eight lines of a ten-line pattern. This spectrum arises from coupling to the phosphorus nucleus and nine equivalent fluorine atoms thus confirming the presence of the three trifluoromethyl groups on phosphorus. The  $^{19}\text{F}$  nmr spectrum showed a doublet of septets arising from coupling to the phosphorus nucleus and six equivalent hydrogen atoms, thus confirming the presence of a single dimethylamine group. Low-temperature  $^{19}\text{F}$  nmr studies of  $(\text{CF}_3)_3\text{PCl}[\text{N}(\text{CH}_3)_2]$  showed a similar behavior to that of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ ; however only partial resolution of the  $\text{CF}_3$  signal into two chemically shifted regions of relative intensity 2:1 with large and small  $^2J_{\text{PF}}$  coupling constants suggestive of equatorial and axial  $\text{CF}_3$  groups, respectively, was achieved for  $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$  at  $-120^\circ$  (the lowest feasible temperature in this case) whereas in  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  these same features were clearly visible in the  $-30^\circ$  spectrum (Figure 3). As a result reliable conclusions regarding the stereochemistry of  $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$  could not be obtained but it seems clear that Cl preferentially occupies an axial site in this compound even though it is thought to possess a lower electronegativity than  $\text{CF}_3$ <sup>23</sup> suggesting that factors other than simple electronegativity considerations are involved in determining locational preferences.

The room-temperature  $^1\text{H}$  spectrum of  $(\text{CF}_3)_2\text{PCl}_2[\text{N}(\text{CH}_3)_2]$  (Figure 4) shows a doublet of septets arising from coupling of the protons to the phosphorus atom ( $^3J_{\text{PH}} = 12.5$  Hz) and to six equivalent F atoms ( $^5J_{\text{FH}} = 1.05$  Hz) thus confirming the presence of two  $\text{CF}_3$  groups on phosphorus. The room-temperature  $^{19}\text{F}$  spectrum (also shown in Figure 4) shows a doublet of septets arising from coupling of the fluorine atoms to a phosphorus atom ( $^2J_{\text{PF}} = 156.9$  Hz) and also to six equivalent protons ( $^3J_{\text{FH}} = 1.09$  Hz), thus confirming the presence of one  $\text{N}(\text{CH}_3)_2$  group attached to a phosphorus atom. The temperature independence (down to  $-120^\circ$ ) of the  $^{19}\text{F}$  and  $^1\text{H}$  nmr spectra and the large value of  $^2J_{\text{PF}}$  strongly suggest that both Cl atoms occupy axial positions and the equatorial positions are occupied by  $\text{CF}_3$  and  $\text{N}(\text{CH}_3)_2$  groups. The  $^{31}\text{P}$  chemical shift of +143.5 ppm vs.  $\text{P}_4\text{O}_6$  and the spin-spin splitting pattern (septet,  $^2J_{\text{PF}}$  159 Hz) confirm the identity of the molecule as a phosphorane and the presence of two  $\text{CF}_3$  groups on P.

If the interpretation is correct, the spectral data indicate that both  $(\text{CF}_3)_3\text{PClN}(\text{CH}_3)_2$  and  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  undergo positional exchange of  $\text{CF}_3$  groups with the former possessing a lower barrier than the latter. The relative barriers are understandable if a Berry<sup>2a</sup> or permutationally equivalent mechanism is responsible since in the latter compound this rearrangement mechanism requires one  $\text{N}(\text{CH}_3)_2$  group to occupy an axial position which is likely a highly unfavorable configuration. In contrast both chloro-substituted compounds can undergo a pseudorotational rearrangement in which  $\text{N}(\text{CH}_3)_2$  groups remain in the equatorial position. The high  $^2J_{\text{PF}}$  value and the temperature independence of the  $^{19}\text{F}$  spectral parameters of  $(\text{CF}_3)_2\text{PCl}_2\text{N}(\text{CH}_3)_2$  lead us to believe that this molecule possesses a structure at ordinary temperatures in which Cl groups preferentially occupy the axial positions. Thus we have in this case a *high* barrier to permutational exchange arising from the destabilization which would result upon replacing axial Cl groups by  $\text{CF}_3$  groups. This suggests that rearrangement barriers are dependent upon *relative* axial preferences which may be predictable as discussed below.

Many other factors must however be considered which could undermine the above interpretation. First we recog-



**Figure 4.** Proton and  $^{19}\text{F}$  nmr spectra of  $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$ . The  $^1\text{H}$  spectrum was measured at 60 MHz on a solution in  $\text{CFCl}_3$  at  $40^\circ$ . The frequency scale is measured relative to TMS with a positive sign denoting resonance to lower field of standard. The  $^{19}\text{F}$  spectrum was measured at 56.4 MHz on a solution in  $\text{CFCl}_3$  at  $40^\circ$ . In this case the frequency scale is measured relative to  $\text{CFCl}_3$  with a positive sign denoting resonance to high field of the standard. The calculated  $^1\text{H}$  spectrum, using the parameters given in Table III, is shown as a stick diagram above the observed spectrum.

nize that the lack of distinction between  $\text{CF}_3$  group environments in  $(\text{CF}_3)_2\text{PCl}_2\text{N}(\text{CH}_3)_2$  does not prove that both  $\text{CF}_3$  groups occupy equivalent equatorial positions since a fast rearrangement with a low barrier, a dissociative, or a catalyzed bimolecular exchange<sup>24</sup> process may prevent the experimental resolution within the temperature range available. We think that all this is unlikely however because the different  $\text{CF}_3$  environments can be resolved in  $(\text{CF}_3)_3\text{PClN}(\text{CH}_3)_2$  although with some difficulty. Additional complications arise in the spectra as a result of the possibility of restricted rotation about P-N bonds, the possibility of inversion at nonplanar nitrogen atoms, and the further complication

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arising from the presence of two  $\text{N}(\text{CH}_3)_2$  groups in  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]$  which may interact with each other as well as with the  $\text{CF}_3$  groups. It is not clear whether the planarity of nitrogen observed in the fluorophosphine<sup>25</sup>  $\text{F}_2\text{PN}(\text{CH}_3)_2$  will persist in trifluoromethyl-substituted aminophosphines or aminophosphoranes where the phosphorus is five-coordinated.

It is worth noting at this point that temperature reduction causes a broadening of resonances assigned to axial  $\text{CF}_3$  groups in the spectra of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  (Figure 3), whereas the line widths of equatorial  $\text{CF}_3$  groups are relatively constant at similar low temperatures. This could be associated with the stabilization of a preferred conformation in which the  $\text{CH}_3$  groups on N interact more strongly with axial  $\text{CF}_3$  groups than with the equatorial  $\text{CF}_3$  groups as a result of restricted rotation about P-N bonds or some similar process. The complexity of the  $^{19}\text{F}$  spectra and the lack of resolution of any features in the  $^1\text{H}$  spectra (down to  $-90^\circ$ ) which could be ascribed to the existence of preferential conformations of  $\text{N}(\text{CH}_3)_2$  groups in the molecule suggest that such interpretations are premature. This interpretation is however consistent with the unchanged spectra of  $(\text{CF}_3)_2\text{PCl}_2\text{N}(\text{CH}_3)_2$  within the temperature range investigated since the proposed exclusive equatorial positioning of both  $\text{CF}_3$  groups would render their interaction with the  $\text{CH}_3$  groups so small as to be probably unobservable. Further the symmetry of this molecule when both Cl groups are fixed in axial positions precludes observation of the effects of "stopped" P-N bond rotation. We hope to apply line shape analysis to the simpler systems<sup>22</sup> now under investigation with the aim of clarifying the averaging processes involved in these molecules.

#### Substitutional Preference of $\text{CF}_3$ Groups—a Suggestion.

The nmr results obtained herein and elsewhere<sup>26</sup> consistently suggest that  $\text{CF}_3$  groups preferentially occupy equatorial positions in halogenophosphoranes even when the  $\text{CF}_3$  group has a lower electronegativity than the halogen. Halogens are thus more "apicophilic,"<sup>24</sup> perhaps because axial bonding is more ionic than equatorial.<sup>2c,4</sup> While calculations suggested<sup>4</sup> that  $\pi$ -bonding groups would favor the equatorial positions as seems to be the case, a superior rationalization of substituent preferences is provided by the association<sup>26</sup> of the relative "apicophilicity" of substituents with the inductive parameter<sup>27</sup>  $\sigma_I$ . Halogens, with large  $\sigma_I$ , prefer axial locations and the  $\text{NR}_2$  group, with a low  $\sigma_I$ , prefers an equatorial location (or avoids axial locations).  $\text{CF}_3$ , with an intermediate  $\sigma_I$  value, shows no strong substitutional preferences and its location is apparently determined by the properties of the other substituents.

Compounds containing  $\text{N}(\text{CH}_3)_2$  groups and less than two halogens are characterized by a low value of  $^2J_{\text{PF}}$ . In the case of  $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ , low-temperature  $^{19}\text{F}$  spectra indicate the existence of two  $\text{CF}_3$  environments, one with a large ( $>100$  Hz) and one with a small ( $<50$  Hz) coupling to phosphorus. Relative intensity distribution suggests that the former is associated with an equatorial  $\text{CF}_3$  group and the latter with the axial  $\text{CF}_3$  groups and the room-temperature value is the weighted average of the two values associated with specific environments. Similar behavior is illustrated by  $(\text{CF}_3)_3\text{PCl}[\text{N}(\text{CH}_3)_2]$  and  $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ <sup>21,22</sup> where, although the spectra are complex and as yet incom-

**Table VI.** Coupling Constants of Trifluoromethylfluoro- and -chlorophosphoranes

	$^2J_{\text{PCF}}$ , Hz	Ref		$^2J_{\text{PCF}}$ , Hz	Ref
$\text{CF}_3\text{PF}_4$	172	28	$\text{CF}_3\text{PCl}_3\text{F}$	149	31
$(\text{CF}_3)_2\text{PF}_3$	175	3, 28	$\text{CF}_3\text{PCl}_2\text{F}_2$	165	32
$(\text{CF}_3)_3\text{PF}_2$	167	28	$(\text{CF}_3)_2\text{PCl}_3$	193 <sup>a</sup>	12, 31
$\text{CF}_3\text{PCl}_4$	154	31	$(\text{CF}_3)_3\text{PCl}_2$	152 <sup>a</sup>	12

<sup>a</sup> This value of the coupling constant remains essentially unchanged down to  $-140^\circ$  suggesting that the  $\text{CF}_3$  groups remain chemically equivalent.<sup>12</sup>

pletely assigned, it is possible to see larger and smaller couplings of  $\text{CF}_3$  to P. Further confirmation is provided by the behavior of  $(\text{CF}_3)_2\text{PCl}_2\text{N}(\text{CH}_3)_2$  where, according to our proposals,<sup>26</sup> Cl should occupy axial sites preferentially and the  $\text{N}(\text{CH}_3)_2$  group should occupy one of the equatorial sites. In this case the  $^{19}\text{F}$  spectrum was essentially temperature invariant and the  $^2J_{\text{PCF}}$  coupling had a value of 156.9 Hz which we think is characteristic of an equatorial  $\text{CF}_3$  substituent.

The fluorophosphoranes  $\text{CF}_3\text{PF}_4$ ,  $(\text{CF}_3)_2\text{PF}_3$ , and  $(\text{CF}_3)_3\text{PF}_2$  all have large  $^2J_{\text{PF}}$  coupling constants<sup>3,28</sup> (Table VI) and, in keeping with the preferential location of F to the axial position, we would consistently assign  $\text{CF}_3$  to equatorial substitutional positions in all these molecules. The original tentative assignments, based mainly on chemical shift and coupling constant (excluding  $^2J_{\text{PF}}$ ) arguments, are in agreement with equatorial positioning of the  $\text{CF}_3$  group with the exception of the case of  $(\text{CF}_3)_2\text{PF}_3$  which was assigned<sup>3</sup> a structure containing two axial  $\text{CF}_3$  groups. We suggest however that equatorial  $\text{CF}_3$  groups are also indicated by the  $^2J_{\text{PF}}$  value in  $(\text{CF}_3)_2\text{PF}_3$ . Vibrational spectroscopy<sup>29</sup> indicates a  $C_{2v}$  (an equatorial  $\text{CF}_3$  group) structure for  $\text{CF}_3\text{PF}_4$  in keeping with the original<sup>3</sup> and present nmr assignments; however a microwave study<sup>30</sup> of  $\text{CF}_3\text{PF}_4$  indicates  $C_{3v}$  (axial  $\text{CF}_3$  structure) symmetry. The reason for this discrepancy is not clear since both vibrational and microwave spectra were obtained on the vapor state of the compound whereas nmr data are obtained from (admittedly dilute) solutions.

It also seems reasonable to suggest that the known trifluoromethylchlorophosphoranes, all of which have large  $^2J_{\text{PF}}$  coupling constants<sup>7,12,31,32</sup> (Table VI), possess only equatorial  $\text{CF}_3$  substituents in solution consistent with the preferential axial location of the Cl suggested herein and elsewhere<sup>26</sup> even though  $\text{CF}_3$  has the higher electronegativity. This is further supported by the fact that  $\text{CF}_3\text{PCl}_2\text{F}_2$ ,<sup>32</sup> which undoubtedly possesses an equatorial  $\text{CF}_3$  substituent and axial F substituents, has a  $^2J_{\text{PCF}}$  coupling constant in good agreement with the other chlorophosphoranes in Table VI. We suggest that  $^2J_{\text{PF}}$  values are a better indicator of  $\text{CF}_3$  location than chemical shift values<sup>3</sup> which are more readily influenced by external perturbations. They may also be a better indicator than directly bound coupling constants which can be dramatically altered by rehybridization of either atom whereas in the case of the indirect coupling constant, the hybridization of one atom (in this case F on C) probably remains relatively unchanged even with large changes in substitution on phosphorus.

It seems reasonable to associate large  $^2J_{\text{PF}}$  values with

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equatorial substitution where the "s" contribution to the bonding is likely to be much greater than in the axial bonds.<sup>4,33</sup> Precise values have not yet been obtained for all possible axial CF<sub>3</sub> coupling constants because of the difficulty of analysis of the nmr spectra of substituted phosphoranes which become very complex at low temperatures; however it seems clear that axial CF<sub>3</sub> groups tend to have a smaller <sup>2</sup>J<sub>PF</sub> value than equatorial CF<sub>3</sub> groups.<sup>26</sup> The equatorial coupling constants may be well established by the large values of <sup>2</sup>J<sub>PF</sub> demonstrated by the chlorophosphoranes and by (CF<sub>3</sub>)<sub>2</sub>PCl<sub>2</sub>[N(CH<sub>3</sub>)<sub>2</sub>].

The proposed exclusive equatorial CF<sub>3</sub> substitution in chlorophosphoranes arising from the present nmr studies is unfortunately at variance with vibrational studies on these molecules. Both CF<sub>3</sub>PCl<sub>4</sub><sup>34</sup> and (CF<sub>3</sub>)<sub>2</sub>PCl<sub>3</sub><sup>35</sup> appear to

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have C<sub>3v</sub> symmetry (axial CF<sub>3</sub> groups). The reason for this inconsistency is not known but may arise from the difference in physical state since vibrational studies were done on gaseous samples (except for some Raman data on the neat liquids)<sup>34,35</sup> whereas nmr studies involve dilute solutions. Further inquiry into this problem is warranted.

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**Registry No.** (CF<sub>3</sub>)<sub>3</sub>PCl<sub>2</sub>, 420-72-4; (CH<sub>3</sub>)<sub>2</sub>NH, 124-40-3; (CF<sub>3</sub>)<sub>3</sub>P[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, 51874-38-5; CF<sub>3</sub>PO<sub>3</sub>H<sup>-</sup>, 51965-63-0; (CF<sub>3</sub>)<sub>2</sub>PCl<sub>3</sub>, 353-77-5; (CF<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>PN(CH<sub>3</sub>)<sub>2</sub>, 51874-47-6; (CF<sub>3</sub>)<sub>3</sub>P(Cl)N(CH<sub>3</sub>)<sub>2</sub>, 52021-56-4; CF<sub>3</sub>P(S)Cl<sub>2</sub>, 18799-78-5; CF<sub>3</sub>P(S)[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, 18894-82-1; CF<sub>3</sub>P(S)Cl[N(CH<sub>3</sub>)<sub>2</sub>], 51965-67-4; CF<sub>3</sub>P(O)Cl<sub>2</sub>, 51965-64-1; CF<sub>3</sub>-P(O)[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, 51965-65-2; CF<sub>3</sub>P(O)Cl[N(CH<sub>3</sub>)<sub>2</sub>], 51965-66-3; (CF<sub>3</sub>)<sub>2</sub>PN(CH<sub>3</sub>)<sub>2</sub>, 432-01-9; CH<sub>3</sub>OH, 67-56-1; CH<sub>3</sub>SH, 74-93-1; H<sub>2</sub>S, 7783-06-4; HCl, 7647-01-0.

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## Investigation of the Reactions of Tetrafluorodiphosphine with Some 3-Substituted Propene Derivatives<sup>1</sup>

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The investigation of the reaction of P<sub>2</sub>F<sub>4</sub> with F<sub>2</sub>PCH<sub>2</sub>CH=CH<sub>2</sub> and H<sub>2</sub>NCH<sub>2</sub>CH=CH<sub>2</sub> has resulted in the formation of the new compounds F<sub>2</sub>PCH<sub>2</sub>CHPF<sub>2</sub>CH<sub>2</sub>PF<sub>2</sub> and F<sub>2</sub>PNHCH<sub>2</sub>CH=CH<sub>2</sub>. (CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>CH=CH<sub>2</sub> reacts in the dark with P<sub>2</sub>F<sub>4</sub> to give unidentified solid products. The formation of PF<sub>2</sub>CH<sub>2</sub>CHPF<sub>2</sub>CH<sub>2</sub>PF<sub>2</sub> proceeds by a free-radical path. The tribasic character of this compound has been demonstrated by the formation of a triadduct with B<sub>2</sub>H<sub>6</sub>. The relative Lewis basicities of the two kinds of phosphorus in F<sub>2</sub>PCH<sub>2</sub>CHPF<sub>2</sub>CH<sub>2</sub>PF<sub>2</sub> have been investigated by an nmr study of a 1:1 mixture of B<sub>2</sub>H<sub>6</sub> and F<sub>2</sub>PCH<sub>2</sub>CHPF<sub>2</sub>CH<sub>2</sub>PF<sub>2</sub>.

### Introduction

The free-radical addition of P<sub>2</sub>F<sub>4</sub> to the double bond of ethene has been recently reported.<sup>2</sup> In this investigation, the generality of the free-radical behavior of P<sub>2</sub>F<sub>4</sub> toward double bonds has been tested in three propene derivatives with phosphorus or nitrogen in the 3 position.

### Experimental Section

**General Techniques.** Standard high-vacuum techniques were used throughout. A uv wavelength of 3000 Å was employed in all irradiations. *N,N*-Dimethylallylamine (Eastman) and allylamine (Aldrich) were dried over Linde 3A molecular sieves and were distilled prior to use. All nmr data were obtained on a Varian XL-100-12 spectrometer. Nmr chemical shifts were obtained by the tube-interchange technique. Ir data were obtained on a Beckman IR-20A spectrometer. Solid-phase ir spectra were obtained at -196° using a low-temperature cell.<sup>3</sup> Mass spectral data were obtained on a Hitachi Perkin-Elmer RMU-6E spectrometer operating at 70 eV. Expected isotope peaks were observed but are omitted for brevity in the data following, as are peaks of mass number 30 or less and others not essential to characterization.

#### Preparation and Properties of 1,2,3-Tris(difluorophosphino)-

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**propane.** In a typical reaction, 1.27 mmol of P<sub>2</sub>F<sub>4</sub><sup>4</sup> and 0.65 mmol of PF<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub><sup>5</sup> were condensed at -196° into a 100-ml quartz reaction tube and allowed to warm to room temperature (both reactants were completely vaporized). The reaction mixture was then irradiated for 20 min. During the course of the irradiation, formation of a green-yellow solid on the sides of the reaction vessel was observed as well as the formation of a liquid in the bottom of the reaction tube. The reaction mixture was condensed to -196° and then distilled through traps held at 0, -45, and -196°. No material was apparent in the trap held at 0°. The trap held at -196° held 0.73 mmol of material which was identified (ir) as a mixture of PF<sub>3</sub> and P<sub>2</sub>F<sub>4</sub>. The trap held at -45° contained 0.48 mmol (mass) of a colorless liquid of low volatility (vp = 1 mm at 25.9°) which was subsequently identified as PF<sub>2</sub>CH<sub>2</sub>CHPF<sub>2</sub>CH<sub>2</sub>PF<sub>2</sub>. The yield of PF<sub>2</sub>CH<sub>2</sub>CHPF<sub>2</sub>CH<sub>2</sub>PF<sub>2</sub> based on the amount of PF<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub> used was 73.5%. The liquid slowly decomposes to a yellow solid if allowed to stand at room temperature as indicated by the presence of a solid, yellow residue after transfer. In the absence of uv irradiation, no F<sub>2</sub>PCH<sub>2</sub>CHPF<sub>2</sub>CH<sub>2</sub>PF<sub>2</sub> was obtained from the reaction mixture. After extended irradiation (1.5 hr) no product was obtained, presumably a result of decomposition. The gas-phase ir of PF<sub>2</sub>CH<sub>2</sub>CHPF<sub>2</sub>CH<sub>2</sub>PF<sub>2</sub> shows the following absorption bands (relative intensity and tentative assignment in parentheses) (cm<sup>-1</sup>): 2880 (vw, ν(C-H)), 1395 (w, δ<sub>s</sub>(PCH<sub>2</sub>)), 1373 (w), 1350 (w, δ(HCH)), 1022 (m), 990 (w), 811 (s, ν(P-F)), 663 (m, ν(P-C)). The solid-phase ir shows absorption bands at 2890 (m, ν(C-H)), 2823 (w,

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