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The Cocondensation Reaction of Difluorosilene with Diborane. New Polyfluoropolysilanes¹

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The cocondensation reaction of SiF_2 with B_2H_6 at a -196° surface gives a product which, by low-temperature evaporation *in vacuo*, yields nonvolatiles and diborane derivatives of the 1,1-fluorosilylated type, possibly of the heterocyclic class 1,1- $(\text{SiF}_2)_n\text{B}_2\text{H}_4$. These decompose very easily at low temperatures (possibly autocatalytically) to form nonvolatiles and polyfluoropolysilanes; such products also come from the original cocondensation reaction. They include the known compounds SiF_4 , HSiF_3 , $(\text{SiF}_3)_2\text{O}$, Si_2F_6 , HSi_2F_5 , and Si_3F_8 and the new compounds H_3SiSiF_3 (mp -65° ; bp estd -19.4°), $\text{H}_2\text{Si}(\text{SiF}_3)_2$ (mp -52° ; volatility estd 1 mm at -78°), probably $\text{HSi}(\text{SiF}_3)_3$ and $\text{Si}(\text{SiF}_3)_4$ (neither very stable), a somewhat unstable $\text{H}(\text{SiF}_2)_2\text{SiF}_3$ (4 mm at -31°), and other volatiles which are more difficult to identify. The 1:1 trimethylamine adducts of H_3SiSiF_3 and $\text{H}_2\text{Si}(\text{SiF}_3)_2$ aid their isolation from other polyfluoropolysilanes, which the amine disproportionates. The mass spectrum of $\text{H}_2\text{Si}(\text{SiF}_3)_2$ includes metastable peaks suggesting transitory formation of at least one isomer of $\text{H}_2\text{Si}_2\text{F}_4$.

Since the discovery (in 1965) that the high-temperature species SiF_2 is relatively stable and unreactive during gas-phase transfer at moderate pressures,² there have been many experiments exploiting its reactivity when cocondensed with various other species. It may abstract hydrogen or halogen³ or insert into various bonds, often forming highly unstable polymer precursors;⁴ or in the oligomeric forms $(\text{SiF}_2)_n$ it can undergo four-center attack upon certain molecules to form either heterocyclic or polymeric species.⁵

In this regard, there is an analogy to polymethylene units, which are known to react with diborane to form a variety of products, including the interesting bicyclic 1,2- μ -polymethylenediboranes.⁶ However, in view of the relative instability of Si-B bonding, no very stable $(\text{SiF}_2)_n\text{-B}$ derivatives could be expected; one might rather hope for interesting chemical reactions or decomposition products of such compounds. Indeed, our experiments on cocondensation reactions of SiF_2 with B_2H_6 did indicate the existence of heterocyclic 1,1- $(\text{SiF}_2)_n\text{B}_2\text{H}_4$ derivatives, stable enough in the gas phase for study of their infrared spectra but extremely unstable in the liquid phase even at low temperatures; and their decomposition products did in fact prove to be numerous.

Experimental Section

The Vacuum Line.—All chemical experiments were done in a greaseless Pyrex vacuum line, including one mercury manometer, a series of U traps, and special equipment for generating and utilizing SiF_2 . The cutoffs mostly were O-ring-sealed, Teflon-plugged screw valves, but large gate valves were used for connection to the oil-diffusion pump, rated at 300 l. sec⁻¹. This pump and the adjacent ionization gauge were always protected by a trap at -196° . Portable devices such as weighing bulbs, infrared cells, or nmr tubes were attached to the line by O-ring joints.

Generation of Difluorosilene.—The "hot molecule" SiF_2 was generated as described by Pease.⁷ The required SiF_4 was pre-

pared by passage through a tube containing steel wool and powdered silicon at 800° , removing a possible SO_2 impurity. It was passed at 1 mm pressure, at a rate of 0.5 mmol/min, through a vertical quartz tube packed with silicon chips (supported by a plug of quartz wool), heated to 1170° . It has been proved by mass spectrometry that the gas stream from such a system consists only of SiF_2 and SiF_4 ;² although the latter is inert toward diborane, we cannot be sure that it plays no role when SiF_2 and diborane are cocondensed.

The Cocondensation Reaction.—The effluents SiF_2 and SiF_4 (traveling horizontally in a tube 25 mm wide) were mixed with diborane, entering at a rate between 0.2 and 0.7 mmol/min (total, 15–30 mmol) at a nozzle 6 cm from the cocondensation surface. This consisted of the curved outer wall of a vertical cylindrical copper bottle (10 cm in diameter), filled with liquid nitrogen. The system provided a very sharp thermal gradient between 25° and the actual cocondensation temperature, so that the gaseous mixture spent minimal time at intermediate temperatures. According to K. G. Sharp (private communication), such a sharp gradient improves the yields of volatiles from any SiF_2 cocondensation reaction; and indeed, when we employed a glass surface with the same geometry as the copper bottle (but slower heat withdrawal), the yields of nonvolatiles increased at the expense of volatile products and hydrogen.

During each run there was a continuous evolution of hydrogen. This was not attributable to the decomposition of back-diffusing diborane at the furnace exit, for only a negligible dark film appeared at that point. It was evident that the initial reaction of diborane with SiF_2 or $(\text{SiF}_2)_n$, either in the gas phase or during cocondensation, was such as to produce some hydrogen.

Products and Results

Behavior of the Cocondensate.—The immediate product at -196° was a lustrous black solid. With the furnace cool, this condensate was allowed to warm slowly to 25° , with continuous pump-off of the volatiles. During this process there were many changes of color and sometimes explosive flaking-off of solids from the copper surface. Some melting occurred near -15° , with a sudden vigorous evolution of hydrogen suggesting that the liquid phase favored this late-stage process. Some of the resulting volatiles were so unstable as to leave a viscous nonvolatile liquid after evaporation from any surface upon which they had been condensed.

The major product now was a nonvolatile, pyrophoric yellow solid. However, approximately 30% of the cocondensed SiF_2 has been used to form a great variety of volatile products, which were separated first by high-vacuum fractional condensation in the simple trap-to-trap manner. Table I lists the temperatures at which the six major fractions condensed, and their components,

(1) The generous support of this research by the Office of Naval Research is gratefully acknowledged.

(2) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *Nature (London)*, **207**, 187 (1965); *J. Amer. Chem. Soc.*, **87**, 2824 (1965).

(3) Y. L. Baay, *Diss. Abstr. B*, **28**, 2315 (1967).

(4) K. G. Sharp and J. L. Margrave, *Inorg. Chem.*, **8**, 2655 (1969).

(5) P. L. Timms, D. D. Stump, R. A. Kent, and J. L. Margrave, *J. Amer. Chem. Soc.*, **88**, 940 (1966).

(6) H. H. Lindner and T. Onak, *ibid.*, **88**, 1886 (1966), and earlier references there cited.

(7) D. C. Pease, U. S. Patent 2,840,588, assigned to E. I. du Pont de Nemours and Co., Wilmington, Del., June 24, 1958.

TABLE I
 COMPONENTS OF FRACTIONS FROM THE $\text{SiF}_2\text{-B}_2\text{H}_6$ COCONDENSATION

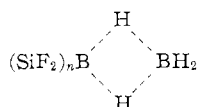
Temp., ^a °C					
-196	-127	-101	-86	-75	-60
B_2H_6	H_3SiSiF_3	$\text{HSiF}_2\text{SiF}_3$	Si_3F_8	Y	$\text{Si}(\text{SiF}_3)_4?$
SiF_4	Si_2F_6	X	$\text{HSi}(\text{SiF}_3)_3$	Si_3F_8	$\text{HSi}(\text{Si}_2\text{F}_5)(\text{SiF}_3)_2??$
HSiF_3	$(\text{SiF}_3)_2\text{O}$	$\text{H}_2\text{Si}(\text{SiF}_3)_2$	Y	$\text{H}(\text{SiF}_2)_2\text{SiF}_3$	
$(\text{SiF}_3)_2\text{O}$	X	$\text{HSi}(\text{SiF}_3)_3$		$\text{HSi}(\text{SiF}_3)_3$	
	Q			$\text{Si}(\text{SiF}_3)_4?$	

^a The temperatures here are the condensation points under high vacuum.

which were further resolved by means of a high-vacuum, low-temperature fractional condensation column.⁸ Here the previously known products were $(\text{SiF}_3)_2\text{O}$ (by action on the quartz tube), HSiF_3 , $\text{HSiF}_2\text{SiF}_3$, and the $\text{SiF}_2\text{-SiF}_4$ cocondensation products Si_2F_6 and Si_3F_8 —all clearly identified by their known nmr, infrared, or mass spectra.

The down-column listing in Table I is in the order of decreasing prevalence in the fraction. All fractions except the first contained at least traces of unidentified components.

X and Y (Table I) were two fractions containing B, H, Si, and F. Infrared and chemical evidence, taken with the argument that an $(\text{SiF}_2)_n\text{B}$ ring could be formed by a proton-hydride reaction of the insertion product $\text{H}(\text{SiF}_2)_n\text{B}_2\text{H}_5$ (and would be more stable than an open-chain Si-B-H compound), leads to the suggestion that X and Y have



structures; but both proved to be too unstable for determination of n . The less volatile Y presumably has the larger value of n , and indeed a higher $\text{SiF}_2\text{:B}_2\text{H}_6$ reactant ratio yielded more Y relative to X. Q may have been an open-chain RB_2H_5 , more volatile than X. Its rapidly disappearing X-like infrared spectrum included an 866-cm^{-1} PQR band, which could represent an SiF_3 group.

Decomposition of X and Y.—In the liquid phase, either X or Y can suddenly decompose at temperatures as low as -65° (or fail to do so even at -35°), as demonstrated by an abrupt change in the nmr spectrum. The apparently autocatalytic process may be strongly affected by impurities. The products are hydrogen, diborane, many of the fluorosilanes listed in Table I, and a nonvolatile viscous liquid. The formation of diborane could correspond to a process of the type $2\text{R}_2\text{BH}(\text{BH}_3) \rightarrow (\text{BH}_3)_2 + (\text{R}_2\text{BH})_2$; then the unstable $(\text{R}_2\text{BH})_2$ would undergo a very complex scrambling process, using some of the B-H bonds as a source of hydrogen for Si-H bonds in the resulting fluorosilanes. No aspect of the process seems to be in any way reversible—in contrast to the reversible BH_2B -bridged polymerization of 1,2- μ -trimethylenediborane.⁶

The vapor-phase decomposition of X or Y is relatively slow even at 25° , again forming nonvolatile viscous liquid material. For the volatiles from both X and Y, analyses based upon the intensities of uniquely recognizable infrared peaks gave the following list of products, with typical relative molar amounts in pa-

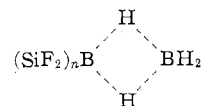
(8) As designed by A. D. Norman, with R. Schaeffer at Indiana University. The operating principle involves a vertical thermal gradient, maintained by a stream of cold nitrogen passing downward through a central tube. A diagram is shown by D. F. Schriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, p 91.

rentheses: B_2H_6 (9), HSiF_3 (13), H_3SiSiF_3 (9), $\text{HSiF}_2\text{-SiF}_3$ (10), $\text{H}_2\text{Si}(\text{SiF}_3)_2$ (13), $\text{HSi}(\text{SiF}_3)_3$ (3), $\text{Si}(\text{SiF}_3)_4$ (trace), and sometimes traces of BF_3 . H_2 (6) was directly measured. Both $\text{HSiF}_2\text{SiF}_3$ and $\text{HSi}(\text{SiF}_3)_3$ seemed to go through maxima during the process, suggesting instability under the reaction conditions.

In view of the prevalence of SiF_3 groups and Si-H bonds in the products of either the liquid or gas-phase decomposition, we cannot strictly rule out the possibility that X and Y are mixtures with compounds containing these features. However, the relatively clean separation into two fractions seems to limit the variety of possible heterocyclic derivatives of diborane; for example, an SiF_3 group attached to the Si_nB ring does not seem probable.

For successful distillation of X or Y in the high-vacuum line, it is best to operate at the lowest possible pressure, with insulation allowing only very slow heat input. This way, it becomes possible to transfer them with little loss, for instrumental studies or for chemical investigations. However, neither X nor Y could be purified completely because their decomposition in the fractional-condensation column produced similarly volatile fluoropolysilanes.

Infrared Spectra of X and Y.—The slow rates of decomposition of X and Y in the vapor phase at 25° made it feasible to study their infrared spectra, but it was quite difficult to evaporate them to sufficiently high pressures without much liquid-phase decomposition. The best procedure employed a Pyrex cell (with KBr windows attached by Apiezon W vacuum wax) having a small sealed-on U tube leading through a Teflon-plugged screw valve to a joint connecting to the vacuum line. Thus a sample of X or Y with similarly volatile fluoropolysilanes could be condensed into the U tube and then quickly evaporated directly into the infrared beam of the Perkin-Elmer No. 337 instrument for a rapid initial scan. Then, by repeated scans at intervals of a few hours, it was possible to observe the disappearance of the bands due to the unstable X or Y species, while the bands for the decomposition products (volatiles and nonvolatile viscous liquid) increased in intensity. Those bands which thus were attributed to X, Y, or deuterated Y (made from B_2D_6), and not obscured by the decomposition products, are compared with the pertinent bands for B_2H_6 and 1,1- $(\text{C}_2\text{H}_5)_2\text{B}_2\text{H}_4$, in Table II. It is quite apparent that both X and Y have the bridging BH_2B and terminal BH_2 groups, as required for the postulated



structural type.

TABLE II
 INFRARED SPECTRA OF X AND Y (GAS PHASE, WITH COMPARISONS)^a

Assignments	B ₂ H ₆ ^b	1,1-Et ₂ B ₂ H ₄ ^c	X	Y	Y-d
$\nu_{16} + \nu_{18}$	3670 (0.8)	3623 (0.2)	3604 (0.4)	3610 (0.4)	2980
$\nu_2 + \nu_{17}$					
B-H _t asym str, ν_{12}	2609 (5.2)	2577 (6.0)	2613 (5.0)	2626 (5.2)	1991
B-H _t sym str, ν_{16}	2520 (5.0)	2506 (5.4)	2533 (6.2)	2544 (8.6)	1867
B-H _b sym in-phase str, ν_2	2102 (0)	2079 (1.0)	2151 (4.1)	2177? (2.7)	1633
B-H _b asym out-of-phase str, ν_8	1988 (0.1)	1718 (1.6)	?	?	?
B-H _b asym in-phase str, ν_{17}	1604 (17)	1543 (17)	1574 (21)	1573 (14)	1176
B(H _t) ₂ bend, in-plane, ν_{18}	1174 (5.5)	1168 (2.4)	1175 (4.4)	1174 (5.7)	832?
?	1032 (2.5)	1032 (1.9)	...
?	923
B(H _t) ₂ out-of-plane wag, ν_9	973 (1.8)	928 (1.0)	972? (?)		
			914? (5.2)	921 (6.7)	725
			857 (?)		
			727 (9.8)	725 (5.0)	612
			582? (1.0)	577 (0.9)	480?
			451? (3.3)	455 (6.6)	429

^a Relative intensities based upon the definition $k = (100/PL) \log (I_0/I)$, for pressure P and path L , both in centimeters. Question marks designate unassigned bands. Et = C₂H₅. Some ambiguous peaks in the Si-F stretching region are omitted. ^b W. E. Anderson and E. F. Barker, *J. Chem. Phys.*, **18**, 698 (1950). ^c W. J. Lehmann, C. O. Wilson, Jr., and I. Shapiro, *ibid.*, **34**, 476 (1961).

As usual, Table II gives the frequencies of the peaks in reciprocal centimeters, with relative intensities in parentheses.

Nmr Spectra of X and Y.—The 100-Mc proton spectra of X and Y showed the broad singlets which are normal for the bridge hydrogen, respectively at τ 10.2 and 10.5. In the BH₂ region, the spectrum for X was unusually broad and obscure, whereas for Y the situation was definite but abnormal: instead of the usual 1:1:1:1 quartet, there was only a broad singlet, at τ 5.96. The half-width of this singlet (62 cps at -68°) increased with temperature (more rapidly than the τ 10.5 peak), as would be expected if quadrupole relaxation were causing coalescence of the usual quartet—an effect which decreases with rising temperature. The situation seemed very like that reported for ClO₃F between -131 and -102° .⁹ A small unresolved multiplet at τ 10.03 (Si-H impurity) showed no change of width with temperature. With rising temperature, the whole proton spectrum of Y tended to be wiped out unpredictably, then being replaced by some 13 broadened peaks.

The 32.1-Mc boron spectrum of X showed the BH₂ group as a relatively sharp complex feature (2 ppm downfield of trimethyl borate), which could be interpreted as a triplet of triplets ($J = 55$ and 145 cps), overlapped by an equally intense triplet with $J \approx 55$ cps—attributable to boron in the (SiF₂)_nB(H₂)_b system. This interpretation conforms to the suggested structural pattern but is not sufficiently dependable to serve as independent evidence.

The boron spectrum of Y, centered at 3.5 ppm downfield of trimethyl borate, looked like a poorly resolved triplet of triplets ($J = ca. 50$ and 83 cps) overlapping a broad singlet with half-width about 520 cps. An interpretation in terms of the 1,1-(SiF₂)_nB₂H₄ structure is possible but not required.

The boron spectra of both X and Y showed a small broad peak at 10.5 ppm downfield of methyl borate, presumably due to the same boron-containing impurity.

(9) J. Bacon, R. J. Gillespie, and J. W. Quail, *Can. J. Chem.*, **41**, 3063 (1963).

Chemical Evidence. The Trimethylamine Reactions.—Diborane derivatives of the 1,1-R₂B₂H₄ type are known to react with 2(CH₃)₃N to form (CH₃)₃NBH₃ and (CH₃)₃NBHR₂,¹⁰ providing a test for this structural type. Accordingly, X and Y in the vapor phase were treated with measured amounts of (CH₃)₃N in a special bulb such that the amine entered from below for ideal mixing. After the rapid reaction, any excess amine was recovered and measured, and the product (CH₃)₃NBH₃ was isolated, identified, and weighed. From X the yield of (CH₃)₃NBH₃ was 1 mol per 2.4 ± 0.3 mol of amine consumed; from Y, 1 mol of (CH₃)₃N per 2.08 ± 0.07 mol of amine consumed. Minor inaccuracies would have been due to the fluoropolysilane impurities, some of which form weak complexes with the amine, but the main conclusion is clear: both X and Y underwent BH₂B bridge cleavage to provide the BH₃ group.

The hypothetical (CH₃)₃NBH(SiF₂)_n aspect could not be observed: if formed at all, it must have been very unstable under the reaction conditions. Both X and Y yielded HSiF₃, SiF₄, and nonvolatile viscous liquids; some very unstable volatile products could not be identified. From the action upon X, no excess amine could be recovered, and considerable yields of H₃SiSiF₃ and H₂Si(SiF₃)₂ were observed; these were not obtained from the Y experiments, wherein excess amine was employed. However, these two fluoropolysilanes are resistant toward catalysis by trimethylamine, in contrast to (SiF₃)₂O, Si₂F₆, Si₃F₈, HSi₂F₅, and HSi₃F₇, all of which are catalytically decomposed by trimethylamine on a cold surface (but not in the vapor phase) to form SiF₄ (and, when possible, HSiF₃) along with nonvolatile white solids which turn orange-brown on warming to room temperature.

Pentafluorodisilane.—The compound HSiF₂SiF₃ was separated with some difficulty from Si₂F₆, which is slightly more volatile. It was clearly identified by its known proton and fluorine nmr spectra, its infrared spectrum (especially, Si-H stretching at 2230 cm⁻¹), and its melting point (-11.5°), all in good agreement

(10) H. I. Schlesinger, N. W. Flodin, and A. B. Burg, *J. Amer. Chem. Soc.*, **61**, 1078 (1939).

with the literature.^{3,4} As a liquid, it proved to be stable at 25° in a clean, greaseless glass container, and the vapor was not wholly decomposed even after a few hours at 160°. In the presence of the polymers formed from X and Y it showed the instability attributed to it by Sharp and Margrave.⁴ Its major presence in the effluent from the original cocondensate suggests that it was formed in the primary reaction, but it was also a major product of the decomposition of Y and probably of X as well. For its direct formation, the Si₂F₄ unit would have to capture an extra F atom (possibly from SiF₄) as well as one H from the boron hydride.

1,1,1-Trifluorodisilane.—The new compound H₃SiSiF₃ was isolated by means of the fractional-condensation column, with some difficulty due to the somewhat more volatile (SiF₃)₂O and the slightly less volatile Si₂F₆. The analogous D₃SiSiF₃ (less volatile than H₃SiSiF₃) could not be isolated by this method.

More conveniently, H₃SiSiF₃ could be converted to its 1:1 complex with trimethylamine, with catalytic destruction of the impurities. The dissociation pressures of H₃SiSiF₃·N(CH₃)₃ were roughly measured in the range -37 to -60°, giving the equation $\log P_{\text{mm}} = 11.90 - 2485/T$ (example, 5.8 mm at -50°). Accordingly, it was possible to evaporate the complex at -78.5°, leaving the somewhat more stable SiF₄·N(CH₃)₃ and (CH₃)₃N·HSiF₃ (products of the disproportionation of impurities) behind at that temperature. The pure sublimate now could be treated with diborane in small excess, liberating H₃SiSiF₃ with formation of (CH₃)₃NBH₃. The components now could be separated quantitatively by fractional condensation and measured to prove the 1:1 composition of the amine complex.

The vapor tensions of solid H₃SiSiF₃ conformed to the equation $\log P_{\text{mm}} = 11.590 - 2046/T$ (example, 12.0 mm at -78.5°). For the liquid, $\log P_{\text{mm}} = 6.784 + 1.75 \log T - 0.008T - 1543/T$ (example, 80 mm at -60.4°), indicating the normal boiling point to be -19.4° and the Trouton constant 21.9 eu. The two equations gave the melting point as -64.9° (obsd, -65.2°, sharp) and the molar enthalpy of fusion as 3.16 kcal. The vapor-phase molecular weight was determined as 115 (calcd, 116.2). The mass spectrum at low ionization voltages showed the parent ion (116) and various expected fragments.

The infrared spectrum of H₃SiSiF₃ (Beckman IR7 instrument) is compared with that of D₃SiSiF₃ in Table III. It is very interesting that the bands assignable to Si-F symmetric stretching have such different frequencies for D₃SiSiF₃ vs. H₃SiSiF₃. It is suggested that the latter molecule undergoes coupling between Si-F symmetric stretching and SiH₃ symmetric deformation, whereas the corresponding asymmetric modes would not couple so effectively.

The many PQR parallel bands correspond to the expected symmetric-top structure. This structure was confirmed very accurately by the microwave spectrum: the spacings agreed well with predictions for the symmetric-top H₃SiSiF₃, and lines were observed for the isotopic combinations 28-28, 28-29, 29-28, 28-30, and 30-28. The full results, showing the Si-Si distance as 2.31 Å (cf. Si₂H₆, 2.32), will be offered for publication under the direction of Dr. R. A. Beaudet.

The vapor of H₃SiSiF₃ inflames spontaneously in air,

TABLE III

INFRARED SPECTRUM OF 1,1,1-TRIFLUORODISILANE ^a		
Suggested assignment	H ₃ SiSiF ₃	D ₃ SiSiF ₃
Combinations?	2373 b (0.5) 2241 b (1.0)	...
Si-H asym str	R2199 sh (5) Q2191 (10)	R1608 (2.9) Q1601 (4.7) P1593 (3.1)
Si-H sym str	Q2180 (7) P2175 sh (4.5)	R1576 (1.7) Q1568 (2.6) P1562 (1.3)
Combinations?	2147 b (0.9) 2127 b (0.7)	
Si-F asym str (SiH ₃ asym def)	R967 (22) Q961 (47) P956 sh (28)	R965 (22) Q959 (50) P950 (26)
Si-F sym str (SiH ₃ sym def)	R833 (33) Q826 (58) P819 (28)	R872 (15) Q866 (18) P861 (10)
Uncertain	...	794 sh (1.8) 788 sh (3.3)
SiD ₃ asym def	...	R781 (5.1) Q774 (6.4) P769 (3.7)
SiD ₃ sym def	...	R661 (10) Q654 (12) P649 (6)
Si-Si str	R539 (1.0) Q532 (2.2)	511 (3.1) 504 sh (7)
SiF ₃ asym def	R512 (6.3) Q505 (12) P498 (5.8)	R499 (9.1) Q493 (12) P486 (7.5)
SiF ₃ sym def	R313 (5.9) Q306 (8.5) P300 (3.7)	305 (6) 298.5 (6)

^a Frequency values in reciprocal centimeters; relative intensities in parentheses. Cf. Table II. sh = shoulder; b = broad band with uncertain maximum absorption frequency.

but the isolated compound is stable as a liquid or gas at 25°; and at 170° (gas) it decomposes only very slowly, to form H₂, HSiF₃, H₂SiF₂, and nonvolatiles. It readily absorbs into the polymers remaining after the decomposition of fractions X and Y but then can be recovered completely by pumping. Very little of this compound was present in the effluent from the original cocondensate; nearly all of it must have come from later reactions of this effluent, including the decomposition of X and Y.

Bis(trifluorosilyl)silane.—The new compound H₂Si(SiF₃)₂ could be isolated almost completely from the slightly more volatile HSiF₂SiF₃ and the less volatile Si₃F₈ by means of the fractional-condensation column. Its large, clear crystals distinguished it from nearby fractions (white sheets or spiny, powdery balls), aiding visual control of the fractionation process. Purification through formation of the 1:1 complex with trimethylamine (and liberating it by action of B₂H₆) is a possible process but somewhat more difficult than the similar procedure for H₃SiSiF₃; slow catalytic decomposition may occur. The volatility of pure H₂Si(SiF₃)₂ is close to 1 mm at -78°; the melting point (not sharp) is near -52°. Its vapor-phase molecular weight was 200.9 (calcd 200.26). In its infrared spectrum (Table IV) the very strong 990-cm⁻¹ peak for Si₃F₈² was not detectable. For the D₂Si(SiF₃)₂ comparison spectrum, however, it was necessary to weed out peaks attributable to impurities such as Si₃F₈, HDSi(SiF₃)₂, and traces of D₃SiSiF₃ and SiF₄. The structure of H₂Si(SiF₃)₂ is proved more dependably by the H and

TABLE IV

INFRARED SPECTRUM OF BIS(TRIFLUOROSILYL)SILANE		
Suggested assignment	H ₂ Si(SiF ₃) ₂	D ₂ Si(SiF ₃) ₂
Si-H asym str	2182 b (1.7)	R1635 (0.3) Q1628 (0.7) P1622 (0.4)
Si-D sym str	...	1595 b (0.8)
Si-F asym str	974 b (26)	974 (31)
Si-H out-of-plane bend	909 b (0.45)	673 (1.2)
Si-F sym str	R860 (14.3) Q856 (14.7) P853 sh (12.4)	R828 (17) Q823 (24) P819 (16)
SiH ₂ sym def	832 b, sh (2.4)	R648 (1.5) Q643 (1.6) P638 (1.2)
SiH ₂ rock	R697 (6) Q694 (9) P691 (12)	R499 (2.3) Q495 (2.2) ?
SiF ₃ asym def	R512 (5) Q507 (8) P498 (3)	Obscured by SiD ₂ rock?
SiF ₃ sym def	R311 (2) Q305 (5) P300 (3)	318 b (4.3) 304 sh (2.3) 295 b (1.5)

F nmr spectra (presented later): the expected features were confirmed by ²⁹Si splittings.

The mass spectrum of this compound (Table V)

TABLE V
MASS SPECTRUM OF H₂Si(SiF₃)₂

Ion mass	Main identity ^a	Amplitude ^b		Ion mass	Main identity ^a	Amplitude ^b	
		20 eV	70 eV			20 eV	70 eV
202	Si ₃ F ₅ H ₂ ⁺	0.3	0.1	96	Si ₂ F ₂ H ₂ ⁺	3.2	2.0
201	Si ₃ F ₅ H ₃ ⁺	0.55	0.3	95	Si ₂ F ₂ H ⁺	0.0	4.1
200	Si ₃ F ₅ H ₂ ⁺	1.8	0.9	94	Si ₂ F ₂ ⁺	0.0	5.1
199	Si ₃ F ₅ H ⁺	4.0	3.6	92	?	2.1	0.6
198	Si ₃ F ₆ ⁺	2.5	2.3	87	SiF ₃ ⁺	0.0	2.2
186	Si ₂ OF ₆	0.8	0.1	86	SiF ₃ ⁺	0.0	3.3
184	Si ₃ F ₅ H ₂ ⁺	0.0	0.2	85	SiF ₃ ⁺	0.9	100
183	Si ₃ F ₅ H ₂ ⁺	0.0	3.2	78	Si ₂ FH ₃ ⁺	1.7	1.0
182	Si ₃ F ₅ H ₂ ⁺	0.0	4.6	75	Si ₂ F ⁺	0.0	1.0
181	Si ₃ F ₅ H ₂ ⁺	0.0	31.2	68	SiF ₂ H ₂ ⁺	0.4	1.0
180	Si ₃ F ₅ H ⁺	0.0	<0.1	67	SiF ₂ H ⁺	0.0	16.7
167	Si ₂ OF ₆ ⁺	0.0	1.1	66	SiF ₂ ⁺	0.0	9.0
144	?	4.5	0.9	49	SiFH ₂ ⁺	2.6	16.8
133	Si ₂ F ₄ H ⁺	0.1	0.7	48	SiFH ⁺	4.0	17.9
132	Si ₂ F ₄ ⁺	0.1	0.5	47	SiF ⁺	16.1	300
117	Si ₂ F ₃ H ₃ ⁺	0.8	0.6	42.5	SiF ₂ ²⁺	0.0	0.2
116	Si ₂ F ₃ H ₃ ⁺	11.2	3.9	42	?	1.2	1.2
115	Si ₂ F ₃ H ₂ ⁺	17.5	11.9	31	SiH ₂ ⁺	0.8	1.8
114	Si ₂ F ₃ H ⁺	100	48.7	30	SiH ₂ ⁺	7.2	9.0
113	Si ₂ F ₃ ⁺	0.6	4.8	29	SiH ⁺	2.5	20.1
104	SiF ₄ ⁺	0.0	0.8	28	Si ⁺	10.1	80.1
97	SiF ₂ SiH ₂ ⁺	0.3	1.4				

^a Where more than one identity is possible, the listed one is presumed to be the most abundant. For example, the intensity of the 202 peak is almost wholly explained by the silicon-isotope effect, whereas two-thirds of the intensity of the 201 peak may be ascribed to H atom transfer. ^b Each amplitude is relative to others at the same voltage but is not to be compared with amplitudes at the other voltage setting. Omitted from the table are peaks assigned to CO₂⁺ (amplitude 0.0 and 2.6) and O₂⁺ (amplitude 1.8 and 7.8).

shows the parent ion only at low intensities; other effects are more interesting. For example, one usually expects easier detachment of H than F, but the 181 peak is far more intense than the 199 peak, and the virtual absence of a 180 peak suggests internal stabilization of the Si₃F₅H₂⁺ species against loss of hydrogen. The similar ions with one ²⁹Si, one ³⁰Si, and ²⁹Si + ³⁰Si appear with exactly the predicted relative intensities, confirming that loss of H is negligible. However, it seems that 20 eV is not enough to remove just one F, for the Si₃F₅H₂⁺ species do not appear at that setting. Most of the other strong peaks were routinely as ex-

pected, but the intense 67 peak for HSiF₂⁺ would require a rearrangement.

The SiF₃⁺ ion, very intense at 70 eV, is almost absent at 20 eV; the pertinent Si-Si bond evidently is not easily broken. However, the extremely intense SiF⁺ ion (requiring the same Si-Si bond cleavage) is still quite prominent at 20 eV, suggesting formation through dissociation of a metastable ion. Indeed, at 70 eV, metastable peaks appear at 12.2 and 11.1 mass units, attributable to the decompositions Si₃F₅H₂⁺ → SiF⁺ + Si₂F₄H₂ (calcd, 12.204) and Si₃F₅H⁺ → SiF⁺ + Si₂F₄H (calcd, 11.101). This interpretation would suggest the first formation of Si₂F₄H₂.

Other notable 20-eV results include higher relative intensity for the parent ion and the related 201 and 202 peaks, which would be attributed to transfer of H to the parent ion. The 114 peak also is relatively much stronger.

Most probably, H₂Si(SiF₃)₂ is formed exclusively from products X and Y.

The Status of 1,1,1,2,2,3,3-Heptafluorotrisilane.—The compound HSiF₂SiF₂SiF₃ could not be completely purified: our best efforts gave only mixtures with Si₃F₈, having 4 mm vapor pressure at -30.7°. Hence the best evidence for its identity is instrumental. Again the strongest evidence is the nmr spectra: both the H and F spectra have the right multiplicity and chemical shifts for the expected three kinds of fluorine and the lone terminal proton. The infrared spectrum (Beckman IR7) showed few strong peaks entirely distinct from those for Si₃F₈; their frequencies (cm⁻¹), with relative intensities, are listed as 316 (3.9), 335 (3.7), 456 (1.2), 517 (0.7), 808 (1.7), and 2222 (0.8). This 2222-cm⁻¹ peak is so near the Si-H stretching frequency in HSiF₂SiF₃ (2230 cm⁻¹) as to confirm the presence of the same terminal HSiF₂ group.

Even the volatility relationships suggest a similar comparison: Si₃F₇H is slightly less volatile than Si₃F₈, just as Si₂F₅H is slightly less volatile than Si₂F₆. It is most probable that HSiF₂SiF₂SiF₃ is formed as a direct product of the SiF₂-B₂H₆ reaction, by a mechanism like that leading to HSiF₂SiF₃. That there is no need to go through products X and Y for its formation is indicated by one result of the SiF₂-H₂S reaction: the mass spectrum of the products includes a peak assigned to Si₃F₇H⁺.¹¹

Our impure samples of HSiF₂SiF₂SiF₃ were slightly unstable, but could be kept for short times as liquid or gas at 25°.

The Presumed Tris(trifluorosilyl)silane.—A still less stable product, showing a single Si-H stretching frequency (2175 cm⁻¹), was indicated by the nmr evidence to be HSi(SiF₃)₃: this formula agrees with the observed single decad for the proton spectrum and the simple doublet with a low coupling constant (4.9 cps) for a set of equivalent F atoms coupling across two Si atoms to one proton. On the fractional condensation column, this product remained liquid at a point between the more volatile H₂Si(SiF₃)₂ and the less volatile Si₃F₈. Its lack of good stability at 25° precluded any very thorough study, such as a molecular weight determination and satisfactory analyses. The microwave spectrum seems confused: no evenly spaced lines (symmetric-top pattern) can be sorted out.

TABLE VI
¹⁹F NMR SPECTRA OF FLUOROPOLYPHOSPHINES FROM THE SiF₂-B₂H₆ REACTION^a

Compd	Struct unit	δ	J_{FSiH}	$J_{\text{FSi}_2\text{H}}$	$J_{\text{FSi}_3\text{H}}$	$J_{\text{FSi}_2\text{F}}$	$J_{\text{FSi}_3\text{F}}$	$J_{\text{F}^{29}\text{Si}}$	$J_{\text{FSi}^{29}\text{Si}}$
HSiF ₂ SiF ₃	SiF ₃ ^b	127.3 (125.3)	...	12.8 d (12.7)	...	12.8 t (12.7)	...	347	63
	SiF ₂	143.8 (142.4)	53.8 d (53.2)	12.4 q (12.7)	...	323	59
H(SiF ₂) ₂ SiF ₃	SiF ₃ ^b	125.0	3.4 d	11.5 t	2.3 t	350	...
	SiF ₂ ^b	140.4	...	5.5 d	...	10.5 q 8.7 t
H ₃ SiSiF ₃	HSiF ₂	143.5	53.3 d	8.5 t	2.2 q
	SiF ₃	116.1	...	5.7 q	347?	...
H ₂ Si(SiF ₃) ₂	SiF ₃	114.5	...	5.3 t	2.8 ^c	342	38
HSi(SiF ₃) ₃	SiF ₃	112.2	...	4.9 d	327?	41
Si(SiF ₃) ₄	SiF ₃	110.8	32
HSi(SiF ₃) ₂ (Si ₂ F ₅)??	(SiF ₃) ₂	111.9	...	5.2 d
	End SiF ₃	125.9	10.6 t
	SiF ₂	130.6	9.3 q

^a δ values in ppm from Cl₃CF; J values in cps. ^b Interpretable overlapping multiplets. ^c Obtained from the ²⁹Si triplet-of-quartets satellites.

Less Certain Products.—Among the less volatile fractions there was a slight yield of a product showing a clean ¹⁹F singlet, confirmed by a small symmetrical splitting ($J = 32$ cps) attributable to a central ²⁹Si in Si(SiF₃)₄; the more complex splitting expected for ²⁹SiF₃ could not be sorted out. Too little of this unstable product was available for any further purification and characterization. Such a compound, having a central Si lacking any π interaction with F (except very weakly across other Si atoms), should be expected to disproportionate for an increase in the total bonding energy.

Another highly uncertain product might be HSi(Si₂F₅)(SiF₃)₂. The least volatile fractions must have included still other products, the nmr spectra of which could not be selected from the results for mixtures.

Comparison of Nmr Spectra

Data.—The data presented in Tables VI and VII

 TABLE VII
 PROTON NMR SPECTRA OF THE FLUOROPOLYSILANES^a

Compd	Struct unit	τ	J_{HSiF}	$J_{\text{HSi}_2\text{F}}$	$J_{\text{HSi}_3\text{F}}$	$J_{\text{H}^{29}\text{Si}}$
HSiF ₂ SiF ₃	SiH	6.15 (6.33)	53.3 t (54.0)	13.3 q (13.3)	...	294
	HSiF ₂ SiF ₂ SiF ₃	SiH ^a	5.41	53.7 t	5.3 t	3.2 q
H ₃ SiSiF ₃	SiH ₃	7.86	...	6.5 q
H ₂ Si(SiF ₃) ₂	SiH ₂	7.84	...	5.2 s	...	206
HSi(SiF ₃) ₃	SiH	7.11	...	4.95 dc

^a τ values in ppm; J values in cps.

were obtained by means of the Varian HA-100 instrument operating in the HR (unlocked) mode, at 94.07 Mc for ¹⁹F and 100 Mc for protons. Most of the chemical shifts were obtained by the tube-replacement method; for fluorine, δ is measured upfield from Cl₃CF, and for protons, τ values (upfield of TMS - 10 ppm) are used. Some very small samples were diluted with Si₂F₆ or Si₃F₈, to provide enough depth of liquid for

good adjustment of homogeneity and also to serve as secondary internal standards. Such dilution could not be expected to have much effect upon the chemical shifts or coupling constants. For moderately unstable samples, temperatures as low as -10° were employed.

The SiF₃ spectrum of HSiF₂SiF₃ and the proton spectrum of HSi(SiF₃)₃ had some complexity of form, suggestive of second-order effects; all others were at least very nearly first order. In both tables, parenthetical values are from the literature. The multiplicity of each feature is indicated: d, doublet; t, triplet; q, quartet; s, septet; dc, decad.

Discussion.—It is interesting that the δ values for SiF₃ groups appear in two small ranges: at lower field when SiF₃ is adjacent to the Si-H bond or at higher field when SiF₂ is interposed. Since this trend is opposite to expectations based upon purely σ bonding, an effect due to F_{2p}-Si_{3d} π bonding may be indicated. However, the SiF₂ group seems less affected by its position in the chain. A small but definite trend of δ for SiF₃ in the series H₃SiSiF₃, H₂Si(SiF₃)₂, HSi(SiF₃)₃, and Si(SiF₃)₄ lends plausibility to the existence of the latter two members; and for HSi(SiF₃)₃ the trend of $J_{\text{FSi}_2\text{H}}$ does the same. However, the differences are so small as to suggest that the electron-withdrawing power of the SiF₃ group is largely neutralized by the suggested F_{2p}-Si_{3d} π back-bonding. Apparently a similar F deshielding occurs in H₃GeSiF₃ (δ 113.8 ppm),¹² whereas in H₃CSiF₃ (δ 138 ppm)¹³ such an effect is not possible.

Also the τ values for protons in the series H₃SiSiF₃, H₂Si(SiF₃)₂, and HSi(SiF₃)₃ differ so little as to confirm the same compensating effect of π back-bonding in the otherwise very electronegative SiF₃ groups. Certainly the differences are far greater when F replaces H in SiH₄.

(12) D. Solan and P. L. Timms, *Inorg. Chem.*, **7**, 2157 (1968); an error of calculation, giving δ as 106, is hereby corrected.

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