Silicon–Nitrogen Compounds. Part X.[1] Dehydrofluorination of Tetrafluorosilane–Amine Adducts with Anionic Hydrides and Related Compounds

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Adducts of tetrafluorosilane and secondary amines NHR_2(R = Me or Et) react, especially when an excess of tetrafluorosilane is present, with the following dehydrofluorinating agents: $LiAlH_4$ (200°); $NaBH_4$ (200°); B_2H_6 (190—200°); electropositive metals (350°). The products are corresponding substituted aminofluorosilanes $SiF_{4-n}(NR_2)_n$ (R = Me, n = 1 or 2; R = Et, n = 1). Tetrafluorosilane slowly reacts at 25° with alkali metals in liquid $NHMe_2$ to give $SiF_2(NMe_2)_2$. Similarly, SiF_4 and primary amines, on heating with $LiAlH_4$ (or in some cases $NaBH_4$), produce corresponding *N*-substituted hexafluorodisilazanes $(SiF_3)_2NR$ (R = H, Me, Et, Ph, or NMe_2). In some cases, evidence for partly-substituted SiF_3NHR or condensed $SiF_3NR(SiF_2NR)_nSiF_3$ derivatives was obtained. The chief or sole product from SiF_4–NH_2R–B_2H_6 reactions is a borazole $B_3H_3N_3R_3$: also the diamine $NHMe[CH_2]_2NHMe$ gives rise to $H\overline{BNMeCH_2CH_2N}Me$. The adduct $SiF_4,2NH_2Me$ is not dehydrofluorinated when heated alone or with added NEt_3, NH_2Ph, zinc, or $Fe(CO)_5$; above 300° some disproportionation of the amine occurs. Physical properties of the products, including the mass spectrum of $(SiF_3)_2NH$ and i.r. spectra are reported; also possible intermediates in dehydrofluorination are discussed.

WE have shown[1] how substituted aminofluorosilanes result from self-dehydrofluorination of SiF_4–amine adducts. Added reagents may also serve to remove the elements of hydrogen fluoride. Thus BF_3 adducts of primary and secondary amines have been converted into B–N compounds by metals[2,3] at 250—300°, metal amides,[4] Grignard reagents,[5] and aliphatic tertiary amines in solution,[6] but not by LiH,[7] pyridine,[6] KF,[3] CsF,[6] $KOBu^t$,[6] $AlCl_3$,[6] CaS,[6] or Al_4C_3;[6] alkali metal tetrahydroborates gave uncertain results.[7]

Less is known concerning SiF_4–amine systems. Apart from our preliminary communication,[8] a patent has described the dehydrofluorination of SiF_4 and tetra-aminobiphenyl using NMe_3,[9] and other reports have shown[10] how various SiF_4–primary amine adducts react in benzene according to equation (1) † with NMe_3, NEt_3, and $NEtPr^i_2$ but not pyridine. The reaction was reversible in boiling benzene, and separation of products was difficult.

$$NH_2R + 3SiF_4 + 2NR_3 \rightleftharpoons \frac{1}{n}(SiF_2NR)_n + 2NHR_3{}^+SiF_5{}^- \qquad (1)$$

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 characterization of products were generally similar to those described previously.[1,11] 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.[1,12] Solvents were dried (CaH_2, Na), then treated with SiF_4 and finally fractionated *in vacuo*. Diborane was made by standard methods[13] or, more conveniently, by heating dry tin(II) chloride and $NaBH_4$ to 200°.[14]

Analysis.—Amine in aminofluorosilanes was determined either (*i*) by treatment with an excess of anhydrous HCl and weighing of the amine salt formed,[1] 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;[12] 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 SiF_4, traces of SiH_4 and $(SiF_3)_2O$, and $(SiF_3)_2NMe$ [21% based on amine used; held at −120°, passed through −85°] [Found: F, 55·0; 55·2; NMe, 14·5, 14·8%;

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† In some cases, other fluorosilicate anions (*e.g.* $Si_2F_{11}{}^{3-}$) were present.

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TABLE 1

Dehydrofluorinations with primary amines and ammonia

Run	SiF_4/mmol	Amine/mmol	Agent/mmol	Reaction time/h	Reaction temp./°C	Products [a]/mmol
1	124	NH_2Me (13)	$LiAlH_4$ (6·5) [b]	10	260	H_2 (25; 95%); $(SiF_3)_2NMe$(1·2; 9%); less volatile oil,[c] grey and white solids.
2	41	NH_2Me (3·3)	B_2H_6 (0·7)	2	175	H_2(2·4; 57%); $(SiF_3)_2NMe$(0·47; 14%); $B_3H_3N_3Me_3$(0·2);[d] solids.[e]
3	60	NH_2Me (3)	$NaBH_4$ (1·5) [f]	10	215	H_2(3·5, 57%); $(SiF_3)_2NMe$(0·64; 21%); solids.
4	5	NH_2Me (70) [g]	Na–K (5)	340	25	H_2; NH_2Me; $SiF_4,2NH_2Me$; liquid *A* (see text);[h] solids.
5	80	NH_2Et (11·2)	$LiAlH_4$ (5·6)	10	225	H_2(16·9; 75%); $(SiF_3)_2NEt$(4·9; 44%); almost involatile liquid silazanes; solids.
6	80	NH_2Et (10)	$NaBH_4$ (5)	10	215	H_2(12·9; 65%); $(SiF_3)_2NEt$(0·4; 4%); probable SiF_3NHEt (*ca.* 10 mg; see text); solids.
7	80	NH_2Ph (8)	$LiAlH_4$ (4·5)	12	300	H_2(9·5; 60%; $(SiF_3)_2NPh$(0·48; 6%); solids.
8	55	NH_2Ph (10·3)	$LiAlH_4$ (5) [i]	12	310	H_2(10; 50%); C_6H_6(0·3); liquid silazanes (*ca.* 20 mg);[j] solids.
9	80 [k]	NH_3 (10·4)	$LiAlH_4$ (5·2)	11	260	H_2(9·5; 46%); $(SiF_3)_2NH$(1·03; 10%); liquid *B* (see text);[l] solids.
10	80	Me_2NNH_2 (10)	$NaBH_4$ (5) [m]	10	260	H_2(9; 45%) SiF_3NMe_2 (trace); $(SiF_3)_2$-$NNMe_2$ (0·27; 3%);[n] solids.

[a] An excess of SiF_4, also traces of SiH_4 and $(SiF_3)_2O$ recovered in all cases except run 4. [b] When SiF_4 (80 mmol) and $LiAlH_4$ (16·9 mmol) were heated together at 370° for 18 h, the volatile products were: H_2 (33·5 mmol); $(SiF_3)_2O$ and SiF_4 (60 mmol). [c] Held at −23°. [d] Held at −64°. Found: *M*, 129. Calc. for $C_3H_{12}B_3N_3$: *M*, 123. I.r. as in: T. Totani, H. Watanabe, and M. Kubo, *Spectrochim. Acta*, 1969, **25A**, 585 and refs. therein. [e] I.r. showed that $SiF_4,2NH_2Me$ was present; on hydrolysis, $(NH_3Me)_2SiF_6$ was appropriately formed. [f] A mixture of SiF_4 and $NaBH_4$, after having been heated under the same conditions, was essentially unchanged. [g] Liquid phase present. [h] Almost involatile at 25°; it contained Si and F, and yielded NH_2Me on hydrolysis. [i] NH_2Ph and $LiAlH_4$ were first allowed to react at 25°, then SiF_4 was introduced. [j] Held at −46°; rapidly decomposed to SiF_4 and solids. [k] With lower $SiF_4 : NH_3$ ratios, no volatile Si–N compounds were isolated. [l] Held at −64°; Found: *M*, 263 Calc. for $(SiF_3NH)_2SiF_2$: 266. I.r. spectrum similar to that of $(SiF_3)_2NH$, but additional weak band at 885 cm^{-1}. [m] $LiAlH_4$ gave similar results. [n] Held at −84°, passes through −64°. Found: *M*, 223. Calc. for $(SiF_3)_2N_2Me_2$: 228. I.r. (gas): 3000ms, 2900ms, 2820m, 1470ms, 1300m, 1240ms, 1180ms, 1100s, 1000vs, 915s, and 825s cm^{-1}.

TABLE 2

Dehydrofluorinations with secondary amines

Run	SiF_4/mmol	Amine/mmol	Agent/mmol	Reaction time/h	Reaction temp./°C	Products [a]/mmol
1	10	$NHMe_2$ (10)	$LiAlH_4$ (2·5) [b]	12	200	H_2(9·0; 90%); SiF_4(0·9); SiF_3NMe_2(4·9; 50%); $SiF_2(NMe_2)_2$(0·2); solids.[c]
2	2·5	$NHMe_2$ (2·2)	B_2H_6 (0·6)	1	190	H_2(1·1; 50%); SiF_4(1·2); SiF_3NMe_2(1·1; 50%); solids.
3	38	$NHMe_2$ (72)	$LiAlH_4$ (19·6)	12	200	H_2(*ca.* 75; 100%); SiF_3NMe_2(trace); $SiF_2(NMe_2)_2$(22; 69%); $SiF(NMe_2)_3$, solids.
4	11·3	$NHMe_2$ (25)	Al (7·4) [d]	12	350	H_2; NMe_3; $SiF_2(NMe_2)_2$ (1·1; 10%; SiF_4,NMe_3; solids.
5	16	$NHMe_2$ (70) [e]	Na (32) [f]	340	25	H_2; $SiF_2(NMe_2)_2$ (6·2; 39%); $SiF(NMe_2)_3$ (trace); solids.
6	55	$NHEt_2$ (5·2)	B_2H_6 (0·65) [g]	2·5	220	H_2; SiF_3NEt_2(3·6; 70%); solids.

[a] SiF_4, and a trace of $(SiF_3)_2O$ were found in all cases except runs 4 and 5; traces of SiH_4 were found in runs 1—3, and 6. [b] $NaBH_4$ was also effective. [c] Partly sublimed at 300°; neither component could be definitely identified (i.r., *X*-ray powder methods). [d] Mg gave similar results, but with lower yields. Zn gave some H_2, but only a trace of aminosilanes. [e] Liquid phase present. [f] K or Na–K alloy gave similar results. [g] $LiAlH_4$ was also effective.

M, 197, 199, 200. Calc. for $(SiF_3)_2NMe$: F, 57·3; NMe, 14·6; *M*, 199], together with white residual solid.

Table 3

Other attempted dehydrofluorinations

Run	SiF_4 mmol	Amine mmol	Agent mmol	Reaction time h	Reaction temp. °C	Products ^{a} mmol
1	0·8	NH_2Me (1·6)	None	2·5	500 ^{b}	H_2(0·02); NMe_3(0·2); $SiF_4,2NH_2Me$; $SiF_4,2NH_3$.^{c}
2	9·7	NH_2Me (19·4)	None	24	350 ^{d,e}	H_2; NMe_3(3·7); SiF_4,NMe_3(0·5); solids.
3	0·6	NH_2Me (1·2)	NEt_3 (1·2)	1	400 ^{g}	H_2(0·11); NEt_3; NH_xMe_{3-x}(x = 0—3) (trace); solids.^{e}
4	0·6	NH_2Me (1·2)	NH_2Ph (1·1)	1	200	NH_2Ph(1·1); $SiF_4,2NH_2Me$(0·6).
5	0·6	NH_2Me (1·2)	NaF (50)	1	200	NH_2Me(1·2); Na_2SiF_6.
6	75	NH_2Me (6)	$Fe(CO)_5$ (6)	1	170 ^{h}	CO; SiF_4; $SiF_4,2NH_2Me$; Fe(CO); solids.
7	6·0	NH_2Me (12)	Zn dust (6) ^{i}	4	350 ^{e}	H_2(1·3); NH_xMe_{3-x}(x = 0—3) (0·027 g); solids.^{j}
8	6·5	NH_2Me (13)	$NaNH_2$ (11)	4	320	H_2(1·0); N_2(0·1); NH_3(10); NH_2Me(8); solids.^{k}
9	^{l}	NH_2Pr^n ^{l}	B_2H_6 ^{l}	3	200	H_2; SiF_4; $B_3H_3N_3Pr^n_3$ ^{m}; solids.
10	10·1	$NHMe_2$ (19·4)	None	18	350 ^{e,p}	H_2(0·14); SiF_4 (*ca.* 1·5); SiF_4,NMe_3; solids.^{n}
11	^{l}	$(NHMeCH_2\text{–})_2$ ^{l}	B_2H_6 ^{l}	3	200	H_2; SiF_4; $\overline{HBNMeCH_2CH_2NMe}$;^{q} solids.
12	83	NH_3 (4·3)	B_2H_6 (1·0)	2	175	H_2(4; 65%); SiF_4; partly-sublimable solids.

[a] In most cases, traces of $(SiF_3)_2O$ were formed. [b] Similar mixtures heated at 220° for 2·5 h were unchanged; after 1 h at 600°, more H_2 and some HCN (*M*, i.r.) were evolved. In all cases the pressure did not exceed 5 atmos., and no liquid adduct was present. [c] Chiefly $SiF_4,2NH_2Me$ (i.r.) but some ammonia was detected after hydrolysis. [d] Pressure was *ca.* 15 atmos.; liquid adduct was present. [e] The reaction vessel was heavily etched. [f] On sublimation, some $SiF_4,2NH_3$ (i.r.) was obtained; on heating with NaF at 200°, the solid gave NH_3 together with some NH_2Me and $NHMe_2$; on hydrolysis, a sample gave 68% of the ammonia calculated for $SiF_4,2NH_3$. [g] No reaction after 1 h at 200°; at 500°, decomposition of NEt_3 was rapid. [h] At higher temperatures, $Fe(CO)_5$ decomposed, but there was no other reaction up to 400°. [i] Similar results were obtained with Mg powder or K; in the latter case, charring was also observed. [j] These comprised a grey powder (containing Zn^{2+},F^-) also a sticky off-white solid which gave some NH_xMe_{3-x} (x = 1—3) on hydrolysis. [k] The light brown residue was free from CN^-; it could not be sublimed up to 300° and hydrolysed very slowly giving F^- and silica. It was resistant to boiling NEt_3 or EtOH, but dissolved in acid or alkali. [l] Excess of SiF_4 and roughly equivalent amounts of amine and B_2H_6 were used. [m] Identified by i.r., n.m.r.; on hydrolysis gave NH_2Pr^n; *cf.* M. P. Brown, R. W. Heseltine, and D. W. Johnson, *J. Chem. Soc.* (*A*), 1967, 597. [n] Pyrolysis with NaF yielded NH_3 and $NHMe_2$; i.r. showed SiF_6^{2-} and $SiF_4,2NH_xMe_{3-x}$ (x = 1 or 3). [p] Liquid adduct phase present (pressure *ca.* 10 atmos.). Mixtures heated up to 400° at pressures below 1 atmos. did not react. [q] M.p., −64°; v.p., 14 mmHg, 21° C. On hydrolysis gave $(HNMeCH_2\text{–})_2$, positive boron test. Found: *M*, 99. Calc. for $C_4H_{11}BN_2$, 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^{-1}. N.m.r. ($SiMe_4$ soln.): τ 7·3 (singlet, CH_3,6*H*); 6·8 (singlet, CH_2,4*H*). B*H* not observed.

Physical properties (see also Table 4). Vapour-pressure equation (187—274 K): $\log p/\text{mmHg} = 8{\cdot}354 - 1640/T$. I.r. spectrum (gas): 2960m, 2912m, 2855m, 1820m, 1460w, 1380w, 1310m, 1235s, 1120m, 1083s, 1016vs, 997vs, 911s, 875m, 828sh, 822s, 605m, 440sh, and 420s cm^{-1}.

(*ii*) N-*Ethylhexafluorodisilazane*. Tetrafluorosilane, ethylamine, and lithium tetrahydroaluminate were heated together as shown in Table 1, run 5. The products were: hydrogen [75% of that required by equation (3)], the excess of SiF_4, traces of SiH_4 and $(SiF_3)_2O$, also $(SiF_3)_2NEt$ [44% based on amine used; held at −96°, passed through −64°] [Found: F, 52·7; NEt, 20·2%; *M*, 214. Calc. for $(SiF_3)_2NEt$: F, 53·5; NEt, 20·2%; *M*, 213], an almost involatile silazane fraction, and a mixture of grey and white solids.

Table 4

Physical properties of some aminofluorosilanes

Compound	M.p. ^{a} °C	B.p.(extrap.) °C	ΔH_{vap} kcal mol^{-1}	ΔS_{vap} cal mol^{-1} K^{-1}
$(SiF_3)_2NH$	*ca.* −35 ^{b}	66 ^{c}	7·2	22 ^{c}
$(SiF_3)_2NMe$	−50	27	7·50	25·0
$(SiF_3)_2NEt$	−75	44	7·64	24·1
SiF_3NMe_2	−108	20·5 ^{d}	6·41 ^{d}	21·8 ^{d}
$SiF_2(NMe_2)_2$ ^{e}	−59 ^{f}	95 ^{g}	8·80 ^{g}	23·9 ^{g}

[a] ± 1° Except for $(SiF_3)_2NH$. [b] Decomposition appreciable at this temperature. [c] Long extrapolation. [d] Supersedes values given in ref. 1. [e] *d*, 1·001 g cm^{-3}, 25 °C. [f] Lit.,[16] −69·5°. [g] Calc from data of ref. 16.

Physical properties (see also Table 4). V.p. equation (187—297 K): $\log p/\text{mmHg} = 8{\cdot}148 - 1670/T$. I.r. spectrum (gas): 3000m, 2920mw, 1490w, 1460w, 1390m, 1360w, 1320ms, 1195s, 1075vs, 1015vs, 987vs, 950ms, 885m, and 830s cm^{-1}.

(*iii*) N-*Phenylhexafluorodisilazane*. The products from pyrolysis of a mixture of SiF_4, aniline, and $LiAlH_4$ 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_4, and slightly impure $(SiF_3)_2NPh$ [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^{-1}] [Found: NPh, 36·2%;* *M*, 249.* Calc. for $(SiF_3)_2NPh$: NPh, 34·9%; *M*, 261], together with a mixture of white and dark grey solids.

In another experiment, the same reactants in mole ratios

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* Consistent with the presence of *ca.* 10% of SiF_3NHPh.

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 $\mathrm{SiF_4}$ and aniline with $\mathrm{NaBH_4}$ or $\mathrm{B_2H_6}$, and of $\mathrm{SiF_4}$ with $\mathrm{LiAl(NHPh)_4}$ (prepared *in situ* from aniline and $\mathrm{LiAlH_4}$) [15] yielded almost no volatile Si–N compounds, although up to 85% of the calculated hydrogen was evolved.

(*iv*) *Hexafluorodisilazane.* When $\mathrm{SiF_4}$, ammonia, and $\mathrm{LiAlH_4}$ 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 $\mathrm{(SiF_3)_2NH}$ [10% yield based on ammonia used; held at −96°, passed through −64°. Found: F, 60·8; NH, 8·0%; *M*, 185 ± 2. Calc. for $\mathrm{(SiF_3)_2NH}$: 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 $\mathrm{(SiF_3)_2NH}$ occurred during fractionation. Attempted preparations using $\mathrm{B_2H_6}$ or $\mathrm{NaBH_4}$ in place of $\mathrm{LiAlH_4}$, or with smaller proportions of $\mathrm{SiF_4}$, were unsuccessful.

Physical properties (see also Table 4). V.p. equation (186—230 K): $\log p/\mathrm{mmHg} = 7{\cdot}68 - 1580/T$. I.r. spectrum (gas): 3400m, 1320m, 1260sh, 1235s, 1145m, 1020vs, 1005vs, 975sh, 940m, 825s, and 685m,br $\mathrm{cm^{-1}}$.

(*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 $\mathrm{SiF_4}$, and $\mathrm{SiF_3NMe_2}$ [50% yield based on amine used; held at −96°, passes −64°. Found: F, 43·5; $\mathrm{NMe_2}$, 34·2%; *M*, 128, 130. Calc. for $\mathrm{SiF_3NMe_2}$: F, 44·1; $\mathrm{NMe_2}$, 34·1%; *M*, 129].

Physical properties (see also Table 4). V.p. equation (241—273 K): $\log p/\mathrm{mmHg} = 7{\cdot}663 - 1405/T$ (lit.,[16] $8{\cdot}416—1606/T$). I.r. spectrum (gas): 2990m, 2915s, 2890sh, 2825m, 1495m, 1460m, 1326s, 1188sh, 1174s, 1090sh, 1078m, 1030s, 980vs, 958vs, 879s, and 665s $\mathrm{cm^{-1}}$.

(*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, $\mathrm{SiF_2(NMe_2)_2}$ [39% yield based on equation (11); held at −64°, passed through −23°. Found: F, 23·6; $\mathrm{NMe_2}$, 56·8%; *M*, 151, 155. Calc. for $\mathrm{SiF_2(NMe_2)_2}$: F, 24·6; $\mathrm{NMe_2}$, 57·2%; *M*, 154. *d*, 1·001 g $\mathrm{ml^{-1}}$ 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 $\mathrm{cm^{-1}}$], 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 must be efficiently removed.[1] Generalized bases that might be used include $\mathrm{H^-}$, $\mathrm{NH_2^-}$, amines, $\mathrm{F^-}$, and metals. We now indicate the scope and limitations of different dehydrofluorinating agents.

$$n\mathrm{SiF_4} + \mathrm{NH}_n\mathrm{R}_{3-n} \rightleftharpoons (\mathrm{SiF_3})_n\mathrm{NR}_{3-n} + n\mathrm{HF} \qquad (2)$$

(a) *Lithium Tetrahydroaluminate and Sodium Tetrahydroborate.*—These two reagents proved to be the most versatile and generally applicable. Thus $\mathrm{LiAlH_4}$ reacted with $\mathrm{SiF_4}$ and $\mathrm{NH_2}$-derivatives according to equation (3) ($\mathrm{M^1 = Li}$, $\mathrm{M^2 = Al}$) when R = Me, Et, Ph,* H,† or $\mathrm{NMe_2}$ (Table 1). The fully-substituted product obtained from $\mathrm{Me_2NNH_2}$ compared with $\mathrm{SiF_3NHNMe_2}$ formed from $\mathrm{SiF_4}$ and $\mathrm{Me_2NNH_2}$ alone.[17] The lithium compound similarly reacted with $\mathrm{SiF_4}$ and secondary amines according to equation (4), $n = 1$, ($\mathrm{M^1 = Li}$, $\mathrm{M^2 = Al}$) 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 $\mathrm{SiF_4}$ in reaction (3); such an excess was also helpful in reaction (4), $n = 1$.

$$\mathrm{M^1M^2H_4 + 4SiF_4 + 2NH_2R \longrightarrow 2(SiF_3)_2NR + M^1F + M^2F_3 + 4H_2} \qquad (3)$$

$$(6-2n)\mathrm{SiF_4} + 4\mathrm{NHR_2} + \mathrm{M^1M^2H_4} \longrightarrow (6-2n)\mathrm{SiF}_{4-n}(\mathrm{NR_2})_n + \mathrm{M^1F + M^2F_3 + 4H_2} \qquad (4)$$

Sodium tetrahydroborate behaved similarly in most cases, although the yields were typically lower [equations (3) and (4); $\mathrm{M^1 = Na}$, $\mathrm{M^2 = B}$]. 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 $\mathrm{LiAlH_4}$. All dehydrofluorinations successful with $\mathrm{NaBH_4}$ could also be effected with $\mathrm{LiAlH_4}$, but the converse was not true: systems with $\mathrm{SiF_4}$, $\mathrm{NaBH_4}$, and ammonia or aniline yielded no disilazane.

The role of $\mathrm{LiAlH_4}$ in the reaction is by no means self-evident. Recent studies by Dilts and Ashby[18] have clarified the stages of thermal decomposition of $\mathrm{LiAlH_4}$, 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) ($\mathrm{M^1 = Li}$, $\mathrm{M^2 = Al}$). Both LiH and aluminium are doubtless produced in a highly reactive form. The latter reacts with $\mathrm{SiF_4}$ and amines even when used as the normal oxide-coated powder (see Table 2 and below) while the former is expected[19] to

$$\mathrm{3LiAlH_4 \longrightarrow Li_3AlH_6 + 3H_2 + 2Al} \qquad (5)$$

$$\mathrm{Li_3AlH_6 \longrightarrow 3LiH + \tfrac{3}{2}H_2 + Al} \qquad (6)$$

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* This compound proved surprisingly difficult to isolate in a pure state, possibly because small amounts of $\mathrm{SiF_3NHPh}$ formed with it tended to induce decomposition.

† No evidence for $\mathrm{(SiF_3)_3N}$ or $\mathrm{SiF_3NH_2}$[11] was found.

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form Li–N derivatives with amine [*e.g.* equation (7)]; these are known[20] to react with SiF_4 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.

$$LiH + NHR_2 \longrightarrow LiNR_2 + H_2 \qquad (7)$$

$$LiNR_2 + SiF_4 \longrightarrow SiF_3NR_2 + LiF \qquad (8)$$

Initial reaction of amine with $LiAlH_4$ to give hydrogen and $LiAlH_n(NR_2)_{4-n}$ (ref. 21) or other Al–N derivatives[22] is unlikely, given the excess of SiF_4 normally present and the very low dissociation pressures of most SiF_4–amine adducts at room temperature.[12] On heating, it is only when the partial pressure of amine becomes significant before $LiAlH_4$ has decomposed that formation of Al–N derivatives is likely; if formed, they are expected however to react readily with SiF_4 (*cf.* ref. 23). In one experiment, aniline and $LiAlH_4$ were allowed to react together before introducing SiF_4; 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_3NHPh (see below). Small amounts of silane arose from slight reduction of SiF_4 by $LiAlH_4$; however, when $LiAlH_4$ and SiF_4 were pyrolysed under more extreme conditions (370° for 18 h), hydrogen was quantitatively released as H_2, and some SiF_4 was removed.

$$LiAlH_4 + 4NH_2R \longrightarrow LiAl(NHR)_4 + 4H_2 \qquad (9)$$

It is concluded that dehydrofluorination can occur directly with $LiAlH_4$ and its pyrolysis and/or reaction products, and indirectly *via* reaction of Li–N and/or Al–N reaction products with SiF_4. Silicon hydrides appear to be unimportant as intermediates.

Sodium tetrahydroborate is known to be more resistant to pyrolysis[24] than $LiAlH_4$, and in this work there was very little reaction when it was heated with SiF_4. Thus B_2H_6, silicon hydrides, or LiH are not likely to be involved as intermediates. Pyrolysis of $NaBH_4$ 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_4 to give Si–N derivatives and BF_3, or that direct abstraction of HF [from (2)] by $NaBH_4$ occurs preferentially. The first possibility, which seems unlikely on grounds of bond energy values, is excluded by the observation that borazoles and SiF_4 were co-products of reactions involving B_2H_6 (see below).

(*b*) *Diborane.*—Equation (10) shows a possible course for dehydrofluorination using diborane. Adducts of BF_3 with amines are stronger than those of SiF_4, and are expected to appear as products, even with an excess of SiF_4. Sufficient amine was therefore added to combine with all the expected BF_3.

$$6SiF_4 + B_2H_6 + (3n + 2)NH_{3-n} \longrightarrow 3n(SiF_3)_{3-n}NR_n + 6H_2 + 2BF_3{,}NH_{3-n}R_n \qquad (10)$$

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.[1]

Primary amines [equation (10): $n = 1$] gave only a low yield of silazane with R = Me, and none at all with R = H, Pr^n, or Ph. Substituted borazoles $(BHNR)_3$ were identified as products when R = Me or Pr^n; there appeared to be no reaction between SiF_4 and these borazoles up to 200°. Analogously, the substituted diamine $NHMe{\cdot}[CH_2]_2{\cdot}NHMe$ gave rise to 1,3-dimethyl-1,3,2-diazaborolidine,[25] $\mathrm{H}\overline{\mathrm{BNMeCH_2CH_2N}}\mathrm{Me}$, but no Si–N products.

It is concluded that diborane is generally less satisfactory than $LiAlH_4$ or $NaBH_4$, 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_4 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[26] at 298 K associated with removal of HF by metals [equation (11)] have the approximate values: M = Mg, −570; Al, −495; K, −295; Zn, −230 kJ mol⁻¹. However, the entropy changes[26] $(-\Delta S)$ 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.

$$M + nHF \longrightarrow MF_n + n/2\,H_2 \qquad (11)$$

Alkali metals also slowly removed HF from reaction mixtures of $SiF_4{,}2NHMe_2$ and liquid dimethylamine [equation (12)]. The large excess of amine and the

$$SiF_4 + nNHMe_2 + nM \longrightarrow SiF_{4-n}(NMe_2)_n + nMF + n/2\,H_2 \qquad (12)$$

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[26] National Bureau of Standards Circular No. 500, Selected Values of Chemical Thermodynamic Properties, Washington, D.C., 1952.

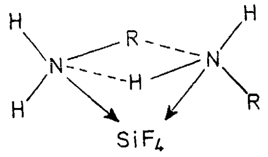
relative susceptibility of SiF_3NMe_2 towards base-catalysed disproportionation [27] ensured that $SiF_2(NMe_2)_2$ was the major product. Further substitution to give $SiF(NMe_2)_3$ is clearly difficult.

Corresponding reactions with primary amines in no case produced hexafluorodisilazanes. At 350°, 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 $(SiF_2NR)_x$. Also about 10% of the original amine disproportionated to give all possible species NH_nR_{3-n} (n = 0—3) when R = Me. Alkali metals with SiF_4 in an excess of methylamine slowly yielded hydrogen and a barely volatile oligomeric silazane (*A*) that showed no tendency to lose SiF_4, and was probably cyclic $(SiF_2NMe)_n$ (see refs. 1, 10, and 28). These observations are all consistent with the known readiness [27] 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 $SiF_4,2NH_2Me$ was pyrolysed at 500° 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 NMe_3 and ammonia (present as the relatively strong adduct $SiF_4,2NH_3$). A small quantity of hydrogen arose from decomposition of methylamine according to: $CH_3NH_2 \longrightarrow HCN + 2H_2$; this was confirmed by isolation of HCN and more hydrogen after pyrolysis at 600°.

When the pressure was sufficiently high to ensure that a liquid phase was present, amine disproportionation occurred at a lower temperature: at 350°, 65% of the methylamine in $SiF_4,2NH_2Me$ had reacted after 24 h. Similar results were obtained with $SiF_4,2NHMe_2$, although it has now been shown that this adduct will undergo self-dehydrofluorination, using milder conditions and added SiF_4.[1] Added tertiary amines were similarly ineffectual under our conditions (*e.g.* Table 3, run 3), although successfully used [10] in benzene solution with an excess of SiF_4. These results reinforce our previous conclusions [1] about the enabling role of SiF_4 in dehydrofluorination.

The disproportionation of methylamines is not well documented. Usually they decompose [29] on heating above *ca.* 450°, but Brown [30] has shown that on heating $BF_3,NHMe_2$ at 240—295°, besides the main products Me_2NBF_2 and $NH_2Me_2^+NF_4^-$, some BF_3,NMe_3 is formed. Considerably more disproportionation was observed with SiF_4 and NH_2Me_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.



(1)

In further experiments with $SiF_4,2NH_2Me$, heating with sodium fluoride led to quantitative displacement of amine, and no $NaHF_2$ was detected; aniline,* also $Fe(CO)_5$ and its decomposition products, were without effect. Sodium amide (used [31] to prepare NH_2BF_2 from BF_3,NH_3) produced 90% of the ammonia required by equation (13), but additional methylamine arose *via*

$$SiF_4,2NH_2Me + 2NaNH_2 \longrightarrow 2NaF + NH_2Me + 2NH_3 + 1/x(SiF_2NMe)_x \quad (13)$$

displacement by F^- from unreacted adduct and/or amine exchange between ammonia and the Si–N product.[32] Hydrogen † and nitrogen were formed by reaction (14); absence of CN^- in the solid products showed that thermolysis of amine and reaction (15) [33]

$$NaNH_2 \longrightarrow NaH + \tfrac{1}{2}H_2 + \tfrac{1}{2}N_2 \quad (14)$$

$$NaNH_2 + NH_2Me \longrightarrow NaCN + NH_3 + 2H_2 \quad (15)$$

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 ΔS_{vap} suggest that intermolecular forces are smallest when the Si : N ratio is unity.‡ In terms of a discussion given [32,34] for corresponding SiH_3 or 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 $(SiF_3)_2NH$ 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 ν_{as}(SiF) and ν_{as}(SiNSi) modes in the region 910—1020 cm^{-1}, and ν_s(SiF) *ca.* 825 cm^{-1}. For $(SiH_3)_2NR$ derivatives, strong bands in the region 1050—1300 cm^{-1}

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* Aniline, like NEt_3, is known [12] not to displace methylamine from $SiF_4,2NH_2Me$.

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

‡ The value of ΔS_{vap} for $(SiF_3)_2NH$ is not strictly comparable with the others, since it refers to the solid–vapour equilibrium.

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have been assigned [23,35] to alkyl rocking and CN stretching vibrations. Somewhat similar bands are observed with $(SiF_3)_2NR$ compounds [R = Me or Et (this work); R = Pr^n, Bu^n, or Bu^s (ref. 1)]. Thus corresponding bands occur in $(SiH_3)_2NEt$ [23] at 1111 * and 1171 cm^{-1}, and in $(SiF_3)_2NEt$ at 1075 and 1195 cm^{-1}. This assignment is consistent with the lack of strong bands for $(SiF_3)_2NH$ in this region.

The spectra of $(SiF_3)_2NH$ and isoelectronic $(SiF_3)_2O$ (refs. 11 and 36) are generally similar, except that (*a*) bands appear in the former at 3400 and 1235 cm^{-1}, reasonably assigned to NH stretching and bending modes,† and (*b*) the $\nu_{as}(SiOSi)$ vibration at 1205 cm^{-1} in $(SiF_3)_2O$ is replaced by $\nu_{as}(SiNSi)$, chiefly associated with a band at 1005 cm^{-1}. The broad bands at 685 cm^{-1} in $(SiF_3)_2NH$ and 605 cm^{-1} in $(SiF_3)_2NMe$ may be tentatively assigned to $\nu_s(SiNSi)$, mixed with other skeletal modes: a similar band was observed [35] at 562 cm^{-1} in the Raman spectrum of $(SiH_3)_2NMe$ and inferred [37a] to lie near 545 cm^{-1} in $(SiH_3)_2NH$.

Because of the low volatility and thermal stability of $(SiF_3)_2NPh$, its i.r. spectrum could not be thoroughly investigated, but band positions appear reasonable by comparison with those of other hexafluorodisilazanes and of $(SiH_3)_2NPh$ (ref. 37*b*). Weak additional bands at 3450 and 1380 cm^{-1} suggested (as did the amine analysis and molecular weight) that some SiF_3NHPh was also present.‡ Similarly in the SiF_4–NH_2Et–$NaBH_4$ reaction, together with $(SiF_3)_2NEt$, a slightly more volatile compound was produced; it contained an N–H bond (i.r., 3400 cm^{-1}), and is thought to be SiF_3NHEt. Like SiF_3NHPh, it decomposed on attempted separation. The i.r. spectrum of $SiF_2(NMe_2)_2$ shows close similarities to those of $SiF_2(NEt_2)_2$ [20] and $SiH_2(NMe_2)_2$: [34] bands at 1305, 1175, and 1070 cm^{-1} can be assigned to mixed $\nu(CN)$ and $\rho(CH_3)$, and those at 1008, 909, and 873 cm^{-1} to mixed $\nu(SiF)$ and $\nu(SiN)$.

Mass Spectrum of $(SiF_3)_2NH$.§ Cleavage of the Si–N bond and loss of SiF_3^+ (85) is an important process; the ions SiF_2^+, SiF^+, and SiF_n^{2+} (n = 1—3) are also found. Stepwise loss of fluorine leads to $Si_2F_5NH^+$ (166), also $Si_2F_4NH^+$ (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[1] in the mass spectrum of SiF_3NEt_2, where $SiF_2NEt_2^+$ is observed, but not $SiFNEt_2^+$; this suggests that $Si_2F_4NH^+$ is the symmetrical species. Other abundant ions include SiF_2NH^+ (81) and SiF_2N^+ (80) (but not SiF_3N^+, $SiFNH^+$, or $SiFN^+$). Minor peaks attributed to $SiHF^+_n$ (n = 0—3) provide some evidence for transfer of H from N to Si. Small amounts of oxygen-containing ions (*e.g.* SiF_3OH^+, SiF_2OH^+, and SiF_2O^+) doubtless arose *via* reaction with traces of water in the spectrometer: the $(SiF_3)_2NH$ used was shown (i.r.) to be initially free from $(SiF_3)_2O$.

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 ir. spectrum and molecular weight appropriate for $(SiF_3NH)_2SiF_2$ was isolated from the reaction of SiF_4 and NH_3 with $LiAlH_4$. The same substance resulted, together with SiF_4, when $(SiF_3)_2NH$ was held for a short time at room temperature. No $(SiF_3)_2NMe$ was isolated from the reaction of SiF_4 with Na–K alloy in liquid methylamine, only an almost involatile liquid (*A*) with properties appropriate for oligomeric $(SiF_2NMe)_x$; similar products were formed in minor amount from the reaction of SiF_4 and NH_2Me with $LiAlH_4$. 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.

$$n(SiF_3)_2NR \begin{cases} \rightarrow SiF_3NR(SiF_2NR)_{n-1}SiF_3 + (n-1)SiF_4 \\ \rightarrow (SiF_2NR)_n + nSiF_4 \end{cases} \qquad (16)$$

We thank the Ministry of Technology for support and Dr. M. N. Lilly for assistance with mass spectra.

[3/1408 *Received*, 6*th July*, 1973]

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

† Corresponding band centres in $(SiH_3)_2NH$ appear at 3425 and 1190 cm^{-1} (ref. 37).

‡ Corresponding bands have been observed for SiF_3NHBu^t (ref. 1), SiH_3NHPh (ref. 37*b*), and $SiMe_3NHPh$ (ref. 38).

§ A Table of mass spectral data for $(SiF_3)_2NH$ 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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