the plots of k_0 vs. $[H^+]$ were found to be $(3.1 \pm 0.3) \times 10^{-4}$, $(8.0 \pm 0.6) \times 10^{-4}$, $(19 \pm 1.1) \times 10^{-4}$, and $(26 \pm 1) \times 10^{-4}$ s^{-1} at 25, 35, 45, and 50°, respectively.

It appears that the nucleophilic attack of OH of the water on phosphorus of the peroxydiphosphate is much easier, as suggested by Franchuk and Brodskii,[11] than the nucleophilic attack[21] of bromide on the oxygen of the peroxydiphosphate; hence the reaction prefers the hydrolytic path rather than a direct redox reaction. The attack by OH on P would be facilitated by the less negative charge on the peroxydiphosphate ion resulting in catalysis by the hydrogen ion. The reaction, therefore, is faster with species $H_3P_2O_8^-$. The mechanism is similar to that of phosphate esters and related compounds.[22]

A comparison of the results of the present investigation with those of the oxidation of iodide[7] shows little similarity between the two. The latter involves a rate law of three terms, of which one refers to hydrolytic reaction and the other two refer to direct reactions of iodide with $H_3P_2O_8^-$ and $H_2P_2O_8^{2-}$. The difference in character probably lies in the difference of the polarizability of the iodide and bromide ions, and thus iodide serves as a better nucleophile[23] for attack on oxygen of the peroxydiphosphate.

Formation of phosphate ion radical $PO_4 \cdot^{2-}$ has been reported in the oxidation of Fe^{II} complexes[7,24,25] and in the photolytic oxidation[26] of water, but no such evidence was found in the present investigation or in the oxidations of arsenic(III)[2] and antimony(III)[3] (absence of any effect of acrylamide on the rate). There is no evidence also in the hydrolytic studies and hence this is another support for the mechanism of the redox reaction suggested earlier.

A comparison of peroxydisulfate and peroxydiphosphate reactions may be of some interest. The decomposition of peroxydiphosphate[27] is slower than that of peroxydisulfate[28] and both of them involve free-radical ions.[28,29] All redox reactions studied so far involving peroxydiphosphate are faster. Peroxydisulfate requires the use of silver(I) as catalyst for the oxidations of manganese(II)[30,31] and vanadyl ions,[32] whereas peroxydiphosphate does so readily even without catalyst. Peroxydiphosphate hydrolyzes more readily than peroxydisulfate.[34] Catalysis by silver(I) and probably by copper(II), also, appears to be a common feature of both anions.

Registry No. $H_3P_2O_8^-$, 58904-54-4; Br^-, 24959-67-9.

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Inorganic Chemistry of Fluorocarbenes. 1. Reactions of Tetrafluoroethylidene with Fluorine-Containing Phosphines

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The interactions of tetrafluoroethylidene with three fluorine-containing phosphines have been investigated. The source of the carbene is the pyrolytic decomposition of $C_2F_5SiF_3$ at 200 °C. The reaction of CF_3CF with PF_3 generates $CF_2{=}CFPF_4$ and PF_5; reaction with $(CF_3)_3P$ leads to $(CF_3)_2PCF(CF_3)_2$; and reaction with $(CF_3)_2PCF(CF_3)_2$ produces the fluorocarbon $(CF_3)_2CFCF(CF_3)_2$. The possibility that the vinylphosphorane product of the PF_3 reaction results from fluorine-transfer rearrangement of $C_2F_5PF_2$ as an intermediate product was discredited by a demonstration that $C_2F_5PF_2$ is thermally stable under the reaction conditions. Other mechanistic pathways are discussed.

Introduction

The direct interaction of fluorocarbenes and volatile inorganic fluorides would seem to be a potentially valuable source of fluoroalkyl derivatives of the main-group elements. To date, however, such a synthetic approach has been severely impeded because of the remarkably low reactivity of CF_2—the most widely investigated fluorocarbene.[1] No reaction occurs between CF_2 and NF_3, PF_3, or BF_3.[2] One of the few inorganic fluorides known to react with CF_2 is PF_5; Mahler[2] has shown that several perfluoro(methylphosphoranes) are interconverted via reversible elision of CF_2

$$(CF_3)_xPF_{5-x} \rightleftharpoons CF_2 + (CF_3)_{x-1}PF_{6-x} \quad (x = 1\text{–}3)$$

Table I. Infrared Spectral Data for New Fluorophosphorus Compounds[a]

$(CF_3)_2PCF(CF_3)_2$	$CF_3CF_2PF_2$	$(CF_2{=}CF)POF_2$
1285 s	1745 vw, br	1745 s
1255 sh	1725 vw, br	1388 s
1245 s	1322 s	1348 m
1172 s	1225 vs	1217 s
1145 s	1167 s	1170 w
1102 m	1130 s	1025 (?) w
1085 sh	1087 m, sh	945 s
963 w	1009 m	888 s
950 w	978 m	685 w
930 m	864 vs	545 s
750 m	754 m, sh	
712 m	749 m	
618 vw	746 m	
555 vw	630 m	
535 w	627 m	
480 vw	623 m, sh	
448 m	590 vw, br	
413 w	540 vw, br	
	487 m	
	433 w	
	410 w	
	404 w	
	376 w	
	370 w	

[a] Spectra run in the vapor phase in 8-cm path length cell equipped with KBr windows. Values in cm^{-1}. Relative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; br, broad, sh, shoulder.

Table II. ^{19}F and ^{31}P NMR Spectral Parameters for $CF_3CF_2PF_2$

	δ[a]		
P	−28.7	$\mathrm{P}F_2$	106.4
$\mathrm{C}F_3$	83.4	$\mathrm{C}F_2$	139.4
	Coupling Constants[b]		
^1PF	1259.3	$\mathrm{C}F_2\mathrm{P}F_2$	9.0
^2PF	101.0	$\mathrm{C}F_3\mathrm{CF_2P}F_2$	6.4
^3PF	7.4	$\mathrm{C}F_3\mathrm{C}F_2$	2.0

[a] ^{31}P shift in ppm from external $(CH_3O)_3P$ (positive shifts are to high field); ^{19}F shifts in ppm upfield from external $CFCl_3$. [b] Absolute values in Hz. Where coupling is observable in both ^{19}F and ^{31}P spectra an average of the two observed values has been given.

Table III. Mass Spectral Data for $C_2F_5PF_2$ (70 eV)

m/e	Intens[a]	Peak identity	*m/e*	Intens[a]	Peak identity
188	w	$C_2F_5PF_2$	69	Major pk	CF_3, F_2P
119	m	C_2F_5, CF_4P	62	m	C_2F_2, CFP
100	s	C_2F_4, CF_3P	50	s	CF_2, FP
88	w	CF_4, F_3P	43	m	C_2F, CP
81	s	C_2F_3, CF_2P	31	s	CF, P

[a] Key: w, weak (<12% of major peak (pk)); m, medium (12–50% of major peak); s, strong (>50% of major peak).

Table IV. NMR Spectral Parameters for $(CF_3)_2PCF(CF_3)_2$

	δ[a]		
P	129.1	$\mathrm{(CF_3)_2PCF(C}F_3)_2$	75.0
$\mathrm{(C}F_3)_2\mathrm{PCF(CF_3)_2}$	49.2	$\mathrm{(CF_3)_2PC}F\mathrm{(CF_3)_2}$	187.2
	J_{P-F}[b]		
$\mathrm{(C}F_3)_2\text{-P}$	88.8	$\mathrm{(CF_3)_2C}F\mathrm{P}$	56.0
$\mathrm{(C}F_3)_2\mathrm{CF\text{-}P}$	15.8		
	J_{F-F}[b]		
$\mathrm{(C}F_3)_2\mathrm{\text{-}P\text{-}CF(C}F_3)_2$	6.1	$\mathrm{P\text{-}C}F\mathrm{(C}F_3)_2$	10.1
$\mathrm{(C}F_3)_2\mathrm{P\text{-}C}F\mathrm{(CF_3)_2}$ ·	8.7		

[a] ^{31}P shift in ppm upfield from external $(CH_3O)_3P$; ^{19}F shifts in ppm upfield from external $CFCl_3$. [b] Absolute values in Hz.

The development of the chemistry of the perfluoro(alkylsilanes)[3,4] has provided—through pyrolytic routes—access to fluorocarbenes of substantially enhanced reactivity vis-a-vis CF_2. This paper will describe the reactions of tetrafluoroethylidene [fluoro(trifluoromethyl)carbene] with PF_3, $(CF_3)_3P$, and the new compound $(CF_3)_2PCF(CF_3)_2$.

Experimental Section

Apparatus and Techniques. Volatile substances were manipulated in a greaseless vacuum system employing borosilicate glass and PTFE stopcocks. The fluorinating agent SbF_3 was handled in a recirculating inert-atmosphere glovebox.

Infrared spectra were recorded in the range 4000–250 cm^{-1} with a double-beam grating spectrophotometer (Beckman Model 20A). Gases were contained in glass cells fitted with KBr windows which were sealed with Viton A O-rings. Fluorine NMR spectra were run on a Varian T-60 and/or a Varian XL-100. Phosphorus spectra were obtained on a Varian XL-100, in the Fourier transform mode.

Gas chromatographic analyses of mixtures and purifications were carried out on a Varian Aerograph Model 920. The column found most useful was 10 ft, $^1/_4$ in., stainless steel packed with 7% OV-101 on 60/80, acid-washed, dimethyldichlorosilane-treated Chromosorb G, operated at room temperature. Gas samples were introduced by use of gastight syringes from glass bulbs equipped with septums.

Mass spectra were obtained on a magnetic single-focusing instrument (Hitachi Model RMU-6E) at 70 eV.

Reagents and Starting Materials. Commercially available reagents were used as received subsequent to purity verification by infrared analysis. The fluorinating agent SbF_3 was outgassed at high vacuum overnight prior to use.

The preparation of $C_2F_5SiF_3$ was carried out as previously described.[4] Pure samples of $(CF_3)_3P$, $(CF_3)_2PI$, and PF_3 were kindly provided by Professor A. B. Burg. Additional quantities of $(CF_3)_3P$ and $(CF_3)_2PI$ were synthesized from the reaction of CF_3I with red phosphorus and iodine at 200–220 °C for 48–64 h.[5]

Synthesis of $C_2F_5PF_2$. A 12.8-mmol amount of C_2F_5I, 44 mmol of red phosphorus, and 5 mmol of I_2 were heated in a sealed glass ampule at 220 °C for 70 h. The product mixture was pumped through a series of cold traps maintained at −24, −84, and −196 °C. $C_2F_5PI_2$, the desired intermediate product, was retained in the −24 °C bath. Fluorination of $C_2F_5PI_2$ (which was not itself characterized) was effected by heating a stirred mixture of the phosphine and excess SbF_3 at 58 °C overnight. Fractionation of the fluorination product mixture through −84 and −196 °C traps led to the collection of pure $C_2F_5PF_2$ (characterization discussed below) in the −196 °C trap. The estimated overall yield of $C_2F_5PF_2$ based on C_2F_5I consumed is 11%.

Alternate Synthesis of $(CF_3)_2PCF(CF_3)_2$. A 2.0-mmol amount of $(CF_3)_2CFI$ and 2.1 mmol of $(CF_3)_2PI$ were added to a 50-ml flask containing 3.0 ml of diglyme which had been distilled from sodium, and 110 mg of a 30% by weight (4.6 mmol of Li) dispersion of Li metal in mineral oil. The system was stirred and maintained at −45 °C for 4 h; then it was kept overnight at room temperature, after which the products were distilled through traps at −78, −95, and −196 °C. The material held at −95 °C, 0.2 mmol, was analyzed by gas chromatography (GC) and found to consist of a mixture of $[(CF_3)_2CF]_2$ (12.1%), $[(CF_3)_2P]_2$ (31.8%) (these compounds were identified via comparison of their infrared spectra and/or GC retention times with those of authentic compounds), and a compound (56.3%) which exhibits an infrared spectrum and GC retention time identical with those attributed to $(CF_3)_2PCF(CF_3)_2$ resulting from the carbene reaction.

Product Characterizations. In general, compounds were purified by means of trap-to-trap fractionation, low-temperature column distillation, and/or gas–liquid chromatography. The phosphorane $CF_2{=}CFPF_4$ was identified via comparison with literature infrared and ^{19}F NMR spectra.[6] The compound $(CF_3)_2CFCF(CF_3)_2$ was characterized by comparison with the literature infrared spectrum[7] and by independent preparation of a compound with identical infrared spectrum and GC retention time from the 2537-Å Hg-sensitized photolysis of $(CF_3)_2CFI$. Details of characterization of the new compounds in this work follow.

$C_2F_5PF_2$. Characterization of $C_2F_5PF_2$ was based on ^{19}F and ^{31}P NMR spectra (all resonances are totally consistent with first-order interactions) (see Table II), its mass spectrum (Table III), its infrared spectrum (Table I), and vapor density molecular weight (calcd 188.0; found 189.0).

$(CF_3)_2PCF(CF_3)_2$. The identity of this product was established by the following methods: vapor density molecular weight (calcd 338.0;

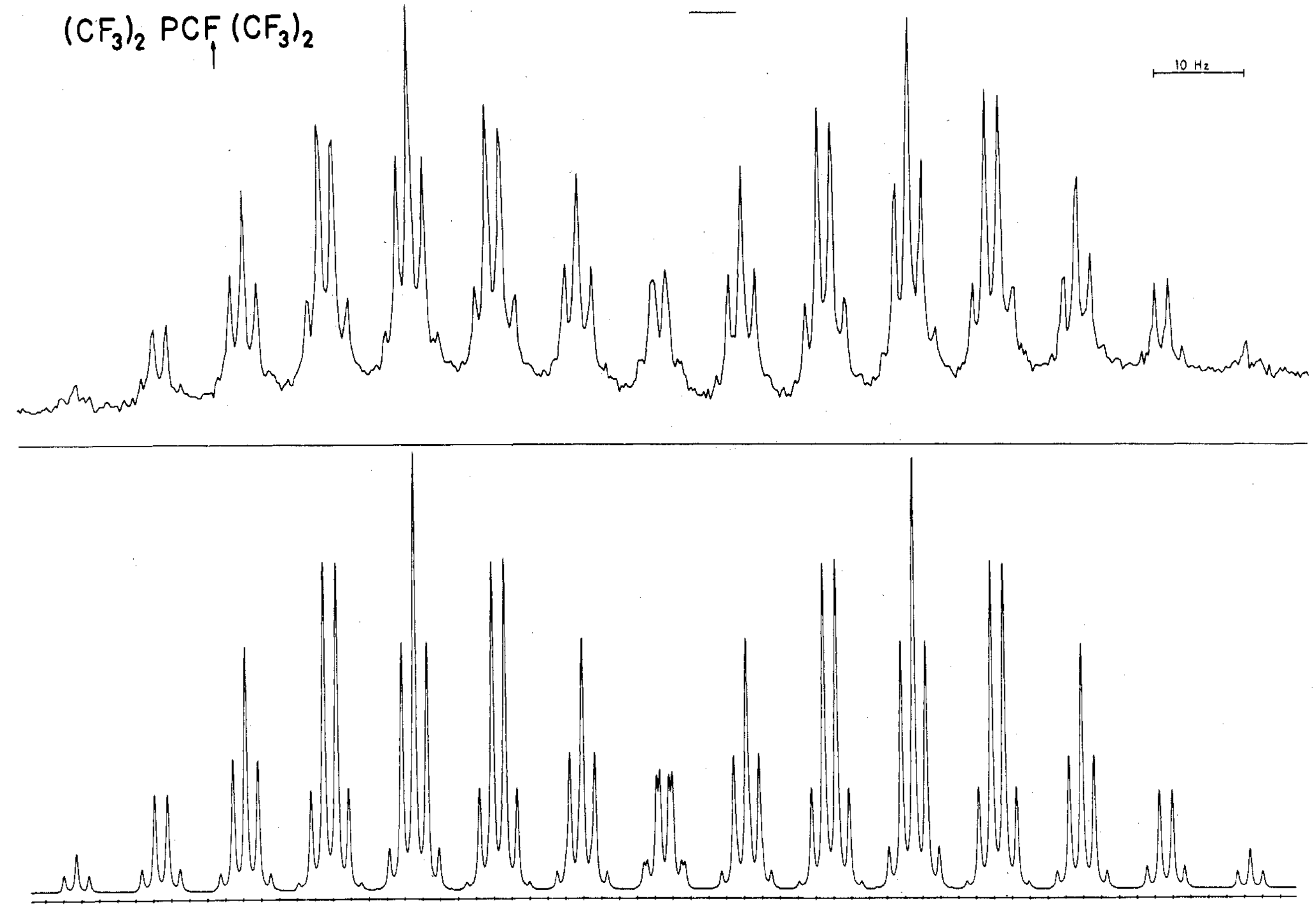


Figure 1. ^{19}F NMR spectra of $(CF_3)_2PCF(CF_3)_2$. The upper spectrum is experimental; the lower spectrum is a computer-based simulation obtained using the parameters given in Table IV. Despite the nominal appearance of the spectrum as alternating quartets and quintets, it is in fact a doublet of septets of septets.

Table V. Mass Spectral Data for $(CF_3)_2PCF(CF_3)_2$ (70 eV)

m/e	Intens[a]	Peak identity	m/e	Intens[a]	Peak identity
338	w	$(CF_3)_2PCF(CF_3)_2$	112	m	C_2F_3P
319	w	$C_4F_{12}P$	107	w	F_4P
269	w	$C_3F_{10}P$	100	s	CF_3P, C_2F_4
250	w	C_3F_9P	93	m	C_2F_2P, C_3F_3
231	w	C_3F_8P	81	m	CF_2P, C_2F_3
181	w	C_3F_6P	74	m	C_2FP
169	w	C_2F_6P, C_3F_7	69	Major pk	F_2P, CF_3
162	w	C_3F_5P			
150	w	C_2F_5P, C_3F_6	62	m	CFP, C_2F_2
143	m	C_3F_4P	50	m	FP, CF_2
131	m	C_2F_4P, C_3F_5	43	w	C_2F, CP
119	m	CF_4P, C_2F_5	31	s	CF, P

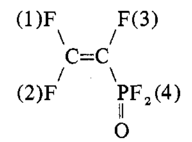
[a] Key: w, weak (<12% of major peak (pk)); m, medium (12–50% of major peak); s, strong (>50% of major peak).

found 342.0); alkaline hydrolysis (5% aqueous NaOH at 24 °C for 2 h) to give a 2:1 mixture of CF_3H–$(CF_3)_2CFH$ in 96% yield; infrared (Table I), fluorine and phosphorus NMR (Table IV), and mass spectral data (Table V). The NMR spectra of the phosphorus atom and of the unique fluorine in the heptafluoroisopropyl group are complex (although first order) 98-line multiplets; consequently, computer-based simulations were employed to verify assignments of coupling constants. Experimental and computed spectra for these two nuclei are presented in Figures 1 ($CF(CF_3)_2$) and 2 (P).

An additional means of characterization of this compound involved its independent synthesis, as described above.

$CF_2{=}CFPOF_2$. Characterization was afforded from analysis of its (first-order) ^{19}F NMR spectrum (Table VI), an infrared spectrum containing a characteristic P=O stretch at 1388 cm^{-1} and C=C stretch at 1745 cm^{-1} (Table I), observation of a molecular ion in the mass spectrum of a mixture also containing $CF_2{=}CFPF_4$, and its hydrolytic formation from $CF_2{=}CFPF_4$.

Table VI. ^{19}F NMR Spectral Parameters for $F_2C{=}CFPOF_2$



	δ^a		Coupling const[b]		Coupling const[b]
F_1	71.6	F_1F_2	16.1	F_2F_4	4.2
F_2	92.9	F_1F_3	29.5	F_2P	20.1
F_3	199.8	F_1F_4	11.9	F_3F_4	8.1
F_4	65.2	F_1P	c	F_3P	<1
		F_2F_3	121.3	F_4P	1090

[a] In ppm upfield from internal $CFCl_3$. [b] Absolute values in Hz. All F–F couplings were consistent to within ±0.2 Hz between both resonances. [c] Coupling not determined due to partial obscuration of the F_1 resonance by impurity peaks.

Reaction Chemistry

Reaction of CF_3CF with PF_3. Pyrolysis of a mixture of $C_2F_5SiF_3$ (0.52 mmol) and PF_3 (2.18 mmol) was carried out at 200 °C and ca. 0.5 atm for 1 h. A small amount of nonvolatile colorless film was observed on the walls of the sealed glass reaction tube after the reaction was completed. Volatile products were passed through a series of traps cooled to −95, −120, and −196 °C. The material held in the −120 °C trap (0.25 mmol) was found to be a mixture of $CF_2{=}CFPF_4$ and $CF_2{=}CFPOF_2$ in a 16:1 ratio. A small amount of material (0.016 g) was retained in the −95 °C trap. This fraction appeared to be a mixture of $CF_2{=}CFPF_4$, $CF_2{=}CFPOF_2$, and at least one other substance. The mixture could not be successfully chromatographed, and the identity of the unknown compound(s) could not be ascertained

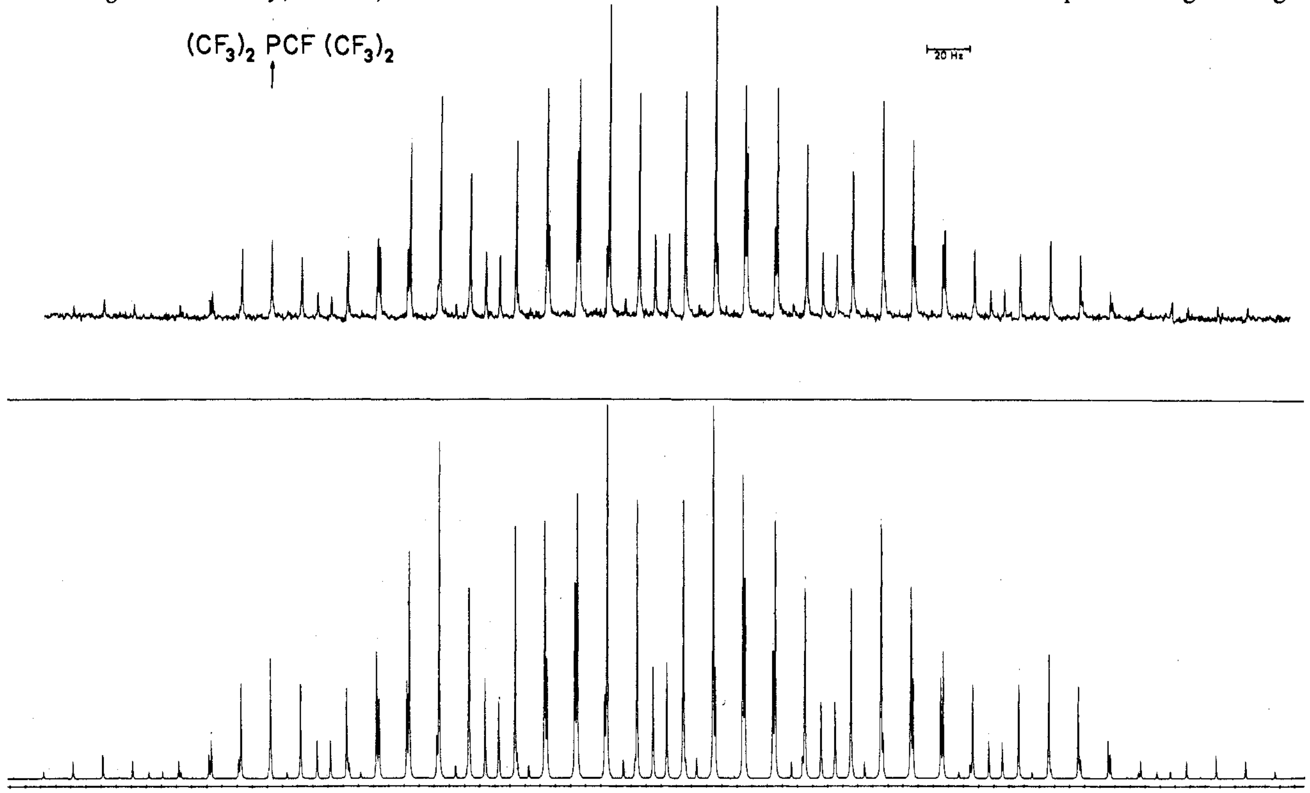


Figure 2. ${}^{31}P$ NMR spectra of $(CF_3)_2PCF(CF_3)_2$. The upper spectrum is experimental; the lower is a computer simulation based on the parameters given in Table IV.

from infrared, NMR, or mass spectral analysis of the mixture. The material retained in the −196 °C bath (2.30 mmol) was analyzed by infrared and ${}^{19}F$ NMR (vapor phase) spectra and found to be a mixture of PF_3 (1.64 mmol), SiF_4 (0.52 mmol), PF_5 (0.12 mmol), and POF_3 (0.04 mmol).

In a control experiment $CF_2{=}CFPF_4$ (0.25 mmol) was heated at 200 °C and ca. 0.6 atm for 2 h. The recovered products (0.23 mmol) consisted of 91 mol % of unreacted $CF_2{=}CFPF_4$ and 9 mol % of a mixture of SiF_4, PF_5, POF_3, and $CF_2{=}CFPOF_2$.

Reaction of CF_3CF with $P(CF_3)_3$. In a typical experiment, a mixture of $C_2F_5SiF_3$ (1.32 mmol) and $P(CF_3)_3$ (1.36 mmol) was heated at 200 °C and ca. 0.5 atm for 1 h. Products were passed through a series of traps cooled to −78, −95, −120, and −196 °C. The material held in the −78 °C trap (0.56 mmol) was shown by gas chromatography to consist of two major components in a 10:1 ratio; several other species with longer retention times were present in much smaller amounts. The two chief components were purified by preparative-scale GC and their identities established as $(CF_3)_2P$-$CF(CF_3)_2$ and $[(CF_3)_2CF]_2$, respectively. The material held in the −95 °C trap (0.11 mmol) was shown by GC to consist of a 1.5:1 mixture of $(CF_3)_2PCF(CF_3)_2$ and $[(CF_3)_2CF]_2$. The contents of the −120 °C trap were demonstrated by infrared analysis to consist of a 3.8:1 mixture of unreacted $P(CF_3)_3$ and *cis*- and *trans*-perfluorobutene-2, respectively. The material retained in the −196 °C bath (1.78 mmol) consisted a mixture of SiF_4, *cis*- and *trans*-C_4F_8-2, $P(CF_3)_3$, and $CF_3CF{=}CF_2$, in the ratio of 16:2.0:1.7:1. The above data correspond to the following yields (based on $C_2F_5SiF_3$ consumed): $(CF_3)_2PCF(CF_3)_2$, 44%; $[(CF_3)_2CF]_2$, 14%; C_3F_6, 7%. In a control experiment, pure $P(CF_3)_3$ was heated at 200 °C for 1 h and underwent no detectable decomposition.

Reaction of CF_3CF with $(CF_3)_2PCF(CF_3)_2$. Pyrolysis of a 1:1 mixture (0.06 mmol each) of $C_2F_5SiF_3$ and $(CF_3)_2PCF(CF_3)_2$ was carried out at 200 °C and 420 Torr for 1 h. Products were passed through a series of traps cooled to −95, −130, and −196 °C. The material held in the −95 °C trap (0.04 mmol) was shown by GC to be a mixture of $(CF_3)_2PCF(CF_3)_2$ and $[(CF_3)_2CF]_2$ in the ratio of 2.6:1. The material which stopped in the −130 °C trap (0.02 mmol) was examined by infrared spectroscopy and shown to be a mixture of *cis*- and *trans*-perfluorobutene-2 and a fluoroalkylphosphine—very likely $(CF_3)_3P$—in the approximate ratio of 7:1. The substance in the −196 °C trap (0.06 mmol) proved to be essentially pure SiF_4. $(CF_3)_2PCF(CF_3)_2$ was independently determined to be thermally stable under the reaction conditions.

Attempted Pyrolysis of $C_2F_5PF_2$. As a test for the possible intermediacy of $C_2F_5PF_2$ in the CF_3CF–PF_3 reaction, the compound was heated to 200 °C for a period of 1 h. Infrared analysis indicated no perceptible change in composition of the material after heating.

Formation of $CF_2{=}CFPOF_2$. Routine handling of $CF_2{=}CFPF_4$ invariably generated small amounts of $CF_2{=}CFPOF_2$, apparently via reaction with glass in the presence of trace amounts of moisture. Indeed, the literature infrared spectrum[6] of $CF_2{=}CFPF_4$ contains several bands which we attribute to $CF_2{=}CFPOF_2$. Deliberate exposure of $CF_2{=}CFPF_4$ to small amounts of air or attempts to chromatograph the compound also led to formation of $CF_2{=}CFPOF_2$ (the conversion is complete in the GC column). The concomitant formation of SiF_4 in samples that were exposed to air in glass vessels strongly suggests hydrolytic decomposition; decomposition in the GC column may occur via interaction of the phosphorane with siloxane moieties in the silicone stationary phase.[8]

Results

A general pathway for thermal decomposition of polyhalo(alkylsilanes) involves α transfer of halogen from carbon to silicon, with release of a carbene.[9] The recent synthesis[3,4] of perfluoro compounds of carbon and silicon has provided a convenient source for the generation of perfluorocarbenes. Substitution of a trifluoromethyl group for fluorine in the disappointingly unreactive CF_2 leads to a substantial increase in reactivity (and presumably electrophilicity) of the resultant carbene; for example, CF_3CF reacts virtually quantitatively with trimethylsilane (via Si–H bond insertion), while reaction of CF_2 with Me_3SiH could not be detected.[4] The present work describes the reactions of CF_3CF—generated from the thermal decomposition of $C_2F_5SiF_3$ at 200 °C—with PF_3, $(CF_3)_3P$, and $(CF_3)_2PCF(CF_3)_2$.

Reaction of CF_3CF with PF_3. The reaction proceeds to generate $CF_2{=}CFPF_4$ as the major product (ca. 54%), along with a smaller quantity of PF_5 and a much smaller amount of a lower volatility substance(s) which was not successfully characterized. The vinylphosphorane product has been synthesized by Cowley and Taylor[6] from the oxidative fluorination of $CF_2{=}CFPCl_2$ with SbF_5. The high efficiency of the CF_3CF–PF_3 reaction is indicated by the complete suppression of the formation of *cis*- and *trans*-perfluorobutene-2, the products of carbene dimerization in the absence of interacting species. Subjection of pure $CF_2{=}CFPF_4$ to the reaction conditions (200 °C for 1 h) results in only slight decomposition of the compound; its thermal degradation cannot account for the amount of PF_5 formed in the reaction.

Reaction of CF_3CF with $(CF_3)_3P$. Except for a small amount of hexafluoropropene, the volatile products of this reaction are the new compound $(CF_3)_2PCF(CF_3)_2$ and perfluoro(2,3-dimethylbutane), $[(CF_3)_2CF]_2$. The latter two species are present in a ratio of ca. 3:1, respectively. A substantial portion of the carbene does not react with the $(CF_3)_3P$ and is recovered as *cis*- and *trans*-C_4F_8-2.

Reaction of CF_3CF with $(CF_3)_2PCF(CF_3)_2$. To explore possible sources of $[(CF_3)_2CF]_2$ in the CF_3CF–$(CF_3)_3P$ reaction, we examined the interaction of the carbene and the primary product of the reaction, $(CF_3)_2PCF(CF_3)_2$. The latter does indeed react with CF_3CF to generate perfluoro(2,3-dimethylbutane) and a smaller amount of $(CF_3)_3P$. No evidence for the formation of $CF_3P[CF(CF_3)_2]_2$ was obtained. The compound $(CF_3)_2PCF(CF_3)_2$ itself is thermally stable under the reaction conditions.

Discussion

The reactions of the carbene CF_3CF with the phosphines PF_3, $(CF_3)_3P$, and $(CF_3)_2PCF(CF_3)_2$ all follow different courses: the PF_3 reaction generates phosphoranes as major products; the $(CF_3)_3P$ reaction leads to what is *formally* the product of P–C bond insertion by the carbene; and the reaction with $(CF_3)_2PCF(CF_3)_2$ does not proceed with incorporation of the carbene into a new phosphine but produces the fluorocarbon formally corresponding to dimerization of the perfluoroisopropyl radical, $[(CF_3)_2CF]_2$.

Previous carbene–phosphine reactions do not allow a secure prediction of behavior in the present systems. Dihalocarbene additions to trialkyl-[10] and triarylphosphines[11–19] to give ylides have been reported, but these were not vapor-phase reactions, and the intermediacy of the free carbene in at least some of the reactions is questionable.[10–12] If the ylide[20] structure is viewed as a donor–acceptor complex between a phosphine and an electrophilic carbene, it is not clear that such complex formation is possible for the very weakly basic fluoro- or fluoroalkylphosphines (it should be recognized, however, that the π-acceptor abilities[21] of these phosphines may well be influential in these systems).

In the CF_3CF–PF_3 reaction, two mechanistic routes to $CF_2{=}CFPF_4$ seemed plausible. The first is ylide formation followed by β-fluorine transfer to phosphorus

$$CF_3CF + PF_3 \rightarrow CF_3CF{=}PF_3 \leftrightarrow CF_3\overset{-}{C}F\overset{+}{P}F_3$$

$$CF_3CF{=}PF_3 \rightarrow CF_2{=}CFPF_4$$

Alternatively, if ylide formation were disfavored, carbene insertion into a P–F bond followed by transfer of *two* fluorines would account for the product

$$CF_3CF + PF_3 \rightarrow CF_3CF_2PF_2 \twoheadrightarrow CF_2{=}CFPF_4$$

Although the latter transformation seemed unlikely to us, we undertook the synthesis and examination of the thermal stability of $C_2F_5PF_2$. The compound proved to be resistant to thermal decomposition under the conditions of the carbene reaction (200 °C for 1 h); we therefore suggest the intermediacy of the ylide in this reaction.

The source of the second major product in the CF_3CF–PF_3 reaction, PF_5, is not known. Thermal degradation of pure $CF_2{=}CFPF_4$ under the reaction conditions does produce a small amount of PF_5 but not enough to account for the abundance of the latter as a reaction product. It seems at least plausible that PF_5 is generated via the decomposition of a high-energy species formed from the exothermic trapping of the carbene by PF_3.

The reaction of CF_3CF with $(CF_3)_3P$ *formally* involves P–C bond insertion by the carbene. However, initial ylide formation followed by the shift of a trifluoromethyl group would of course also account for the observed product. Such a rearrangement would presumably be related to SNi reactions such as the Stevens rearrangement; the P–C bond in perfluoroalkylphosphines is readily cleaved by strong base.[22] If the reaction does proceed through the ylide intermediate, the CF_3 shift must be considerably faster than the β-fluorine transfer invoked for the PF_3 reaction; neither $(CF_3)_3PF(CF{=}CF_2)$ nor evidence for the presence of CF_2 (a likely decomposition product of the preceding molecule) was observed in this system.

The reaction of CF_3CF and $(CF_3)_2PCF(CF_3)_2$ is apparently the source of the fluorocarbon product $(CF_3)_2CFCF(CF_3)_2$ in the $(CF_3)_3P$ reaction. A possible explanation of this reaction is that the disubstituted product $CF_3P[CF(CF_3)_2]_2$ is sufficiently sterically encumbered to undergo homolytic cleavage of the P–C bond in the perfluoroisopropyl groups at 200 °C. Another possibility would be elision of the fluorocarbon product from a single molecule. We have at present no direct evidence in support of either of these mechanisms. The phosphorus "sink" in this reaction is apparently a compound (or polymer) of too low a volatility to be readily transferred in the vacuum system.

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Registry No. $(CF_3)_2PCF(CF_3)_2$, 58734-88-6; $CF_3CF_2PF_2$, 58734-89-7; $(CF_2{=}CF)POF_2$, 58734-90-0; P, 7723-14-0; C_2F_5I, 354-64-3; $(CF_3)_2CFI$, 677-69-0; $(CF_3)_2PI$, 359-64-8; CF_3CF, 58734-91-1; PF_3, 7783-55-3; $P(CF_3)_3$, 432-04-2; $C_2F_5SiF_3$, 354-89-2.

References and Notes

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