

## Silicon–Nitrogen Compounds. Part X.<sup>1</sup> Dehydrofluorination of Tetrafluorosilane–Amine Adducts with Anionic Hydrides and Related Compounds

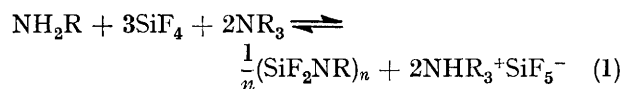
By Mellis Allan, Bernard J. Aylett,\* Ian A. Ellis, and Christopher J. Porritt, Chemistry Department, Westfield College, Hampstead, London NW3 7ST

Adducts of tetrafluorosilane and secondary amines  $\text{NHR}_2$  ( $\text{R} = \text{Me}$  or  $\text{Et}$ ) react, especially when an excess of tetrafluorosilane is present, with the following dehydrofluorinating agents:  $\text{LiAlH}_4$  ( $200^\circ$ );  $\text{NaBH}_4$  ( $200^\circ$ );  $\text{B}_2\text{H}_6$  ( $190$ – $200^\circ$ ); electropositive metals ( $350^\circ$ ). The products are corresponding substituted aminofluorosilanes  $\text{SiF}_{4-n}(\text{NR}_2)_n$  ( $\text{R} = \text{Me}$ ,  $n = 1$  or  $2$ ;  $\text{R} = \text{Et}$ ,  $n = 1$ ). Tetrafluorosilane slowly reacts at  $25^\circ$  with alkali metals in liquid  $\text{NHMe}_2$  to give  $\text{SiF}_2(\text{NMe}_2)_2$ . Similarly,  $\text{SiF}_4$  and primary amines, on heating with  $\text{LiAlH}_4$  (or in some cases  $\text{NaBH}_4$ ), produce corresponding *N*-substituted hexafluorodisilazanes  $(\text{SiF}_3)_2\text{NR}$  ( $\text{R} = \text{H}$ ,  $\text{Me}$ ,  $\text{Et}$ ,  $\text{Ph}$ , or  $\text{NMe}_2$ ). In some cases, evidence for partly-substituted  $\text{SiF}_3\text{NHR}$  or condensed  $\text{SiF}_3\text{NR}(\text{SiF}_2\text{NR})_n\text{SiF}_3$  derivatives was obtained. The chief or sole product from  $\text{SiF}_4$ – $\text{NH}_2\text{R}$ – $\text{B}_2\text{H}_6$  reactions is a borazole  $\text{B}_3\text{H}_3\text{N}_3\text{R}_3$ ; also the diamine

$\text{NHMe}[\text{CH}_2]_2\text{NHMe}$  gives rise to  $\text{HBNMeCH}_2\text{CH}_2\text{NMe}$ . The adduct  $\text{SiF}_4 \cdot 2\text{NH}_2\text{Me}$  is not dehydrofluorinated when heated alone or with added  $\text{NEt}_3$ ,  $\text{NH}_2\text{Ph}$ , zinc, or  $\text{Fe}(\text{CO})_5$ ; above  $300^\circ$  some disproportionation of the amine occurs. Physical properties of the products, including the mass spectrum of  $(\text{SiF}_3)_2\text{NH}$  and i.r. spectra are reported; also possible intermediates in dehydrofluorination are discussed.

We have shown<sup>1</sup> how substituted aminofluorosilanes result from self-dehydrofluorination of  $\text{SiF}_4$ –amine adducts. Added reagents may also serve to remove the elements of hydrogen fluoride. Thus  $\text{BF}_3$  adducts of primary and secondary amines have been converted into B–N compounds by metals<sup>2,3</sup> at  $250$ – $300^\circ$ , metal amides,<sup>4</sup> Grignard reagents,<sup>5</sup> and aliphatic tertiary amines in solution,<sup>6</sup> but not by  $\text{LiH}$ ,<sup>7</sup> pyridine,<sup>6</sup>  $\text{KF}$ ,<sup>3</sup>  $\text{CsF}$ ,<sup>6</sup>  $\text{KOBu}^t$ ,<sup>6</sup>  $\text{AlCl}_3$ ,<sup>6</sup>  $\text{CaS}$ ,<sup>6</sup> or  $\text{Al}_4\text{C}_3$ ;<sup>6</sup> alkali metal tetrahydroborates gave uncertain results.<sup>7</sup>

Less is known concerning  $\text{SiF}_4$ –amine systems. Apart from our preliminary communication,<sup>8</sup> a patent has described the dehydrofluorination of  $\text{SiF}_4$  and tetraaminobiphenyl using  $\text{NMe}_3$ ,<sup>9</sup> and other reports have shown<sup>10</sup> how various  $\text{SiF}_4$ –primary amine adducts react in benzene according to equation (1) † with  $\text{NMe}_3$ ,  $\text{NEt}_3$ , and  $\text{NEtPr}_2$  but not pyridine. The reaction was



reversible in boiling benzene, and separation of products was difficult.

We now give a detailed account of the preparation of monomeric and condensed aminofluorosilanes by means of a range of dehydrofluorinating agents.

### EXPERIMENTAL

High-vacuum and dry-box techniques were employed throughout. Procedures for separation and characteriza-

† In some cases, other fluorosilicate anions (e.g.  $\text{Si}_2\text{F}_{11}^{3-}$ ) were present.

<sup>1</sup> Part IX: B. J. Aylett, I. A. Ellis, and C. J. Porritt, *J.C.S. Dalton*, 1973, 83.

<sup>2</sup> V. I. Spitsyn, I. D. Kolli, R. A. Rodionov, and T. G. Sevast'yanova, *Doklady Akad. Nauk S.S.S.R.*, 1965, **160**, 1101.

<sup>3</sup> L. L. Shchukovskaya, M. G. Voionkov, and O. V. Pavlova, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1962, 366.

<sup>4</sup> C. A. Kraus and E. H. Brown, *J. Amer. Chem. Soc.*, 1930, **52**, 4414.

tion of products were generally similar to those described previously.<sup>1,11</sup> I.r. spectra were recorded on a Perkin-Elmer 137 or 337, n.m.r. spectra on a Varian A60-A, and mass spectra using a modified A.E.I. MS 10 instrument.

Tetrafluorosilane was prepared and amines were purified as already described.<sup>1,12</sup> Solvents were dried ( $\text{CaH}_2$ , Na), then treated with  $\text{SiF}_4$  and finally fractionated *in vacuo*. Diborane was made by standard methods<sup>13</sup> or, more conveniently, by heating dry tin(II) chloride and  $\text{NaBH}_4$  to  $200^\circ$ .<sup>14</sup>

**Analysis.**—Amine in aminofluorosilanes was determined either (i) by treatment with an excess of anhydrous  $\text{HCl}$  and weighing of the amine salt formed,<sup>1</sup> or (ii) by hydrolysis of the sample with alkali and subsequent pumping of the evolved amine through a known excess of standard acid. Fluorine was estimated by the usual titrimetric procedure with thorium nitrate;<sup>12</sup> as usual, results were always a little low.

**Preparative Routes.**—Experimental conditions and quantities are summarized in Tables 1–3. Illustrative procedures are given below for selected compounds.

(i) *N-Methylhexafluorodisilazane.* Tetrafluorosilane, methylamine, and sodium tetrahydroborate were sealed together in a thick-walled tube and heated as indicated in Table 1, run 3. Some white solid was present, and more deposited on the walls as they cooled. Fractionation yielded hydrogen [57% of that required by equation (3)], the excess of  $\text{SiF}_4$ , traces of  $\text{SiH}_4$  and  $(\text{SiF}_3)_2\text{O}$ , and  $(\text{SiF}_3)_2\text{NMe}$  [21% based on amine used; held at  $-120^\circ$ , passed through  $-85^\circ$ ] [Found: F, 55.0; 55.2; NMe, 14.5, 14.8%];

<sup>5</sup> A. Dornow and H. H. Gehrt, *Z. anorg. Chem.*, 1958, **294**, 81.

<sup>6</sup> J. J. Harris and B. Rudner, *Inorg. Chem.*, 1969, **8**, 1258.

<sup>7</sup> C. W. Heitsch, *Inorg. Chem.*, 1964, **3**, 767.

<sup>8</sup> M. Allan, B. J. Aylett, and I. A. Ellis, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 261.

<sup>9</sup> J. J. Harris, U.S.P. 3,304,160/1967.

<sup>10</sup> J. J. Harris and B. Rudner, *J. Amer. Chem. Soc.*, 1968, **90**, 515; *J. Inorg. Nuclear Chem.*, 1972, **34**, 75.

<sup>11</sup> B. J. Aylett, I. A. Ellis, and J. R. Richmond, *J.C.S. Dalton*, 1973, 981.

<sup>12</sup> B. J. Aylett, I. A. Ellis, and C. J. Porritt, *J.C.S. Dalton*, 1972, 1953.

<sup>13</sup> H. C. Brown and P. A. Tierney, *J. Amer. Chem. Soc.*, 1958, **80**, 1552; G. F. Freeguard and L. H. Long, *Chem. and Ind.*, 1965, 471.

<sup>14</sup> W. Jeffers, *Chem. and Ind.*, 1961, 431.

TABLE 1  
Dehydrofluorinations with primary amines and ammonia

Run	SiF <sub>4</sub> mmol	Amine mmol	Agent mmol	Reaction time h	Reaction temp. °C	Products <sup>a</sup> mmol
1	124	NH <sub>2</sub> Me (13)	LiAlH <sub>4</sub> (6.5) <sup>b</sup>	10	260	H <sub>2</sub> (25; 95%); (SiF <sub>3</sub> ) <sub>2</sub> NMe(1.2; 9%); less volatile oil, <sup>c</sup> grey and white solids.
2	41	NH <sub>2</sub> Me (3.3)	B <sub>2</sub> H <sub>6</sub> (0.7)	2	175	H <sub>2</sub> (2.4; 57%); (SiF <sub>3</sub> ) <sub>2</sub> NMe(0.47; 14%); B <sub>3</sub> H <sub>3</sub> N <sub>3</sub> Me <sub>3</sub> (0.2); <sup>d</sup> solids. <sup>e</sup>
3	60	NH <sub>2</sub> Me (3)	NaBH <sub>4</sub> (1.5) <sup>f</sup>	10	215	H <sub>2</sub> (3.5, 57%); (SiF <sub>3</sub> ) <sub>2</sub> NMe(0.64; 21%); solids.
4	5	NH <sub>2</sub> Me (70) <sup>g</sup>	Na-K (5)	340	25	H <sub>2</sub> ; NH <sub>2</sub> Me; SiF <sub>4</sub> .2NH <sub>2</sub> Me; liquid A (see text); <sup>h</sup> solids.
5	80	NH <sub>2</sub> Et (11.2)	LiAlH <sub>4</sub> (5.6)	10	225	H <sub>2</sub> (16.9; 75%); (SiF <sub>3</sub> ) <sub>2</sub> NEt(4.9; 44%); almost involatile liquid silazanes; solids.
6	80	NH <sub>2</sub> Et (10)	NaBH <sub>4</sub> (5)	10	215	H <sub>2</sub> (12.9; 65%); (SiF <sub>3</sub> ) <sub>2</sub> NEt(0.4; 4%); probable SiF <sub>3</sub> NHEt (ca. 10 mg; see text); solids.
7	80	NH <sub>2</sub> Ph (8)	LiAlH <sub>4</sub> (4.5)	12	300	H <sub>2</sub> (9.5; 60%); (SiF <sub>3</sub> ) <sub>2</sub> NPh(0.48; 6%); solids.
8	55	NH <sub>2</sub> Ph (10.3)	LiAlH <sub>4</sub> (5) <sup>i</sup>	12	310	H <sub>2</sub> (10; 50%); C <sub>6</sub> H <sub>6</sub> (0.3); liquid silazanes (ca. 20 mg); <sup>j</sup> solids.
9	80 <sup>k</sup>	NH <sub>3</sub> (10.4)	LiAlH <sub>4</sub> (5.2)	11	260	H <sub>2</sub> (9.5; 46%); (SiF <sub>3</sub> ) <sub>2</sub> NH(1.03; 10%); liquid B (see text); <sup>l</sup> solids.
10	80	Me <sub>2</sub> NNH <sub>2</sub> (10)	NaBH <sub>4</sub> (5) <sup>m</sup>	10	260	H <sub>2</sub> (9; 45%); SiF <sub>3</sub> NMe <sub>2</sub> (trace); (SiF <sub>3</sub> ) <sub>2</sub> -NNMe <sub>2</sub> (0.27; 3%); <sup>n</sup> solids.

<sup>a</sup> An excess of SiF<sub>4</sub>, also traces of SiH<sub>4</sub> and (SiF<sub>3</sub>)<sub>2</sub>O recovered in all cases except run 4. <sup>b</sup> When SiF<sub>4</sub> (80 mmol) and LiAlH<sub>4</sub> (16.9 mmol) were heated together at 370° for 18 h, the volatile products were: H<sub>2</sub> (33.5 mmol); (SiF<sub>3</sub>)<sub>2</sub>O and SiF<sub>4</sub> (60 mmol). <sup>c</sup> Held at -23°. <sup>d</sup> Held at -64°. Found: *M*, 129. Calc. for C<sub>3</sub>H<sub>12</sub>B<sub>3</sub>N<sub>3</sub>: *M*, 123. I.r. as in: T. Totani, H. Watanabe, and M. Kubo, *Spectrochim. Acta*, 1969, **25A**, 585 and refs. therein. <sup>e</sup> I.r. showed that SiF<sub>4</sub>.2NH<sub>2</sub>Me was present; on hydrolysis, (NH<sub>2</sub>Me)<sub>2</sub>SiF<sub>6</sub> was appropriately formed. <sup>f</sup> A mixture of SiF<sub>4</sub> and NaBH<sub>4</sub>, after having been heated under the same conditions, was essentially unchanged. <sup>g</sup> Liquid phase present. <sup>h</sup> Almost involatile at 25°; it contained Si and F, and yielded NH<sub>2</sub>Me on hydrolysis. <sup>i</sup> NH<sub>2</sub>Ph and LiAlH<sub>4</sub> were first allowed to react at 25°, then SiF<sub>4</sub> was introduced. <sup>j</sup> Held at -46°; rapidly decomposed to SiF<sub>4</sub> and solids. <sup>k</sup> With lower SiF<sub>4</sub>:NH<sub>3</sub> ratios, no volatile Si-N compounds were isolated. <sup>l</sup> Held at -64°; Found: *M*, 263. Calc. for (SiF<sub>3</sub>NH)<sub>2</sub>SiF<sub>2</sub>: 266. I.r. spectrum similar to that of (SiF<sub>3</sub>)<sub>2</sub>NH, but additional weak band at 885 cm<sup>-1</sup>. <sup>m</sup> LiAlH<sub>4</sub> gave similar results. <sup>n</sup> Held at -84°, passes through -64°. Found: *M*, 223. Calc. for (SiF<sub>3</sub>)<sub>2</sub>N<sub>2</sub>Me<sub>2</sub>: 228. I.r. (gas): 3000ms, 2900ms, 2820m, 1470ms, 1300m, 1240ms, 1180ms, 1100s, 1000vs, 915s, and 825s cm<sup>-1</sup>.

TABLE 2  
Dehydrofluorinations with secondary amines

Run	SiF <sub>4</sub> mmol	Amine mmol	Agent mmol	Reaction time h	Reaction temp. °C	Products <sup>a</sup> mmol
1	10	NHMe <sub>2</sub> (10)	LiAlH <sub>4</sub> (2.5) <sup>b</sup>	12	200	H <sub>2</sub> (9.0; 90%); SiF <sub>4</sub> (0.9); SiF <sub>3</sub> NMe <sub>2</sub> (4.9; 50%); SiF <sub>2</sub> (NMe <sub>2</sub> ) <sub>2</sub> (0.2); solids. <sup>c</sup>
2	2.5	NHMe <sub>2</sub> (2.2)	B <sub>2</sub> H <sub>6</sub> (0.6)	1	190	H <sub>2</sub> (1.1; 50%); SiF <sub>4</sub> (1.2); SiF <sub>3</sub> NMe <sub>2</sub> (1.1; 50%); solids.
3	38	NHMe <sub>2</sub> (72)	LiAlH <sub>4</sub> (19.6)	12	200	H <sub>2</sub> (ca. 75; 100%); SiF <sub>3</sub> NMe <sub>2</sub> (trace); SiF <sub>2</sub> (NMe <sub>2</sub> ) <sub>2</sub> (22; 69%); SiF(NMe <sub>2</sub> ) <sub>3</sub> solids.
4	11.3	NHMe <sub>2</sub> (25)	Al (7.4) <sup>d</sup>	12	350	H <sub>2</sub> ; NMe <sub>3</sub> ; SiF <sub>2</sub> (NMe <sub>2</sub> ) <sub>2</sub> (1.1; 10%); SiF <sub>4</sub> , NMe <sub>3</sub> ; solids.
5	16	NHMe <sub>2</sub> (70) <sup>e</sup>	Na (32) <sup>f</sup>	340	25	H <sub>2</sub> ; SiF <sub>2</sub> (NMe <sub>2</sub> ) <sub>2</sub> (6.2; 39%); SiF(NMe <sub>2</sub> ) <sub>3</sub> (trace); solids.
6	55	NHMe <sub>2</sub> (5.2)	B <sub>2</sub> H <sub>6</sub> (0.65) <sup>g</sup>	2.5	220	H <sub>2</sub> ; SiF <sub>3</sub> NEt <sub>2</sub> (3.6; 70%); solids.

<sup>a</sup> SiF<sub>4</sub>, and a trace of (SiF<sub>3</sub>)<sub>2</sub>O were found in all cases except runs 4 and 5; traces of SiH<sub>4</sub> were found in runs 1—3, and 6. <sup>b</sup> NaBH<sub>4</sub> was also effective. <sup>c</sup> Partly sublimed at 300°; neither component could be definitely identified (i.r., X-ray powder methods). <sup>d</sup> Mg gave similar results, but with lower yields. Zn gave some H<sub>2</sub>, but only a trace of aminosilanes. <sup>e</sup> Liquid phase present. <sup>f</sup> K or Na-K alloy gave similar results. <sup>g</sup> LiAlH<sub>4</sub> was also effective.

*M*, 197, 199, 200. Calc. for (SiF<sub>3</sub>)<sub>2</sub>NMe: F, 57.3; NMe, 14.6; *M*, 199], together with white residual solid.

*Physical properties* (see also Table 4). Vapour-pressure equation (187—274 K):  $\log p/\text{mmHg} = 8.354 - 1640/T$ . I.r. spectrum (gas): 2960m, 2912m, 2855m, 1820m, 1460w,

of SiF<sub>4</sub>, traces of SiH<sub>4</sub> and (SiF<sub>3</sub>)<sub>2</sub>O, also (SiF<sub>3</sub>)<sub>2</sub>NEt [44% based on amine used; held at -96°, passed through -64°] [Found: F, 52.7; NEt, 20.2%; *M*, 214. Calc. for (SiF<sub>3</sub>)<sub>2</sub>NEt: F, 53.5; NEt, 20.2%; *M*, 213], an almost involatile silazane fraction, and a mixture of grey and white solids.

TABLE 3

Run	SiF <sub>4</sub> mmol	Amine mmol	Other attempted dehydrofluorinations			Products <sup>a</sup> mmol
			Agent mmol	Reaction time h	Reaction temp. °C	
1	0.8	NH <sub>2</sub> Me (1.6)	None	2.5	500 <sup>b</sup>	H <sub>2</sub> (0.02); NMe <sub>3</sub> (0.2); SiF <sub>4</sub> , 2NH <sub>2</sub> Me; SiF <sub>4</sub> , 2NH <sub>3</sub> . <sup>c</sup>
2	9.7	NH <sub>2</sub> Me (19.4)	None	24	350 <sup>d,e</sup>	H <sub>2</sub> ; NMe <sub>3</sub> (3.7); SiF <sub>4</sub> , NMe <sub>3</sub> (0.5); solids.
3	0.6	NH <sub>2</sub> Me (1.2)	NEt <sub>3</sub> (1.2)	1	400 <sup>f</sup>	H <sub>2</sub> (0.11); NEt <sub>3</sub> ; NH <sub>2</sub> Me <sub>3-x</sub> (x = 0—3) (trace); solids. <sup>g</sup>
4	0.6	NH <sub>2</sub> Me (1.2)	NH <sub>2</sub> Ph (1.1)	1	200	NH <sub>2</sub> Ph(1.1); SiF <sub>4</sub> , 2NH <sub>2</sub> Me(0.6).
5	0.6	NH <sub>2</sub> Me (1.2)	NaF (50)	1	200	NH <sub>2</sub> Me(1.2); Na <sub>2</sub> SiF <sub>6</sub> .
6	75	NH <sub>2</sub> Me (6)	Fe(CO) <sub>5</sub> (6)	1	170 <sup>h</sup>	CO; SiF <sub>4</sub> ; SiF <sub>4</sub> , 2NH <sub>2</sub> Me; Fe(CO); solids.
7	6.0	NH <sub>2</sub> Me (12)	Zn dust (6) <sup>i</sup>	4	350 <sup>e</sup>	H <sub>2</sub> (1.3); NH <sub>2</sub> Me <sub>3-x</sub> (x = 0—3) (0.027 g); solids. <sup>l</sup>
8	6.5	NH <sub>2</sub> Me (13)	NaNH <sub>2</sub> (11)	4	320	H <sub>2</sub> (1.0); N <sub>2</sub> (0.1); NH <sub>3</sub> (10); NH <sub>2</sub> Me(8); solids. <sup>k</sup>
9	l	NH <sub>2</sub> Pr <sup>n</sup> l	B <sub>2</sub> H <sub>6</sub> l	3	200	H <sub>2</sub> ; SiF <sub>4</sub> ; B <sub>3</sub> H <sub>3</sub> N <sub>3</sub> Pr <sub>3</sub> <sup>m</sup> ; solids.
10	10.1	NHMe <sub>2</sub> (19.4)	None	18	350 <sup>e,p</sup>	H <sub>2</sub> (0.14); SiF <sub>4</sub> (ca. 1.5); SiF <sub>4</sub> , NMe <sub>3</sub> ; solids. <sup>n</sup>
11	l	(NHMeCH <sub>2</sub> ) <sub>2</sub> l	B <sub>2</sub> H <sub>6</sub> l	3	200	H <sub>2</sub> ; SiF <sub>4</sub> ; $\overline{\text{HNMeCH}_2\text{CH}_2\text{NMe}}$ ; solids.
12	83	NH <sub>3</sub> (4.3)	B <sub>2</sub> H <sub>6</sub> (1.0)	2	175	H <sub>2</sub> (4; 65%); SiF <sub>4</sub> ; partly-sublimable solids.

<sup>a</sup> In most cases, traces of (SiF<sub>3</sub>)<sub>2</sub>O were formed. <sup>b</sup> Similar mixtures heated at 220° for 2.5 h were unchanged; after 1 h at 600°, more H<sub>2</sub> and some HCN (*M*, i.r.) were evolved. In all cases the pressure did not exceed 5 atmos., and no liquid adduct was present. <sup>c</sup> Chiefly SiF<sub>4</sub>, 2NH<sub>2</sub>Me (i.r.) but some ammonia was detected after hydrolysis. <sup>d</sup> Pressure was ca. 15 atmos.; liquid adduct was present. <sup>e</sup> The reaction vessel was heavily etched. <sup>f</sup> On sublimation, some SiF<sub>4</sub>, 2NH<sub>3</sub> (i.r.) was obtained; on heating with NaF at 200°, the solid gave NH<sub>3</sub> together with some NH<sub>2</sub>Me and NHMe<sub>2</sub>; on hydrolysis, a sample gave 68% of the ammonia calculated for SiF<sub>4</sub>, 2NH<sub>3</sub>. <sup>g</sup> No reaction after 1 h at 200°; at 500°, decomposition of NEt<sub>3</sub> was rapid. <sup>h</sup> At higher temperatures, Fe(CO)<sub>5</sub> decomposed, but there was no other reaction up to 400°. <sup>i</sup> Similar results were obtained with Mg powder or K; in the latter case, charring was also observed. <sup>j</sup> These comprised a grey powder (containing Zn<sup>2+</sup>, F<sup>-</sup>) also a sticky off-white solid which gave some NH<sub>2</sub>Me<sub>3-x</sub> (x = 1—3) on hydrolysis. <sup>k</sup> The light brown residue was free from CN<sup>-</sup>; it could not be sublimed up to 300° and hydrolysed very slowly giving F<sup>-</sup> and silica. It was resistant to boiling NEt<sub>3</sub> or EtOH, but dissolved in acid or alkali. <sup>l</sup> Excess of SiF<sub>4</sub> and roughly equivalent amounts of amine and B<sub>2</sub>H<sub>6</sub> were used. <sup>m</sup> Identified by i.r., n.m.r.; on hydrolysis gave NH<sub>2</sub>Pr<sup>n</sup>; cf. M. P. Brown, R. W. Heseltine, and D. W. Johnson, *J. Chem. Soc. (A)*, 1967, 597. <sup>n</sup> Pyrolysis with NaF yielded NH<sub>3</sub> and NHMe<sub>2</sub>; i.r. showed SiF<sub>6</sub><sup>2-</sup> and SiF<sub>4</sub>, 2NH<sub>2</sub>Me<sub>3-x</sub> (x = 1 or 3). <sup>p</sup> Liquid adduct phase present (pressure ca. 10 atmos.). Mixtures heated up to 400° at pressures below 1 atmos. did not react. <sup>q</sup> M.p., -64°; v.p., 14 mmHg, 21° C. On hydrolysis gave (HNMeCH<sub>2</sub>)<sub>2</sub>, positive boron test. Found: *M*, 99. Calc. for C<sub>4</sub>H<sub>11</sub>BN<sub>2</sub>, 98. I.r. spectrum (gas): 2990s, 2870vs, 2800s, 2560s, 1520s, 1450s, 1420s, 1360m, 1300s, 1235s, br, 1075s, 1065sh, 1035sh, 1030s, 995s, 945w, 878m, 865m, 820w, 638w, and 595 cm<sup>-1</sup>. N.m.r. (SiMe<sub>4</sub> soln.): τ 7.3 (singlet, CH<sub>3</sub>, 6H); 6.8 (singlet, CH<sub>2</sub>, 4H). BH not observed.

1380w, 1310m, 1235s, 1120m, 1083s, 1016vs, 997vs, 911s, 875m, 828sh, 822s, 605m, 440sh, and 420s cm<sup>-1</sup>.

(ii) *N-Ethylhexafluorodisilazane*. Tetrafluorosilane, ethylamine, and lithium tetrahydroaluminate were heated

TABLE 4

Physical properties of some aminofluorosilanes

Compound	M.p. <sup>a</sup> °C	B.p.(extrap.) °C	Δ <i>H</i> <sub>vap</sub> kcal mol <sup>-1</sup>	Δ <i>S</i> <sub>vap</sub> cal mol <sup>-1</sup> K <sup>-1</sup>
(SiF <sub>3</sub> ) <sub>2</sub> NH	ca. -35 <sup>b</sup>	66 <sup>c</sup>	7.2	22 <sup>c</sup>
(SiF <sub>3</sub> ) <sub>2</sub> NMe	-50	27	7.50	25.0
(SiF <sub>3</sub> ) <sub>2</sub> NEt	-75	44	7.64	24.1
SiF <sub>3</sub> NMe <sub>2</sub>	-108	20.5 <sup>d</sup>	6.41 <sup>d</sup>	21.8 <sup>d</sup>
SiF <sub>2</sub> (NMe <sub>2</sub> ) <sub>2</sub> <sup>e</sup>	-59 <sup>f</sup>	95 <sup>g</sup>	8.80 <sup>g</sup>	23.9 <sup>g</sup>

<sup>a</sup> ± 1° Except for (SiF<sub>3</sub>)<sub>2</sub>NH. <sup>b</sup> Decomposition appreciable at this temperature. <sup>c</sup> Long extrapolation. <sup>d</sup> Supersedes values given in ref. 1. <sup>e</sup> *d*, 1.001 g cm<sup>-3</sup>, 25 °C. <sup>f</sup> Lit.<sup>16</sup> -69.5°. <sup>g</sup> Calc from data of ref. 16.

together as shown in Table 1, run 5. The products were: hydrogen [75% of that required by equation (3)], the excess

*Physical properties* (see also Table 4). V.p. equation (187—297 K):  $\log p/\text{mmHg} = 8.148 - 1670/T$ . I.r. spectrum (gas): 3000m, 2920mw, 1490w, 1460w, 1390m, 1360w, 1320ms, 1195s, 1075vs, 1015vs, 987vs, 950ms, 885m, and 830s cm<sup>-1</sup>.

(iii) *N-Phenylhexafluorodisilazane*. The products from pyrolysis of a mixture of SiF<sub>4</sub>, aniline, and LiAlH<sub>4</sub> in mole ratios of 18 : 1.8 : 1 (Table 1, run 7) were: hydrogen [60% of that required by equation (3)], the excess of SiF<sub>4</sub>, and slightly impure (SiF<sub>3</sub>)<sub>2</sub>NPh [6% based on amine used; held at -85°, passed through -46°; liquid at room temperature; v.p.: 1.5 mmHg/23°. I.r. spectrum (gas): 3450vw, 3060w, 1615m, 1510m, 1480w, 1380mw, 1315w, 1290m, 1135w, 1030vs, 1010sh, 975m, 845m, and 748m cm<sup>-1</sup>] [Found: NPh, 36.2%; *M*, 249.\* Calc. for (SiF<sub>3</sub>)<sub>2</sub>NPh: NPh, 34.9%; *M*, 261], together with a mixture of white and dark grey solids.

In another experiment, the same reactants in mole ratios

\* Consistent with the presence of ca. 10% of SiF<sub>3</sub>NHPh.

of 5 : 0.7 : 1, after 10 h at 250°, gave a white solid, held at -23° but volatile at room temperature. Its i.r. spectrum was very similar to that recorded above, and it gave aniline on hydrolysis.

Other attempted reactions of SiF<sub>4</sub> and aniline with NaBH<sub>4</sub> or B<sub>2</sub>H<sub>6</sub>, and of SiF<sub>4</sub> with LiAl(NHPh)<sub>4</sub> (prepared *in situ* from aniline and LiAlH<sub>4</sub>)<sup>15</sup> yielded almost no volatile Si-N compounds, although up to 85% of the calculated hydrogen was evolved.

(iv) *Hexafluorodisilazane*. When SiF<sub>4</sub>, ammonia, and LiAlH<sub>4</sub> were pyrolysed together in mole ratios of 16 : 2 : 1 (Table 1, run 9), the volatile products included hydrogen [46% of that required by equation (3)] and (SiF<sub>3</sub>)<sub>2</sub>NH [10% yield based on ammonia used; held at -96°, passed through -64°. Found: F, 60.8; NH, 8.0%; *M*, 185 ± 2. Calc. for (SiF<sub>3</sub>)<sub>2</sub>NH: F, 61.6; NH, 8.1%; *M*, 185]. The mixture of white and dark grey solids remaining in the tube smelled strongly of ammonia when exposed to air. Extensive decomposition of (SiF<sub>3</sub>)<sub>2</sub>NH occurred during fractionation. Attempted preparations using B<sub>2</sub>H<sub>6</sub> or NaBH<sub>4</sub> in place of LiAlH<sub>4</sub>, or with smaller proportions of SiF<sub>4</sub>, were unsuccessful.

*Physical properties* (see also Table 4). V.p. equation (186–230 K): log *p*/mmHg = 7.68 - 1580/*T*. I.r. spectrum (gas): 3400m, 1320m, 1260sh, 1235s, 1145m, 1020vs, 1005vs, 975sh, 940m, 825s, and 685m, br cm<sup>-1</sup>.

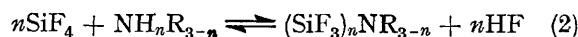
(v) *Dimethylaminotrifluorosilane*. Tetrafluorosilane, dimethylamine, and diborane were heated together as shown in Table 2, run 2. Only a little viscous liquid could be seen in the hot reaction vessel; on cooling to room temperature, the liquid set to a gum and additional white solid was deposited on the tube walls. The volatile products were hydrogen [50% of that required by equation (10)], excess of SiF<sub>4</sub>, and SiF<sub>3</sub>NMe<sub>2</sub> [50% yield based on amine used; held at -96°, passes -64°. Found: F, 43.5; NMe<sub>2</sub>, 34.2%; *M*, 128, 130. Calc. for SiF<sub>3</sub>NMe<sub>2</sub>: F, 44.1; NMe<sub>2</sub>, 34.1%; *M*, 129].

*Physical properties* (see also Table 4). V.p. equation (241–273 K): log *p*/mmHg = 7.663 - 1405/*T* (lit.<sup>16</sup> 8.416 - 1606/*T*). I.r. spectrum (gas): 2990m, 2915s, 2890sh, 2825m, 1495m, 1460m, 1326s, 1188sh, 1174s, 1090sh, 1078m, 1030s, 980vs, 958vs, 879s, and 665s cm<sup>-1</sup>.

(vi) *Bisdimethylaminodifluorosilane*. Tetrafluorosilane and sodium were sealed with liquid dimethylamine in a small tube as shown in Table 2, run 5. After 2 weeks at room temperature, with occasional shaking, the dark-coloured reaction mixture yielded hydrogen, excess of amine, SiF<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub> [39% yield based on equation (11)]; held at -64°, passed through -23°. Found: F, 23.6; NMe<sub>2</sub>, 56.8%; *M*, 151, 155. Calc. for SiF<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub>: F, 24.6; NMe<sub>2</sub>, 57.2%; *M*, 154. *d*, 1.001 g ml<sup>-1</sup> at 25°. I.r. spectrum (gas): 2960m, 2875s, 2855sh, 2800s, 2160w, 1910w, 1750w, 1610w, 1460sh, 1440m, 1395w, 1305s, 1175s, 1070m, 1008vs, 909s, 873s, and 746m cm<sup>-1</sup>], and small amounts of the tris- and tetrakis-derivatives.

## RESULTS AND DISCUSSION

In order to make Si-N compounds by condensations such as that shown in equilibrium (2), hydrogen fluoride

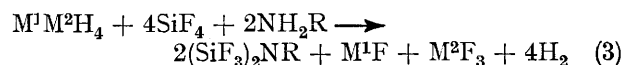


\* This compound proved surprisingly difficult to isolate in a pure state, possibly because small amounts of SiF<sub>3</sub>NHPh formed with it tended to induce decomposition.

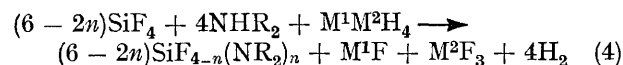
† No evidence for (SiF<sub>3</sub>)<sub>3</sub>N or SiF<sub>3</sub>NH<sub>2</sub><sup>12</sup> was found.

must be efficiently removed.<sup>1</sup> Generalized bases that might be used include H<sup>-</sup>, NH<sub>2</sub><sup>-</sup>, amines, F<sup>-</sup>, and metals. We now indicate the scope and limitations of different dehydrofluorinating agents.

(a) *Lithium Tetrahydroaluminate and Sodium Tetrahydroborate*.—These two reagents proved to be the most versatile and generally applicable. Thus LiAlH<sub>4</sub> reacted with SiF<sub>4</sub> and NH<sub>2</sub>-derivatives according to equation (3) (M<sup>1</sup> = Li, M<sup>2</sup> = Al) when R = Me, Et,



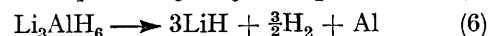
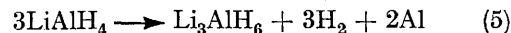
Ph,\* H,† or NMe<sub>2</sub> (Table 1). The fully-substituted product obtained from Me<sub>2</sub>NNH<sub>2</sub> compared with SiF<sub>3</sub>NHNMe<sub>2</sub> formed from SiF<sub>4</sub> and Me<sub>2</sub>NNH<sub>2</sub> alone.<sup>17</sup> The lithium compound similarly reacted with SiF<sub>4</sub> and secondary amines according to equation (4), *n* = 1, (M<sup>1</sup> = Li, M<sup>2</sup> = Al) when R = Me or Et; with an excess of dimethylamine, further substitution occurred, as in equation (4), *n* = 2 (Table 2). To obtain reasonable



yields of disilazanes, it was essential to restrict disproportionation by using a large excess of SiF<sub>4</sub> in reaction (3); such an excess was also helpful in reaction (4), *n* = 1.

Sodium tetrahydroborate behaved similarly in most cases, although the yields were typically lower [equations (3) and (4); M<sup>1</sup> = Na, M<sup>2</sup> = B]. A comparison of runs 5 and 6 in Table 1 shows that although the extent of reaction (as measured by hydrogen evolution) was similar, side-reactions leading to loss of product were less serious with LiAlH<sub>4</sub>. All dehydrofluorinations successful with NaBH<sub>4</sub> could also be effected with LiAlH<sub>4</sub>, but the converse was not true: systems with SiF<sub>4</sub>, NaBH<sub>4</sub>, and ammonia or aniline yielded no disilazane.

The role of LiAlH<sub>4</sub> in the reaction is by no means self-evident. Recent studies by Dilts and Ashby<sup>18</sup> have clarified the stages of thermal decomposition of LiAlH<sub>4</sub>, and under the conditions used in the present work, reactions (5) and (6) would be complete. These can



account for some 36% of the hydrogen required by equations (3) and (4) (M<sup>1</sup> = Li, M<sup>2</sup> = Al). Both LiH and aluminium are doubtless produced in a highly reactive form. The latter reacts with SiF<sub>4</sub> and amines even when used as the normal oxide-coated powder (see Table 2 and below) while the former is expected<sup>19</sup> to

<sup>15</sup> N. G. Gaylord, 'Reduction with Complex Metal Hydrides,' Interscience, New York, 1956.

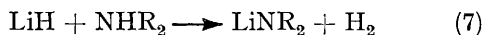
<sup>16</sup> H. Grosse-Ruyken and R. Kleesaat, *Z. anorg. Chem.*, 1961, **308**, 122.

<sup>17</sup> G. G. Strathdee, Ph.D. thesis, McGill University, Montreal, 1967; M. Onyszchuk, personal communication.

<sup>18</sup> J. A. Dilts and E. C. Ashby, *Inorg. Chem.*, 1972, **11**, 1230.

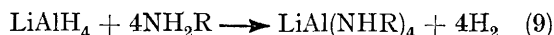
<sup>19</sup> Cf. B.P. 293 040/1928; R. N. Hader, R. L. Nielsen, and M. G. Herre, *Ind. and Eng. Chem.*, 1951, **43**, 2636.

form Li-N derivatives with amine [*e.g.* equation (7)]; these are known<sup>20</sup> to react with SiF<sub>4</sub> to give aminosilanes [equation (8)]. The extent to which these reactions



compete with direct reaction of HF [from equilibrium (2)] with LiH, *etc.*, is not known.

Initial reaction of amine with LiAlH<sub>4</sub> to give hydrogen and LiAlH<sub>n</sub>(NR<sub>2</sub>)<sub>4-n</sub> (ref. 21) or other Al-N derivatives<sup>22</sup> is unlikely, given the excess of SiF<sub>4</sub> normally present and the very low dissociation pressures of most SiF<sub>4</sub>-amine adducts at room temperature.<sup>12</sup> On heating, it is only when the partial pressure of amine becomes significant before LiAlH<sub>4</sub> has decomposed that formation of Al-N derivatives is likely; if formed, they are expected however to react readily with SiF<sub>4</sub> (*cf.* ref. 23). In one experiment, aniline and LiAlH<sub>4</sub> were allowed to react together before introducing SiF<sub>4</sub>; after pyrolysis, the hydrogen evolved corresponded exactly to that required by equation (9), but was only 50% of that demanded by



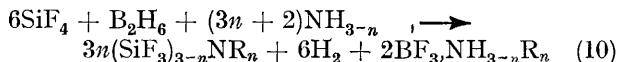
equation (3). Some C-N bond cleavage had occurred to give benzene, but the only volatile silazane product was a small quantity of thermally unstable liquid, thought to be SiF<sub>3</sub>NHPh (see below). Small amounts of silane arose from slight reduction of SiF<sub>4</sub> by LiAlH<sub>4</sub>; however, when LiAlH<sub>4</sub> and SiF<sub>4</sub> were pyrolysed under more extreme conditions (370° for 18 h), hydrogen was quantitatively released as H<sub>2</sub>, and some SiF<sub>4</sub> was removed.

It is concluded that dehydrofluorination can occur directly with LiAlH<sub>4</sub> and its pyrolysis and/or reaction products, and indirectly *via* reaction of Li-N and/or Al-N reaction products with SiF<sub>4</sub>. Silicon hydrides appear to be unimportant as intermediates.

Sodium tetrahydroborate is known to be more resistant to pyrolysis<sup>24</sup> than LiAlH<sub>4</sub>, and in this work there was very little reaction when it was heated with SiF<sub>4</sub>. Thus B<sub>2</sub>H<sub>6</sub>, silicon hydrides, or LiH are not likely to be involved as intermediates. Pyrolysis of NaBH<sub>4</sub> with salts of primary or secondary amines can lead to borazoles or aminoboranes, but these were not detected here. This implies either that any B-N compounds formed react completely with SiF<sub>4</sub> to give Si-N derivatives and BF<sub>3</sub>, or that direct abstraction of HF [from (2)] by NaBH<sub>4</sub> occurs preferentially. The first possibility, which seems unlikely on grounds of bond energy values, is excluded by the observation that borazoles and SiF<sub>4</sub> were co-products of reactions involving B<sub>2</sub>H<sub>6</sub> (see below).

(b) *Diborane*.—Equation (10) shows a possible course for dehydrofluorination using diborane. Adducts of BF<sub>3</sub>

with amines are stronger than those of SiF<sub>4</sub>, and are expected to appear as products, even with an excess of



SiF<sub>4</sub>. Sufficient amine was therefore added to combine with all the expected BF<sub>3</sub>.

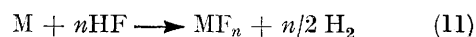
Good yields were obtained with secondary amines [equation (10); *n* = 2, R = Me or Et]; all reactants were volatile, making it easy to fill reaction vessels, and no volatile boron-containing products were detected. At the reaction temperatures used, the contents of the vessel were entirely gaseous: at higher pressures and with a condensed phase present self-dehydrofluorination occurs, especially when R is large.<sup>1</sup>

Primary amines [equation (10): *n* = 1] gave only a low yield of silazane with R = Me, and none at all with R = H, Pr<sup>n</sup>, or Ph. Substituted borazoles (BHN<sub>2</sub>)<sub>3</sub> were identified as products when R = Me or Pr<sup>n</sup>; there appeared to be no reaction between SiF<sub>4</sub> and these borazoles up to 200°. Analogously, the substituted diamine NHMe·[CH<sub>2</sub>]<sub>2</sub>·NHMe gave rise to 1,3-dimethyl-1,3,2-diazaborolidine,<sup>25</sup> HBNMeCH<sub>2</sub>CH<sub>2</sub>NMe, but no Si-N products.

It is concluded that diborane is generally less satisfactory than LiAlH<sub>4</sub> or NaBH<sub>4</sub>, although it has some use in the preparation of dialkylamino-derivatives.

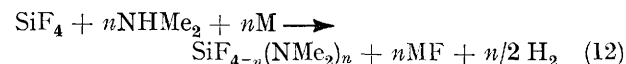
(c) *Metals*.—Powdered aluminium, magnesium, and zinc were able to remove HF from heated gaseous mixtures of SiF<sub>4</sub> and dimethylamine. There was little reaction below 300°, but at 350° small yields of dimethylaminofluorosilanes were obtained, decreasing in the order Al > Mg > Zn. Such high temperatures are probably needed to break the protective oxide coating on the metal surface.

The enthalpy changes<sup>26</sup> at 298 K associated with removal of HF by metals [equation (11)] have the approx-



imate values: M = Mg, -570; Al, -495; K, -295; Zn, -230 kJ mol<sup>-1</sup>. However, the entropy changes<sup>26</sup> (-ΔS) lie in the order: Al > Mg ~ Zn > K. The observed order of efficacy is therefore reasonable at high temperatures. Disproportionation of amine (*e.g.* Table 2, run 4) was equally apparent in systems without added metals, and will be discussed under (d) below.

Alkali metals also slowly removed HF from reaction mixtures of SiF<sub>4</sub>·2NHMe<sub>2</sub> and liquid dimethylamine [equation (12)]. The large excess of amine and the



<sup>20</sup> U. Wannagat, H. Bürger, and F. Höfler, *Monatsh.*, 1968, **99**, 1198.

<sup>21</sup> A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69**, 1199.

<sup>22</sup> R. G. Beach and E. C. Ashby, *Inorg. Chem.*, 1971, **10**, 1888.

<sup>23</sup> C. Glidewell and D. W. H. Rankin, *J. Chem. Soc. (A)*, 1970, 279.

<sup>24</sup> D. S. Stasinevich and G. A. Egorenko, *Russ. J. Inorg. Chem.*, 1968, **13**, 341; H. I. Schlesinger and H. C. Brown, *J. Amer. Chem. Soc.*, 1940, **62**, 3429.

<sup>25</sup> E. F. Rothgery, P. J. Busse, and K. Niedenzu, *Inorg. Chem.*, 1971, **10**, 2343.

<sup>26</sup> National Bureau of Standards Circular No. 500, Selected Values of Chemical Thermodynamic Properties, Washington, D.C., 1952.

relative susceptibility of  $\text{SiF}_3\text{NMe}_2$  towards base-catalysed disproportionation<sup>27</sup> ensured that  $\text{SiF}_2(\text{NMe}_2)_2$  was the major product. Further substitution to give  $\text{SiF}(\text{NMe}_2)_3$  is clearly difficult.

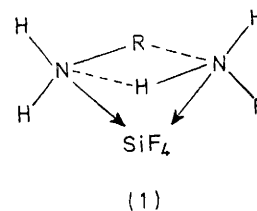
Corresponding reactions with primary amines in no case produced hexafluorodisilazanes. At  $350^\circ$ , zinc, magnesium, or potassium removed some HF (ca. 20% measured by evolution of hydrogen), but no volatile Si-N compounds were detected. Evidently further reaction led to species such as polymeric  $(\text{SiF}_2\text{NR})_x$ . Also about 10% of the original amine disproportionated to give all possible species  $\text{NH}_n\text{R}_{3-n}$  ( $n = 0-3$ ) when  $\text{R} = \text{Me}$ . Alkali metals with  $\text{SiF}_4$  in an excess of methylamine slowly yielded hydrogen and a barely volatile oligomeric silazane (A) that showed no tendency to lose  $\text{SiF}_4$ , and was probably cyclic  $(\text{SiF}_2\text{NMe})_n$  (see refs. 1, 10, and 28). These observations are all consistent with the known readiness<sup>27</sup> of hexafluorodisilazanes to disproportionate.

(d) *Other Dehydrofluorinating Agents.*—The simplest procedure would appear to be pyrolysis of the 1 : 2 adduct, either alone or with added amine. When  $\text{SiF}_4 \cdot 2\text{NH}_2\text{Me}$  was pyrolysed at  $500^\circ$  in the gas phase (Table 3, run 1) no volatile silazanes were detected, and the chief reaction was disproportionation of the amine (ca. 40%), leading to free  $\text{NMe}_3$  and ammonia (present as the relatively strong adduct  $\text{SiF}_4 \cdot 2\text{NH}_3$ ). A small quantity of hydrogen arose from decomposition of methylamine according to:  $\text{CH}_3\text{NH}_2 \rightarrow \text{HCN} + 2\text{H}_2$ ; this was confirmed by isolation of HCN and more hydrogen after pyrolysis at  $600^\circ$ .

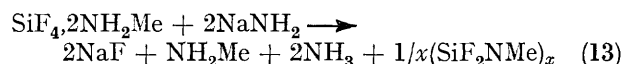
When the pressure was sufficiently high to ensure that a liquid phase was present, amine disproportionation occurred at a lower temperature: at  $350^\circ$ , 65% of the methylamine in  $\text{SiF}_4 \cdot 2\text{NH}_2\text{Me}$  had reacted after 24 h. Similar results were obtained with  $\text{SiF}_4 \cdot 2\text{NHMe}_2$ , although it has now been shown that this adduct will undergo self-dehydrofluorination, using milder conditions and added  $\text{SiF}_4$ .<sup>1</sup> Added tertiary amines were similarly ineffectual under our conditions (e.g. Table 3, run 3), although successfully used<sup>10</sup> in benzene solution with an excess of  $\text{SiF}_4$ . These results reinforce our previous conclusions<sup>1</sup> about the enabling role of  $\text{SiF}_4$  in dehydrofluorination.

The disproportionation of methylamines is not well documented. Usually they decompose<sup>29</sup> on heating above ca.  $450^\circ$ , but Brown<sup>30</sup> has shown that on heating  $\text{BF}_3 \cdot \text{NHMe}_2$  at  $240-295^\circ$ , besides the main products  $\text{Me}_2\text{NBF}_2$  and  $\text{NH}_2\text{Me}_2^+\text{NF}_4^-$ , some  $\text{BF}_3 \cdot \text{NMe}_3$  is formed. Considerably more disproportionation was observed with  $\text{SiF}_4$  and  $\text{NH}_2\text{Me}_2$  in this work since self-dehydrofluorination did not compete, and higher temperatures could be

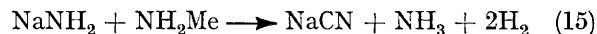
used. Free-radical processes are expected to lead to methane, which was not observed; an intermediate such as (1), with both amines co-ordinated to silicon, seem possible.



In further experiments with  $\text{SiF}_4 \cdot 2\text{NH}_2\text{Me}$ , heating with sodium fluoride led to quantitative displacement of amine, and no  $\text{NaHF}_2$  was detected; aniline,\* also  $\text{Fe}(\text{CO})_5$  and its decomposition products, were without effect. Sodium amide (used<sup>31</sup> to prepare  $\text{NH}_2\text{BF}_2$  from  $\text{BF}_3 \cdot \text{NH}_3$ ) produced 90% of the ammonia required by equation (13), but additional methylamine arose *via*



displacement by  $\text{F}^-$  from unreacted adduct and/or amine exchange between ammonia and the Si-N product.<sup>32</sup> Hydrogen† and nitrogen were formed by reaction (14); absence of  $\text{CN}^-$  in the solid products showed that thermolysis of amine and reaction (15)<sup>33</sup>



could be disregarded. A disadvantage of this reagent is that evolved ammonia may react with the Si-N product and make it disproportionate; rather high temperatures are also needed.

*Simple Silicon-Nitrogen Products.*—Physical properties of some of the volatile compounds prepared are shown in Table 4. Values of m.p. and  $\Delta S_{\text{vap}}$  suggest that intermolecular forces are smallest when the Si : N ratio is unity.‡ In terms of a discussion given<sup>32,34</sup> for corresponding  $\text{SiH}_3$  or  $\text{SiH}_2$  compounds, enhanced Lewis acid character results when this ratio increases, and enhanced base character when it falls. The relatively high m.p. of  $(\text{SiF}_3)_2\text{NH}$  can be rationalized in terms of intermolecular N-H...F bonding.

I.r. spectra of these compounds can be interpreted similarly to those in ref. 1: hexafluorodisilazanes show mixed  $\nu_{\text{as}}(\text{SiF})$  and  $\nu_{\text{as}}(\text{SiNSi})$  modes in the region  $910-1020 \text{ cm}^{-1}$ , and  $\nu_{\text{s}}(\text{SiF})$  ca.  $825 \text{ cm}^{-1}$ . For  $(\text{SiH}_3)_2\text{NR}$  derivatives, strong bands in the region  $1050-1300 \text{ cm}^{-1}$

\* Aniline, like  $\text{NEt}_3$ , is known<sup>12</sup> not to displace methylamine from  $\text{SiF}_4 \cdot 2\text{NH}_2\text{Me}$ .

† Additional hydrogen arose *via* reaction of  $\text{H}^-$  [from (14)] with adduct.

‡ The value of  $\Delta S_{\text{vap}}$  for  $(\text{SiF}_3)_2\text{NH}$  is not strictly comparable with the others, since it refers to the solid-vapour equilibrium.

<sup>27</sup> M. Allan, B. J. Aylett, and I. A. Ellis, *Chem. and Ind.*, 1966, 1417.

<sup>28</sup> W. Airey, G. M. Sheldrick, B. J. Aylett, and I. A. Ellis, *Spectrochim. Acta*, 1971, **27A**, 1505.

<sup>29</sup> H. J. Emeléus and L. J. Jolley, *J. Chem. Soc.*, 1935, 929.

<sup>30</sup> J. F. Brown, *J. Amer. Chem. Soc.*, 1952, **74**, 1219.

<sup>31</sup> C. W. Keenan and W. K. McDowell, *J. Amer. Chem. Soc.*, 1953, **75**, 6348.

<sup>32</sup> B. J. Aylett and M. J. Hakim, *J. Chem. Soc. (A)*, 1969, 1788.

<sup>33</sup> H. S. Fry and W. V. Culp, *Rec. Trav. chim.*, 1935, **54**, 838.

<sup>34</sup> B. J. Aylett and L. K. Peterson, *J. Chem. Soc.*, 1964, 3429; 1965, 4043.

have been assigned<sup>23,35</sup> to alkyl rocking and CN stretching vibrations. Somewhat similar bands are observed with  $(\text{SiF}_3)_2\text{NR}$  compounds [R = Me or Et (this work); R = Pr<sup>n</sup>, Bu<sup>n</sup>, or Bu<sup>s</sup> (ref. 1)]. Thus corresponding bands occur in  $(\text{SiH}_3)_2\text{NEt}$ <sup>23</sup> at 1111\* and 1171 cm<sup>-1</sup>, and in  $(\text{SiF}_3)_2\text{NEt}$  at 1075 and 1195 cm<sup>-1</sup>. This assignment is consistent with the lack of strong bands for  $(\text{SiF}_3)_2\text{NH}$  in this region.

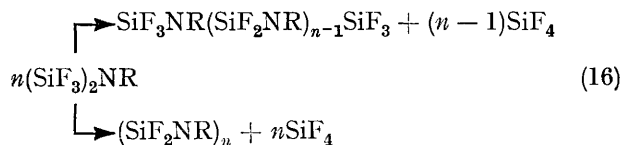
The spectra of  $(\text{SiF}_3)_2\text{NH}$  and isoelectronic  $(\text{SiF}_3)_2\text{O}$  (refs. 11 and 36) are generally similar, except that (a) bands appear in the former at 3400 and 1235 cm<sup>-1</sup>, reasonably assigned to NH stretching and bending modes,<sup>†</sup> and (b) the  $\nu_{\text{as}}(\text{SiOSi})$  vibration at 1205 cm<sup>-1</sup> in  $(\text{SiF}_3)_2\text{O}$  is replaced by  $\nu_{\text{as}}(\text{SiNSi})$ , chiefly associated with a band at 1005 cm<sup>-1</sup>. The broad bands at 685 cm<sup>-1</sup> in  $(\text{SiF}_3)_2\text{NH}$  and 605 cm<sup>-1</sup> in  $(\text{SiF}_3)_2\text{NMe}$  may be tentatively assigned to  $\nu_{\text{s}}(\text{SiNSi})$ , mixed with other skeletal modes: a similar band was observed<sup>35</sup> at 562 cm<sup>-1</sup> in the Raman spectrum of  $(\text{SiH}_3)_2\text{NMe}$  and inferred<sup>37a</sup> to lie near 545 cm<sup>-1</sup> in  $(\text{SiH}_3)_2\text{NH}$ .

Because of the low volatility and thermal stability of  $(\text{SiF}_3)_2\text{NPh}$ , its i.r. spectrum could not be thoroughly investigated, but band positions appear reasonable by comparison with those of other hexafluorodisilazanes and of  $(\text{SiH}_3)_2\text{NPh}$  (ref. 37b). Weak additional bands at 3450 and 1380 cm<sup>-1</sup> suggested (as did the amine analysis and molecular weight) that some  $\text{SiF}_3\text{NPh}$  was also present.<sup>‡</sup> Similarly in the  $\text{SiF}_4\text{-NH}_2\text{Et-NaBH}_4$  reaction, together with  $(\text{SiF}_3)_2\text{NEt}$ , a slightly more volatile compound was produced; it contained an N-H bond (i.r., 3400 cm<sup>-1</sup>), and is thought to be  $\text{SiF}_3\text{NHet}$ . Like  $\text{SiF}_3\text{NPh}$ , it decomposed on attempted separation. The i.r. spectrum of  $\text{SiF}_2(\text{NMe}_2)_2$  shows close similarities to those of  $\text{SiF}_2(\text{NEt}_2)_2$ <sup>20</sup> and  $\text{SiH}_2(\text{NMe}_2)_2$ :<sup>34</sup> bands at 1305, 1175, and 1070 cm<sup>-1</sup> can be assigned to mixed  $\nu(\text{CN})$  and  $\rho(\text{CH}_3)$ , and those at 1008, 909, and 873 cm<sup>-1</sup> to mixed  $\nu(\text{SiF})$  and  $\nu(\text{SiN})$ .

**Mass Spectrum of  $(\text{SiF}_3)_2\text{NH}$ .** § Cleavage of the Si-N bond and loss of  $\text{SiF}_3^+$  (85) is an important process; the ions  $\text{SiF}_2^+$ ,  $\text{SiF}^+$ , and  $\text{SiF}_n^{2+}$  ( $n = 1-3$ ) are also found. Stepwise loss of fluorine leads to  $\text{Si}_2\text{F}_5\text{NH}^+$  (166), also  $\text{Si}_2\text{F}_4\text{NH}^+$  (147) and the corresponding hydrogen-

free ion, but further loss of fluorine seems to lead to Si-N bond cleavage. A similar situation has been noted<sup>1</sup> in the mass spectrum of  $\text{SiF}_3\text{NEt}_2$ , where  $\text{SiF}_2\text{NEt}_2^+$  is observed, but not  $\text{SiFNEt}_2^+$ ; this suggests that  $\text{Si}_2\text{F}_4\text{NH}^+$  is the symmetrical species. Other abundant ions include  $\text{SiF}_2\text{NH}^+$  (81) and  $\text{SiF}_2\text{N}^+$  (80) (but not  $\text{SiF}_3\text{N}^+$ ,  $\text{SiF}_3\text{NH}^+$ , or  $\text{SiFN}^+$ ). Minor peaks attributed to  $\text{SiHF}_n^+$  ( $n = 0-3$ ) provide some evidence for transfer of H from N to Si. Small amounts of oxygen-containing ions (e.g.  $\text{SiF}_3\text{OH}^+$ ,  $\text{SiF}_2\text{OH}^+$ , and  $\text{SiF}_2\text{O}^+$ ) doubtless arose *via* reaction with traces of water in the spectrometer: the  $(\text{SiF}_3)_2\text{NH}$  used was shown (i.r.) to be initially free from  $(\text{SiF}_3)_2\text{O}$ .

**More Condensed Silicon-Nitrogen Products.**—Most dehydrofluorination experiments with primary amines or ammonia yielded, in addition to the simple compounds already described, liquids or solids of low volatility. Thus a fraction (B) with i.r. spectrum and molecular weight appropriate for  $(\text{SiF}_3\text{NH})_2\text{SiF}_2$  was isolated from the reaction of  $\text{SiF}_4$  and  $\text{NH}_3$  with  $\text{LiAlH}_4$ . The same substance resulted, together with  $\text{SiF}_4$ , when  $(\text{SiF}_3)_2\text{NH}$  was held for a short time at room temperature. No  $(\text{SiF}_3)_2\text{NMe}$  was isolated from the reaction of  $\text{SiF}_4$  with Na-K alloy in liquid methylamine, only an almost involatile liquid (A) with properties appropriate for oligomeric  $(\text{SiF}_2\text{NMe})_x$ ; similar products were formed in minor amount from the reaction of  $\text{SiF}_4$  and  $\text{NH}_2\text{Me}$  with  $\text{LiAlH}_4$ . Other examples can be found in the Tables. In all cases the products are consistent with those shown in equation (16). Systems with R = H or



Ph seemed particularly prone to this decomposition.

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\* Assigned by the original authors to  $\nu(\text{CC})$ .

† Corresponding band centres in  $(\text{SiH}_3)_2\text{NH}$  appear at 3425 and 1190 cm<sup>-1</sup> (ref. 37).

‡ Corresponding bands have been observed for  $\text{SiF}_3\text{NHBu}^+$  (ref. 1),  $\text{SiH}_3\text{NPh}$  (ref. 37b), and  $\text{SiMe}_3\text{NPh}$  (ref. 38).

§ A Table of mass spectral data for  $(\text{SiF}_3)_2\text{NH}$  has been deposited in Supplementary Publication No. SUP 20846 (3 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full size copies.)

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