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Perfluoro(alkylsilanes). II. Trifluoro(trifluoromethyl)silane and Trifluoro(pentafluoroethyl)silane[1]

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The perfluoro(alkylsilanes) CF_3SiF_3 (I) and $C_2F_5SiF_3$ (II) have been prepared and characterized. Synthesis was effected by fluorination of the corresponding difluoroiodo(perfluoroalkyl)silanes, obtained by the reaction of SiF_2 with the appropriate perfluoroalkyl iodide. Both compounds are stable at room temperature. Products from thermolysis of I at *ca.* 80° or above and of II at 160° or above, as pure compounds or in the presence of added reagents, are consistent with a decomposition mechanism involving α-fluorine transfer and the intermediacy of the carbenes $:CF_2$ and $CF_3\ddot{C}F$, respectively. Basic and aqueous hydrolytic behaviors are described.

Introduction

Despite the large number of perfluoroalkyl derivatives of the main-group elements now known[3-5] and the greatly increased level of activity in silicon–fluorine chemistry over the past few years, the perfluoro analogs of the well-known alkylsilanes, $RSiH_3$, have remained essentially uncharacterized until very recently.

The synthesis of CF_3SiF_3, other perfluoro(alkylsilanes), and perfluoroalkylhalosilanes was claimed by Simons and Dunlap, in a 1953 patent,[6] to result from the reactions of perfluoroalkyl bromides with Si–Cu alloy at 400–500°. A contemporary patent,[7] however, claimed only the synthesis of perfluoroalkylhalosilanes, $(R_f)_nSiX_{4-n}$ (n = 1-3, $X \neq F$), from very similar systems. A further apparent contradiction arises from the somewhat earlier report[8] that the reaction of perfluoroalkyl chlorides with silicon or Si–Cu alloy at 500–1000° leads to complete transfer of halogen to silicon without production of fluoroalkylsilanes. While very low yields of CF_3SiF_3 (I) have been reported[9] from the reaction of CF_3I with Si–Cu at 450–500°, other workers[10] have been unsuccessful in attempts to reproduce specifically the synthesis of this compound from CF_3Br by the procedure of Simons and Dunlap. Details of product characterization in all of these early investigations are quite sparse; indeed, from what is now known of the thermal stability of polyfluoroalkylsilanes in general and of I in particular, it seems most unlikely that the compound could be generated and recovered in high yield at the elevated temperatures used in the "direct" reaction.

A number of alternative routes have been applied successfully to the synthesis of fluoroalkylsilicon compounds.[11] These include reaction of fluoroalkyllithium or Grignard reagents with silicon halides, addition of the Si–H function across the double bond in fluoroolefins, and free-radical reactions of perfluoroalkyl halides with unsaturated organosilanes. These procedures have not, however, yielded fully fluorinated derivatives.

Synthesis in silicon–fluorine chemistry has been greatly extended in recent years by the development of the low-temperature chemistry of silicon difluoride.[12] Thus, the production of CF_3SiF_2I[13] from the reaction of SiF_2 with CF_3I suggested a potential route to the previously uncharacterized CF_3SiF_3. In a recent communication,[1] we have described the synthesis of this compound in high yield. We report here synthesis of the next higher homolog, $C_2F_5SiF_3$, together with some aspects of the chemistry of both species.

Experimental Section[14]

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

Infrared spectra were recorded in the range 4000–400 cm^{-1} with a commercial double-beam grating spectrophotometer (Perkin-Elmer Model 337). Gases were contained in borosilicate glass cells fitted with KBr windows which were sealed with Viton-A O rings.

Mass spectra were obtained on a 180° sector single-focusing magnetic instrument (AEI MS-10). Samples were generally vaporized directly into the ion-source region from a gas infrared cell; infrared spectra were taken both prior to and subsequent to sampling.

Fluorine nmr spectra were run on a modified Varian HR-60 (56.4 MHz)[15] and/or a Bruker HFX-11 (84.67 MHz) spectrometer. Proton spectra were obtained on a Varian A-60. Observation of satellite spectra was facilitated with the use of signal-averaging techniques. Chemical shifts were, unless otherwise indicated, determined relative to the external references $CFCl_3$ and $(CH_3)_4Si$.

Molecular weights reported were obtained from vapor density measurements.

Reagents.—Materials used as reactants were obtained from commercial sources. Identities of gases were verified by means of infrared spectra prior to use. Purities were deemed suitable, except for HBr which was further purified *via* vacuum-line fractionation. Antimony(III) fluoride was supplied as a gray powder. Vacuum sublimation yielded a pure white solid whose

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[1] Part I: K. G. Sharp and T. D. Coyle, *J. Fluorine Chem.*, **1**, 249 (1971).

[2] NRC-NBS Postdoctoral Research Associate, 1969–1971.

[3] R. E. Banks and R. N. Haszeldine, *Advan. Inorg. Chem. Radiochem.*, **3**, 337 (1961).

[4] P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, **1**, 143 (1964).

[5] R. E. Banks, "Fluorocarbons and Their Derivatives," Olbourne Press, London, 1964.

[6] J. H. Simons and R. D. Dunlap, U. S. Patent 2,651,651 (1953).

[7] H. J. Passino and L. C. Rubin, U. S. Patent 2,686,194 (1953).

[8] E. F. Izard and S. L. Kwolek, *J. Amer. Chem. Soc.*, **73**, 1156 (1951).

[9] R. N. Haszeldine and K. Leedham, unpublished results cited in ref 3.

[10] F. E. Brinckman, private communication (see ref 1).

[11] See, for example, ref 3–5 and references cited therein.

[12] Two recent reviews of SiF_2 chemistry: J. L. Margrave, K. G. Sharp, and P. W. Wilson, *Top. Current Chem.*, in press; J. L. Margrave and P. W. Wilson, *Accounts Chem. Res.*, **4**, 145 (1971).

[13] J. L. Margrave, K. G. Sharp, and P. W. Wilson, *J. Inorg. Nucl. Chem.*, **32**, 1917 (1970).

[14] Certain commercial equipment, instruments, or materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

[15] R. B. Johannesen, T. C. Farrar, F. E. Brinckman, and T. D. Coyle, *J. Chem. Phys.*, **44**, 962 (1966).

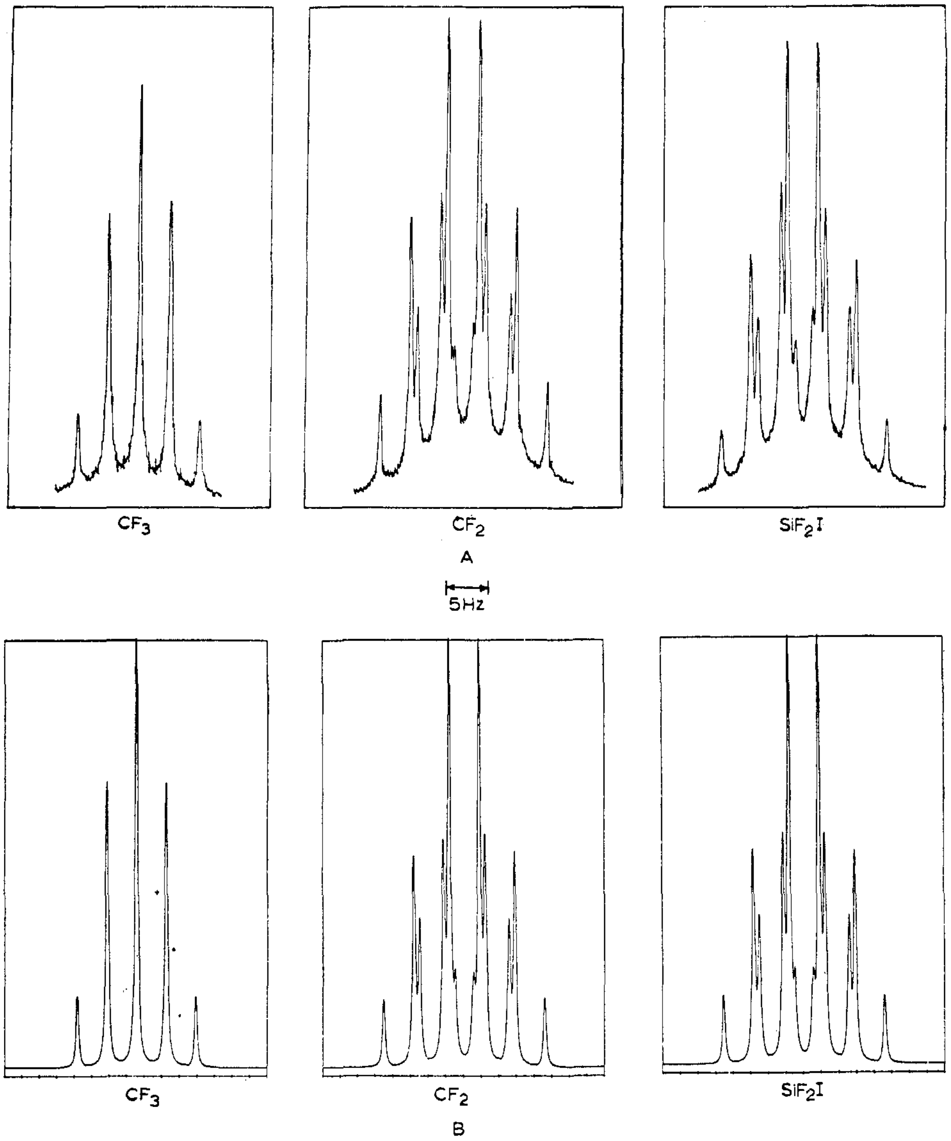

Figure 1.—Multiplets in the ^{19}F nmr spectrum of $CF_3CF_2SiF_2I$: A, experimental spectra; B, computer simulation obtained using the parameters summarized in Table I.

efficiency as a fluorinating agent was not, however, enhanced; the SbF_3 was thus generally used as received.

Purification of Products.—Low-temperature column distillation was found to be the most generally useful means of separating product mixtures. The arrangement used was a modification of one described elsewhere.[16] We find that the particular geometry of the column is less important than effective insulation of the cold nitrogen gas source and transfer tubing.

Preparation of CF_3SiF_2I and $C_2F_5SiF_2I$.—Silicon difluoride was generated from the reaction of SiF_4 with elemental Si at 1200°.[17] Reactants CF_3I or C_2F_5I were cocondensed with the SiF_2–SiF_4 mixture at −196° so as to provide a slight excess of the fluorocarbon (a 60% conversion of SiF_4 to SiF_2 was assumed). The desired products were obtained in 40–60% yields (based on the assumed SiF_2 production) on warm-up of the low-temperature condensate and generally constituted 60–80% of the total products. Unreacted SiF_4 and fluorocarbon were removed from the systems by means of trap-to-trap fractionation. CF_3SiF_2I or $C_2F_5SiF_2I$ was subsequently purified on the low-temperature distillation column. Purity of the CF_3SiF_2I was established from its infared spectrum.[18] Identity of the new compound, $C_2F_5SiF_2I$, was established from the molecular weight (calcd, 312.0; found, 313.0), infrared spectrum [1321 (s), 1228 (vs), 1153 (s), 1109 (s), 987 (s), 891 (s), 845 (w), 748 (w), 613 (w), 587 (w), 551 (m), 500 (s), 484 (s) cm^{-1}] which exhibits bands characteristic of Si–F stretches and the C_2F_5 function, and ^{19}F nmr spectrum (Table I, Figure 1).

Synthesis of Perfluoro(alkylsilanes).—The difluoroiodo(perfluoroalkyl)silanes were distilled into 200-ml borosilicate glass bulbs containing an excess of finely powdered SbF_3. The bulbs, which were equipped with 15-mm O-ring connectors and greaseless stopcocks, were removed from the vacuum system and the contents were agitated on warm-up from liquid nitrogen temperature. The color of the solid in the bulb began changing (eventually to an orange-red) well below room temperature. Slight amounts of moisture in the SbF_3 were found to lead to slight hydrolysis of CF_3SiF_2I and I. Partial decomposition of I to SiF_4 and C_2F_4 was at times also observed in the fluorination process. Samples of SbF_3 were consequently often "seasoned" with impure CF_3SiF_2I prior to use. The corresponding pentafluoroethyl system was much less sensitive to moisture. Perfluorinated products could be recovered in >80% yield in both systems.

Characterization of I was based on molecular weight and infrared (Figure 2), mass, and nmr (Table I) spectral evidence, as described previously.[1] The new compound $C_2F_5SiF_3$ (II) was identified on the basis of its molecular weight (calcd, 204.1; found, 202.4), infrared spectrum (Figure 2), mass spectrum (Table II), nmr spectrum (Table I, Figure 3), and reaction chemistry.

Thermal Reaction Studies.—Pyrolyses of I and II, as pure

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[16] E. J. Spanier, Ph.D. Thesis, University of Pennsylvania, 1964.

[17] P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Amer. Chem. Soc.*, **87**, 2824 (1965).

TABLE I

NMR SPECTRAL PARAMETERS FOR PERFLUORO(ALKYLSILANES) AND RELATED COMPOUNDS[a]

	$\delta(CF_3)$	$\delta(CF_2)$	$\delta(SiF_2)$	$\delta(SiF_3)$	J_{F-F}[b] 1–2	1–3	2–3	J_{Si-F}	Ref
CF_3SiF_2I	69.9	. . .	120.1	. . .	6.9	. . .	. . .	342.4	*c, d*
CF_3SiF_3	69.4	. . .	. . .	153.8	11.0	. . .	. . .	273.2	*d, f*
$CF_3CF_2SiF_2I$	82.7	130.6	117.0	. . .	3.38	3.38	4.06	346.2	*c, e*
$CF_3CF_2SiF_3$	86.5	134.4	. . .	150.2	3.59	2.81	4.92	275.3	*e, f*
CF_3CF_3	91.0	. . .	. . .	. . .	3.50	. . .	. . .	. . .	*g*
SiF_3SiF_3	. . .	. . .	. . .	125.6	20.9	. . .	. . .	321.8	*h*
$CF_3CF_2CF_3$	83.0	131.5	. . .	. . .	0.70	7.3	0.70	. . .	*i*
$SiF_3SiF_2SiF_3$	. . .	. . .	139.6	127.1	10.8	3.61	10.8	344.4	*j*

[a] Chemical shifts in ppm from external CCl_3F reference. Estimated uncertainties in the reported values for this work are ±0.4 ppm. *J* values in Hz. [b] Equivalent groups of fluorines are numbered from the left side of the molecule as written. [c] Spectrum obtained for neat liquid. [d] Uncertainty in *J* is ±0.1 Hz. [e] Uncertainty in *J* is ±0.04 Hz. [f] Spectrum obtained for *ca.* 40% solution in *c*-C_4F_8. [g] R. J. Abraham and L. Cavalli, *Mol. Phys.*, **9**, 67 (1965). [h] Reference 15. [i] G. V. D. Tiers, *J. Phys. Chem.*, **66**, 945 (1962). [j] R. B. Johannesen, *J. Chem. Phys.*, **47**, 955 (1967).

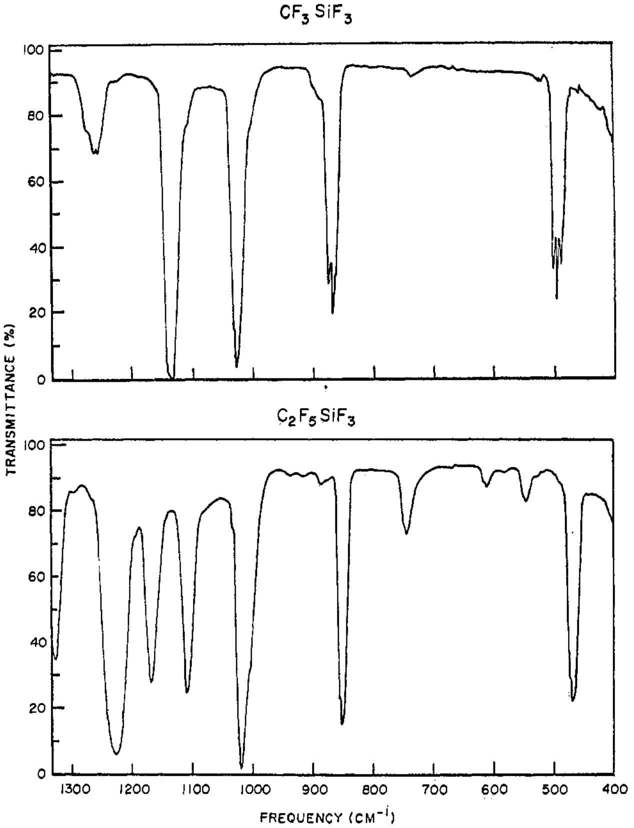

Figure 2.—Infrared spectra of CF_3SiF_3 (I) and $C_2F_5SiF_3$ (II).

TABLE II

MASS SPECTRUM OF TRIFLUORO(PENTAFLUOROETHYL)SILANE (70 EV)

m/e	Peak identity	Rel intens	*m/e*	Peak identity	Rel intens
31	CF^+	27.0	85	SiF_3^+	59.8
47	SiF^+	3.3	100	$C_2F_4^+$	12.4
50	CF_2^+	4.4	116	$CSiF_4^+$	1.9
62	$C_2F_2^+$	1.9	119	$C_2F_5^+$	2.0
66	SiF_2^+	3.0	135	$CSiF_5^+$	100.0
69	CF_3^+	20.9	185	$C_2SiF_7^+$	12.0
81	$C_2F_3^+$	74.5	204	$C_2SiF_8^+$	<0.2

compounds or in the presence of potential reactants, were performed in sealed glass ampoules with all reactants in the gas phase. Reactions of I were generally carried out at 100° and 50–200 Torr for 30–60 min; those involving II, at 200° for 90 min.

CF_3SiF_3.—Pyrolytic decomposition proceeded rapidly at temperatures in excess of 100° and occurred at a moderate pace (<16 hr for complete decomposition) at temperatures as low as 78°. Although a detailed kinetic study was not attempted, the half-life of I at 100° and 50 Torr was determined to be approximately 7 min, with no marked dependence on pressure.

Thermal decomposition generated three products: SiF_4, C_2F_4, and *c*-C_3F_6, with the two last species in a ratio of 10:1. In a typical run, 0.29 mmol of I yielded 0.29 mmol of SiF_4, 0.13 mmol of C_2F_4, and 0.01 mmol of *c*-C_3F_6. All species were identified by comparison with known infrared spectra. Physical separation of SiF_4 and C_2F_4 was difficult; the fraction containing these species was thus distilled into aqueous NaOH to destroy the SiF_4. C_2F_4 was then determined directly and SiF_4 by difference.

Compound I (0.20 mmol) was distilled into a 35-ml bulb with excess HBr (0.26 mmol) and heated to 102° for 45 min. Infrared spectra revealed the presence of only two materials, SiF_4 and bromodifluoromethane. These species and unreacted HBr (not readily observed in the infrared spectra) could not be efficiently separated either by trap-to-trap fractionation or by low-temperature column distillation. Neither C_2F_4 nor *c*-C_3F_6 was detected, and if present, these compounds constitued less than 1% of the products. Thus, the apparent yield of CF_2HBr was quite high. Bromodifluoromethane was identified from its known infrared spectrum.[18]

Pyrolysis of a 4:1 mixture of vinyl fluoride and I at 100° for 60 min yielded a series of products which could be separated into only two fractions. The more volatile fraction (emerging from the column at −150°) consisted of SiF_4, C_2F_4, and unreacted C_2H_3F, as indicated by the infrared spectrum. The less volatile fraction (volatile at −122°) contained *c*-C_3F_6, identified by its infrared spectrum,[19] and an approximately equal amount of a substance believed to be 1,1,2-trifluorocyclopropane, the expected product of addition of $:CF_2$ to the fluoroethylene. This material was obtained in roughly 5% yields and could not be generated in sufficient quantities for nmr analysis.

In further efforts to assess the reactivity of I, the compound was pyrolyzed in the presence of CF_3I and $(CH_3)_3SiH$. In both these investigations, the potential reactants were present in excess by at least a factor of 2 with respect to I. After being heated to 100° until destruction of I was complete, the mixtures in both cases showed no evidence of reaction between $:CF_2$ and the reactant in question.

$C_2F_5SiF_3$.—Thermal decomposition of II did not occur to an appreciable extent at temperatures below 160°. At 180° and 10–200 Torr, the half-life of the compound was found to be *ca.* 28 min. Two products constituted over 98% of the volatile species recovered from the pyrolysis: SiF_4 and a mixture of *cis*- and *trans*-perfluorobutene-2, identified from the infrared spectrum.[19] In a typical run, 0.24 mmol of II yielded 0.24 mmol of SiF_4, 0.11 mmol of C_4F_8, and a much smaller amount (*ca.* 1%) of a less volatile material exhibiting infrared bands in the C–F stretching region (1150–1300 cm^{-1}) but not in the Si–F (800–1030 cm^{-1}) region.

When II was pyrolyzed in the presence of excess HBr, no perfluorobutene was detected among the products. In a typical experiment, HBr (0.22 mmol) and II (0.15 mmol) were allowed to react at 200° for 95 min. Products were separated on the low-temperature column into a fraction containing SiF_4 and unreacted HBr (volatile at −150°) and a much less volatile fraction (−105°) shown to be 1-bromo-1,2,2,2-tetrafluoroethane

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(18) E. K. Plyler and N. Acquista, *J. Res. Nat. Bur. Stand.*, **48**, 92 (1952).

(19) J. Heicklen, F. Wachi, and V. Knight, *J. Phys. Chem.*, **69**, 693 (1965).

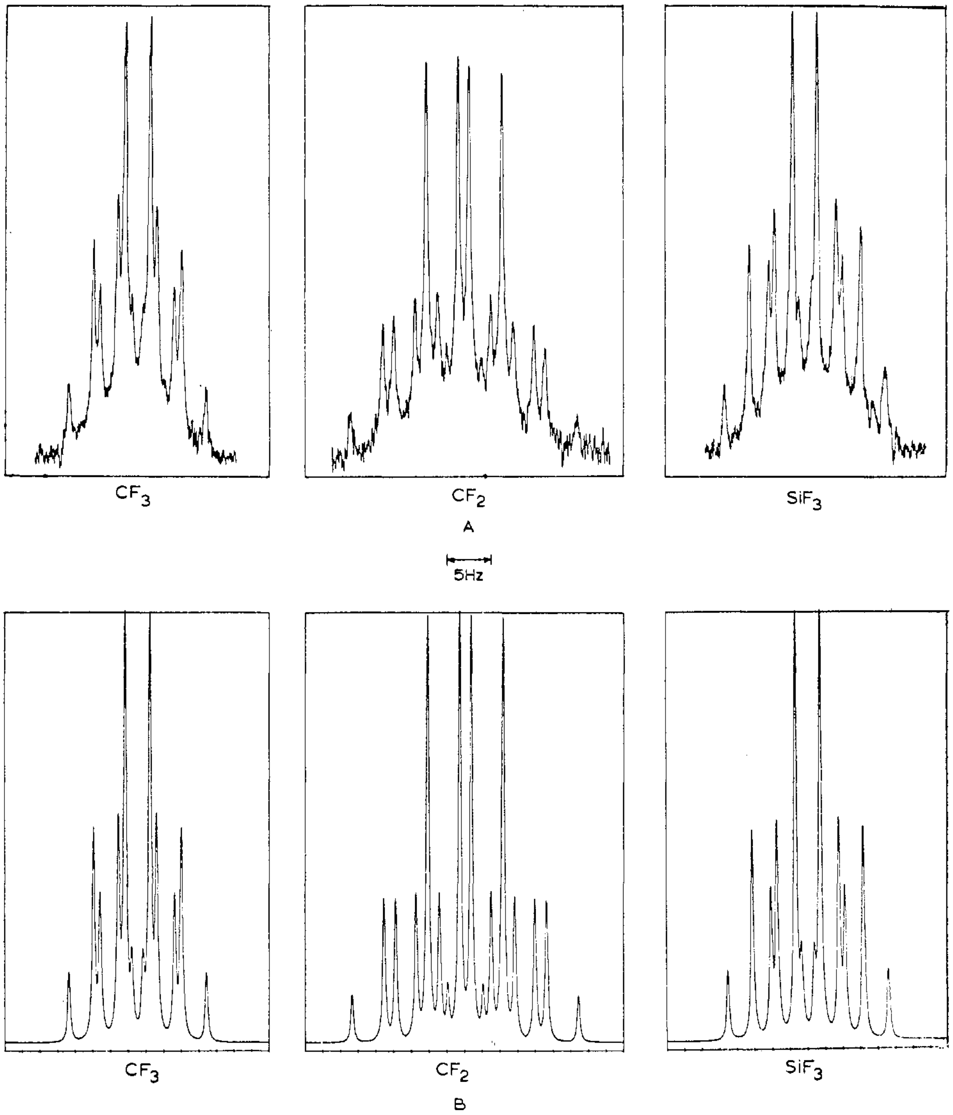

Figure 3.—Multiplets in the ^{19}F nmr spectrum of II: A, experimental spectra; B, computer simulations using parameters given in Table I.

(0.14 mmol) on the basis of molecular weight (calcd, 180.9; found, 179.9), infrared spectrum [2997 (w), 1367 (m), 1292 (s), 1262 (m), 1216 (vs), 1210 (sh), 1154 (vs), 1105 (s), 865 (m), 758 (m), 694 (m), 568 (w), 522 (w) cm^{-1}], and proton and fluorine nmr spectra which gave, from first-order analysis, the parameters listed in Table III.

Table III

Nmr Spectral Parameters for $CF_3\ddot{C}F$ Insertion Products

CF_3CFHBr

δ(H) −6.35 ppm, δ(C*F*$_3$) 84.2, δ(C*F*H) 163.6

$J(H\text{–}F)_{gem}$ = 48.6 Hz, $J(H\text{–}F)_{vic}$ = 4.6, $J(F\text{–}F)$ = 13.0

$CF_3CFHSi(CH_3)_3$

δ(H) 4.44 ppm, δ(C*H*$_3$) −0.34, δ(C*F*$_3$) 75.1, δ(C*F*H) 240.5

$J(H\text{–}F)_{gem}$ = 46.0 Hz, $J(H\text{–}F)_{vic}$ = 10.7, $J(F\text{–}F)$ = 16.7, $J(C\mathit{F}H\text{-}Si\text{-}C\text{-}\mathit{H}) \leq 0.4$, $J(C\mathit{F}_3\text{-}C\text{-}Si\text{-}C\text{-}\mathit{H}) = 0.7$

In contrast to our experience with I, decomposition of II in the presence of $(CH_3)_3SiH$ resulted in effective reaction involving the Si–H function. In one experiment 0.24 mmol of $(CH_3)_3SiH$ and 0.16 mmol of I were heated at 200° for 130 min. Separation of products could be effected either by trap-to-trap fractionation or on the low-temperature column. SiF_4 (0.17 mmol) was removed from the column at −130°; unreacted $(CH_3)_3SiH$ at −100°. Material retained at −100° (0.16 mmol) was identified as the new compound trimethyl-1,2,2,2-tetrafluoroethylsilane on the basis of molecular weight (calcd, 174.2; found, 173.7) and first-order analysis of the nmr spectra which yielded the parameters listed in Table III. The infrared spectrum exhibited bands typical of the $(CH_3)_3Si$ moiety as well as C–F and C–H stretches: 2965 (m), 2910 (w), 1347 (s), 1281 (s), 1262 (s), 1175 (vs), 1118 (s), 1044 (m), 893 (m), 850 (vs), 758 (w), 703 (w), 662 (w), 622 (w) cm^{-1}. $(CH_3)_3SiCFHCF_3$ is resistant to thermal decomposition at 220° for at least 1 hr.

Hydrolyses.—Basic hydrolysis was effected by distilling I or II into a small bulb containing a concentrated aqueous solution of NaOH. The bulb was isolated from the vacuum system and shaken as the contents warmed from liquid nitrogen temperature. Volatile products were pumped through a −95° trap for removal of water vapor. The basic hydrolysis of I yielded CF_3H as the only volatile product (91% recovery). Similarly, hydrolysis of II generated C_2F_5H as the sole product (95% recovery).

The reactions of I and II with water vapor were studied with the use of a gas-mixing cell in tandem with an infrared cell. System compositions were followed qualitatively by means of infrared spectroscopy. Reaction of water vapor with I yielded CF_3H and SiF_4 but no siloxanes or other oxygen-containing volatiles. Reaction was accompanied by appearance of a prominent absorption at 730 cm^{-1} on the cell window. With II, destruction of the compound was observed without cleavage of the Si–C bond. These observations are discussed more fully in the following section.

Results and Discussion

The reaction sequence described here provides straightforward, high-yield routes to the heretofore elusive perfluoro(alkylsilanes)

$$R_fI + SiF_2 \longrightarrow R_fSiF_2I \quad (R_f = CF_3, C_2F_5)$$

$$R_fSiF_2I \xrightarrow[\text{or AgF}]{SbF_3,\ AsF_3,} R_fSiF_3$$

Although the interaction of SiF_2 and CF_3I[13] or C_2F_5I has been shown to produce a large and complex array of products, if an excess of the fluoroalkyl iodide is employed, high yields of the respective R_fSiF_2I species result. Separation of these products from the other reaction products and from unreacted starting materials is not difficult, and the Si–I bond may be smoothly fluorinated with antimony(III) fluoride to give the perfluoro compounds in high yields (80–90%). As previously described,[1] fluorination of CF_3SiF_2I may also be effected with AsF_3 or AgF at 25°.

CF_3SiF_3 and $C_2F_5SiF_3$ are stable in the gas phase or in solution in inert solvents at room temperature. The former compound is quite sensitive to moisture or to traces of base, while the latter is significantly more robust in these respects as well as more resistant to thermolysis. The observed thermal behavior (*vide infra*) strongly suggests, however, that neither substance has the requisite stability to survive for long periods under the rigorous conditions cited[6] for the "direct" synthesis of such compounds.

Spectral Properties.—The infrared spectra of CF_3SiF_3 and $C_2F_5SiF_3$ are reproduced in Figure 2. The similarity of the bands in the Si–F stretching region (1030–800 cm^{-1}) is apparent, while the bands resulting from C–F stretching vibrations resemble those of the corresponding perfluoroalkyl halides.

The 70-eV mass spectrum of $C_2F_5SiF_3$ is presented in Table II. As reported previously,[1] the mass spectrum of I is complicated by the occurrence of thermal decomposition of the compound in the ion source of the spectrometer. In the high-voltage spectra, the molecular ions of both I and II are of very low intensity, as has been observed for various saturated fluorocarbons and fluorosilanes. Fragmentation to the [parent − F] ion is the predominant process for CF_3SiF_3, as it is for C_2F_6[20] and Si_2F_6.[21] With II, however, the [parent − F] ion, $C_2SiF_7^+$, is of rather low relative intensity; the most abundant ion in the 70-eV spectrum is $CSiF_5^+$. Preferred thermal processes (*i.e.*, α-fluorine transfer) are apparently reflected in the low-voltage (<18 eV) fragmentation patterns of I and II. Thus, the CF_2^+ species is at least an order of magnitude more intense than any other in the spectrum of I at 15 eV, suggesting fragmentation to the stable neutral SiF_4. With II, the m/e 135 peak ($CSiF_5^+$) is still the most intense at 15 eV, but the ion corresponding to $C_2F_4^+$ ranks second in abundance, suggesting a process paralleling the low-voltage fragmentation of I.

Fluorine nmr spectral parameters of the compounds reported here and of related molecules are listed in Table I. Figures 1 and 3 present traces of the various multiplet spectra in $C_2F_5SiF_2I$ and II, respectively, along with computed simulations of the spectra in which the relative coupling constants have been selected to provide the best fit of observed spectra. The spectra are all interpretable *via* first-order analysis: δ/J is in each case >250 (at 86.67 MHz) and the multiplets exhibit the required symmetry. Chemical shifts determined for the various groups are quite consistent with those observed for related species. The spectrum of $CF_3CF_2SiF_2I$ is noteworthy in that the resonances of the CF_2 and SiF_2I groups are essentially identical. This behavior implies that the two groups in question are precisely equally coupled to the CF_3 group. The situation is confirmed by appearance of the CF_3 multiplet as a 1:4:6:4:1 quintet with only a slight suggestion of additional splitting.

The magnitudes of the F–F coupling constants in II are of interest in comparison to those of perfluoropropyl groups which exhibit large long-range (J_{1-3}) coupling—from 9 to 13 Hz—and small vicinal couplings.[22] The latter are in some instances <1 Hz. In contrast, we find that the long-range F–F coupling in II (*i.e.*, $J_{CF_3-SiF_3}$) is the smallest of the three, with $J_{CF_2-SiF_3}$ the largest. The behavior of II more closely resembles that of perfluorotrisilane, where $J_{1-3} = 3.6$ Hz and $J_{1-2} = 11.0$ Hz.[23] Consideration of the series C_2F_6, CF_3SiF_3, and Si_2F_6 discloses the same trend in coupling constants: J_{F-F} is 3.5, 10.9, and 21.0 Hz, respectively. Several groups of workers have proposed correlations between J_{F-F} and substituent electronegativities for fluoroethanes.[24–26] On the basis of such a correlation, the sign of J_{F-F} in C_2F_6 was assigned as positive.[26] Attempts to fit J_{F-F} for the C_2F_5 group in II or $C_2F_5SiF_2I$ to such schemes suggest the sign of the coupling constant is negative. It will be of substantial interest to determine the signs of the F–F coupling constants in II; work in this area is now in progress.

The ^{29}Si–F coupling constants for the directly bonded atoms are very similar for $^{29}SiF_3CF_3$ and $^{29}SiF_3C_2F_5$. That for $^{29}SiF_2IC_2F_5$ is substantially higher in accordance with those observed for other fluoroiodosilanes such as SiF_3I[27] and SiF_2ICF_3.[13]

For SiF_3X species, there is a rough correlation between J_{Si-F} and substituent electronegativity, with J_{Si-F} increasing with less electronegative groups.[28] On this basis J_{Si-F} for I and II is somewhat larger than might be anticipated; indeed, the coupling constants are close to those observed in the analogous alkyltrifluorosilanes.[28]

Pyrolysis Chemistry.—The results of thermal decomposition experiments on I and II, alone or in the presence of added reagents, are described in the Experimental Section. The perfluoroethyl derivative is substantially more resistant to thermal decomposition than the perfluoromethyl homolog. Thus, while I decomposes significantly below 100°, pyrolysis of II is not appreciable below about 160°.

The extensive studies of Haszeldine and his coworkers[29] have revealed the general thermolytic behavior to be expected for polyfluoroalkylsilanes. These

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(20) F. L. Mohler, V. H. Dibeler, and R. M. Reese, *J. Res. Nat. Bur. Stand.*, **49**, 343 (1952).

(21) J. B. McDonald, C. H. Williams, J. C. Thompson, and J. L. Margrave, *Advan. Chem. Ser.*, **No. 72**, 261 (1968).

(22) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, Chapter 11.

(23) R. B. Johannesen, *J. Chem. Phys.*, **47**, 955 (1967).

(24) S. Ng and C. H. Sederholm, *ibid.*, **40**, 2090 (1964).

(25) R. J. Abraham and L. Cavalli, *Mol. Phys.*, **9**, 67 (1965).

(26) R. E. Graves and R. A. Newmark, *J. Chem. Phys.*, **47**, 368 (1967).

(27) J. L. Margrave, K. G. Sharp, and P. W. Wilson, *J. Inorg. Nucl. Chem.*, **32**, 1813 (1970).

(28) R. B. Johannesen, F. E. Brinckman, and T. D. Coyle, *J. Phys. Chem.*, **72**, 660 (1968).

(29) R. N. Haszeldine, "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, London, 1968, Chapter 5.

workers have shown that compounds containing fluorine atoms on the α-carbon atom decompose by a unimolecular α shift of fluorine to silicon, liberating the corresponding carbene which, depending on the particular species, may then rearrange to olefin, dimerize, or be trapped in the presence of a suitable added reagent. For β-fluoroalkylsilanes, decomposition *via* an internal nucleophilic attack of fluorine on silicon, leading to olefin elimination, has been proposed. Compounds containing both α- and β-fluorine atoms appear to decompose preferentially by α transfer, often resulting in the generation of novel asymmetrical carbenes.[30,31]

The thermal behavior observed in this study for I and II is completely consistent with exclusive operation of the α-elimination process. Thus, the observed decomposition products of I

$$CF_3SiF_3 \longrightarrow SiF_4 + C_2F_4\ (90\%) + c\text{-}C_3F_6\ (10\%)$$

suggest the presence of difluorocarbene as a primary decomposition product. Presence of a moderate excess of HBr in the pyrolysis reaction completely suppresses the formation of C_2F_4 and c-C_3F_6 and leads to formation of bromodifluoromethane in high yield. Mahler, who used fluoro(trifluoromethyl)phosphoranes as sources of CF_2, reported HCl to be one of the few inorganic substances studied which react with CF_2.[32]

Thermal decomposition of II leads almost exclusively to formation of a mixture of cis and trans isomers of perfluorobutene-2, which can be formed by dimerization of fluoro(trifluoromethyl)carbene

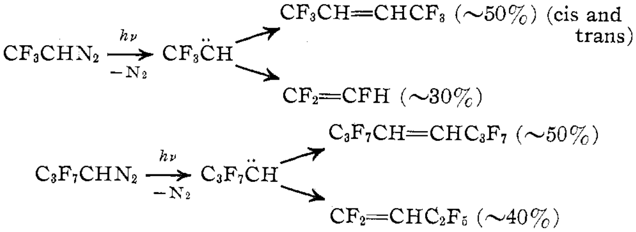
$$CF_3CF_2SiF_3 \xrightarrow{-SiF_4} CF_3\ddot{C}F \longrightarrow CF_3{-}CF{=}CF{-}CF_3\ \text{(cis and trans)}$$

It is particularly noteworthy that tetrafluoroethylene, which could arise from rearrangement of the carbene formed by α elimination and would be the expected product of β elimination, is absent from the reaction mixture.

As with $:CF_2$, dimerization of $CF_3\ddot{C}F$ is effectively inhibited in the presence of HBr, and the insertion product, CF_3CFHBr, can be obtained in high yield from the reaction mixture.

It is surprising that the fate of $CF_3\ddot{C}F$ is exclusively dimer formation, since the structurally related carbenes $CF_2H\ddot{C}F$ and $CFH_2\ddot{C}F$ are reported[29,30] to undergo rearrangement to C_2 olefins without formation of the corresponding butene derivatives.

Both reaction modes (dimerization and rearrangement) have been reported for the carbenes $CF_3\ddot{C}H$ and $C_3F_7\ddot{C}H$ obtained by photolysis of the corresponding fluorodiazoalkanes[33] (following reactions).



$$CF_3CHN_2 \xrightarrow[-N_2]{h\nu} CF_3\ddot{C}H \rightarrow \begin{cases} CF_3CH{=}CHCF_3\ (\sim 50\%)\ \text{(cis and trans)} \\ CF_2{=}CFH\ (\sim 30\%) \end{cases}$$

$$C_3F_7CHN_2 \xrightarrow[-N_2]{h\nu} C_3F_7\ddot{C}H \rightarrow \begin{cases} C_3F_7CH{=}CHC_3F_7\ (\sim 50\%) \\ CF_2{=}CHC_2F_5\ (\sim 40\%) \end{cases}$$

Mahler[34] has briefly cited evidence for the generation of $CF_3\ddot{C}F$ by thermolysis of $C_2F_5PF_4$ at 240° in platinum but reported only C_2F_4 as the fluorocarbon product of the pyrolysis. A mixture of perfluorobutene-2 and -1 has been observed as a product of thermal decomposition of bis(perfluoroethyl)iron tetracarbonyl.[35]

Although resembling $:CF_2$ in its tendency to dimerize, $CF_3\ddot{C}F$ more closely resembles $CF_2H\ddot{C}F$ with respect to insertion into Si–H bonds. Thus, pyrolysis of II in the presence of $(CH_3)_3SiH$ gave the new compound $(CH_3)_3SiCHFCF_3$ in almost quantitative yield, while no reaction was observed in the parallel experiment with I. The similar system of $CHF_2CF_2SiF_3$ with $(CH_3)_3SiH$ gives the corresponding insertion product in 55% yield.[28] In accord with the relatively low reactivity reported for $:CF_2$ from other sources, we find no effect of added CF_3I on the pyrolysis of I and only small amounts (*ca.* 5%) of what is believed to be the addition product 1,1,2-trifluorocyclopropane when pyrolysis is carried out in the presence of vinyl fluoride.

Hydrolysis Chemistry.—Basic hydrolysis of I and II in aqueous NaOH yields CF_3H and C_2F_5H, respectively, as the only volatile products. Similar behavior is well known for polyfluoroalkylsilanes.[29]

When gaseous I is allowed to mix with a deficiency of water vapor, reaction is rapid to produce CF_3H, SiF_4, and an involatile polymer. No evidence for the formation of hexafluorodisiloxane or any other volatile oxy species was found. When larger amounts of water are admitted to the system, the formation of polymer is favored over formation of additional CF_3H and SiF_4.

With II, interaction with water vapor also takes place, but cleavage of the Si–C bond does not occur. The amount of II in the system is depleted as more water vapor is added, but removal of II appears to proceed *via* a moderately stable hydrate which can be transported under its own vapor pressure at temperatures slightly above room temperature. The hydrate apparently slowly decomposes to polymeric materials which exhibit window absorptions in the infrared spectrum similar to those seen in the I–H_2O system. No SiF_4 is formed in the process.

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(30) G. Fishwick, R. N. Haszeldine, L. Parkinson, P. J. Robinson, and R. F. Simmons, *Chem. Commun.*, 382 (1965).

(31) W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. Ind.* (*London*), 789 (1961).

(32) W. Mahler, *Inorg. Chem.*, **2**, 230 (1963).

(33) R. Fields and R. N. Haszeldine, *Proc. Chem. Soc., London*, 22 (1960).

(34) W. Mahler, *J. Amer. Chem. Soc.*, **90**, 523 (1968).

(35) R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *ibid.*, **83**, 3604 (1961).