Silicon–Nitrogen Compounds. Part IX.[1] Self-dehydrofluorination of Tetrafluorosilane–Amine Adducts as a Route to Substituted Aminofluorosilanes

By **B. J. Aylett,* I. A. Ellis, and C. J. Porritt**, Chemistry Department, Westfield College, London N.W.3

Adducts of tetrafluorosilane and secondary amines readily undergo self-dehydrofluorination on moderate heating to yield as volatile products substituted aminofluorosilanes, SiF_3NR_2 (R = Me, Et, Pr^n, Bu^n; $R_2 = C_4H_8$, C_5H_{10}). Similar adducts of primary amines less readily give disilazanes, $(SiF_3)_2NR$ (R = Pr^n, Bu^n, Bu^s) or the silylamine SiF_3NHBu^t. Yields are increased if an excess of SiF_4 is present. Entirely gaseous SiF_4–amine mixtures do not react under these conditions: a liquid phase must be present for high yields. I.r., mass, and n.m.r. spectra of the new compounds are discussed. Tetrafluorogermane and diethylamine do not react in a gas–liquid system at 130 °C.

ADDUCTS of BF_3 and amines often rearrange on being heated[2] or in solution[3] to give dehydrofluorinated products and tetrafluoroborate salt [*e.g.*, equation (1);

$$2BF_3,NHR_2 \longrightarrow BF_2NR_2 + NH_2R_2BF_4 \qquad (1)$$

R = H (ref. 2*e*); Me (ref. 2*b*); and Et (refs. 2*c*, 2*d*)]. Similarly adducts of TiF_4, PF_3, PF_5, and organo-derivatives of the last two compounds yield substituted amino-compounds of the types TiF_3,NR_2,[4] $R_xPF_y(NR_2)_{3-x-y}$,[5] and $R_xPF_y(NR_2)_{5-x-y}$.[6]

In contrast, it has been generally supposed until recently that adducts of tetrafluorosilane with ammonia and amines remain unchanged on heating, apart from undergoing reversible dissociation. For example, $SiF_4,2NH_3$ is reported[7] to be stable at 300 °C, while adducts of ethylenediamine,[8] pyrrolidine,[8] piperidine,[8] aniline,[9] and the methylamines[10,11] sublime essentially unchanged at moderate temperatures. Various dehydrofluorinating agents such as metal hydrides,[12] diborane,[12] and adducts of tertiary amines[9] have been recommended for the production of aminofluorosilanes from these adducts.

During our studies of the dissociation of SiF_4–amine adducts[10] it was found that $SiF_4,2NHEt_2$ melted at 66 °C and underwent slow irreversible changes above that temperature, yielding *NN*-diethyl(trifluorosilyl)amine, SiF_3NEt_2. We now augment the preliminary account[13] of the scope of this reaction; it has been found independently[14] that tetrafluorosilane and trimethyl- or *unsym*-dimethyl-hydrazine when heated together form $Me_2N{\cdot}NMe{\cdot}SiF_3$ and $Me_2N{\cdot}NH{\cdot}SiF_3$ respectively.

EXPERIMENTAL

General.—High-vacuum and dry-box techniques were employed throughout. I.r. spectra were recorded (gas phase, 10 cm cell, for volatile compounds) on a Perkin-Elmer 337, n.m.r. spectra using a Varian A60-A, and mass spectra using a modified A.E.I. MS 10 instrument. Vapour pressures were measured with wide-bore manometers of Veridia tubing, and temperatures were determined with calibrated mercury or alcohol thermometers. A Stock-type apparatus was used to find m.p.s. Molecular weights were routinely checked by vapour-density determinations.

Amines were commercial samples; they were distilled, dried (CaH_2), and redistilled, all *in vacuo.* Molecular weights and i.r. spectra of middle fractions indicated no impurity.

Tetrafluoro-silane and -germane were prepared by the pyrolysis *in vacuo* at 400 °C or 700 °C of barium hexafluoro-silicate or -germanate respectively; they were purified by repeated fractionation.

Preparation of NN-*Diethyltrifluorosilylamine.*—In a typical experiment, diethylamine (8·2 mmol) was heated in a thick-walled tube (*ca.* 100 ml) with tetrafluorosilane (21 mmol) for 4·5 h at 110—120 °C. The volatile products were tetrafluorosilane (*ca.* 14 mmol), hexafluorodisiloxane (trace), and *NN*-diethyltrifluorosilylamine (4·1 mmol, 100%; held at −96 °C, passed through −64 °C) (Found: *M*, 159. Calc. for SiF_3NEt_2: *M*, 157). The white solid (0·5530 g) remaining in the tube [Found: $NHEt_2$, 54·1. Calc. for $(NH_2Et_2)_2SiF_6$, 50·5; for NH_2Et_2F, 78·5; for $NH_2Et_2SiF_5$, 37·0%] gave an i.r. spectrum characteristic of $NH_2Et_2^+$ and SiF_6^{2-} ions, and dissolved completely in water, from which it could be recovered unchanged.

---

[1] Part VIII, B. J. Aylett and M. J. Hakim, *J. Chem. Soc.* (*A*), 1969, 1788.

[2] (*a*) A. W. Laubengayer and G. F. Condike, *J. Amer. Chem. Soc.*, 1948, **70**, 2274; (*b*) J. F. Brown, *J. Amer. Chem. Soc.*, 1952, **74**, 1219; (*c*) I. G. Ryss and D. B. Donskaya, *Zhur. neorg. Khim.*, 1960, **5**, 2251; (*d*) V. I. Spitsyn, I. D. Kolli, R. A. Rodionov, and T. G. Sevast'yanova, *Doklady Akad. Nauk S.S.S.R.*, 1965, **160**, 1101; (*e*) I. G. Ryss and N. G. Parkhomenko, *Zhur. neorg. Khim.*, 1966, **11**, 103. For unsuccessful attempts, however, see: I. G. Ryss and S. L. Idel's *Zhur. neorg. Khim.*, 1959, **4**, 1990; J. J. Harris and B. Rudner, *Inorg. Chem.*, 1969, **8**, 1258.

[3] R. S. Satchell and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1967, 36.

[4] E. L. Muetterties, *J. Amer. Chem. Soc.*, 1960, **82**, 1082; J. A. Chandler, J. E. Wuller, and R. S. Drago, *Inorg. Chem.*, 1962, **1**, 65; J. A. Chandler and R. S. Drago, *ibid.*, p. 356.

[5] R. G. Cavell, *J. Chem. Soc.*, 1964, 1992; M. A. Fleming, R. J. Wyma, and R. C. Taylor, *Spectrochim. Acta*, 1965, **21**, 1189; J. S. Harman and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1970, 1935; J. F. Nixon and J. R. Swain, *ibid.*, p. 2075.

[6] R. Schmutzler and G. S. Reddy, *Inorg. Chem.*, 1965, **4**, 191; G. S. Reddy and R. Schmutzler, *ibid.*, 1966, **5**, 164; D. H. Brown, G. W. Fraser, and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1966, 171; J. J. Harris and B. Rudner, *J. Org. Chem.*, 1968, **33**, 1392; J. S. Harman and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1970, 1138.

[7] D. B. Miller and H. H. Sisler, *J. Amer. Chem. Soc.*, 1955, **17**, 4998.

[8] J. P. Guertin and M. Onyszchuk, *Canad. J. Chem.*, 1969, **47**, 1275.

[9] J. J. Harris and B. Rudner, *J. Inorg. Nuclear Chem.*, 1972, **34**, 75.

[10] B. J. Aylett, I. A. Ellis, and C. J. Porritt, *J.C.S. Dalton*, 1972, 1953.

[11] A. P. Hagen and B. W. Callaway, *J. Inorg. Nuclear Chem.*, 1972, **34**, 487.

[12] M. Allan, B. J. Aylett, and I. A. Ellis, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 261.

[13] B. J. Aylett, I. A. Ellis, and C. J. Porritt, *Chem. and Ind.*, 1970, 499.

[14] G. G. Strathdee, Ph.D. Thesis, McGill University, Montreal, 1967; M. Onyszchuk, personal communication.

Other Preparative Reactions.—In the separation of other mixtures of reaction products, aminofluorosilanes were held at −96 °C and passed through −64 °C baths, except in the cases of $SiF_3NPr^n_2$ and $SiF_3NBu^n_3$, which were held at −64 °C and passed through −46 °C or −23 °C respectively. The involatile solid products were completely soluble in water in the case of high-yielding reactions involving $NHPr^n_2$, $NHBu^n_2$, NH_2Bu^s, and NH_2Bu^t; in other cases, silica was precipitated and amine was liberated, indicating that unchanged adduct was present.

Reaction of Tetrafluorogermane and Diethylamine.—When an excess of GeF_4 and diethylamine were allowed to warm from −196 °C in a thick-walled tube, a white solid formed after the amine had melted. A cloudy viscous liquid was present at room temperature; the tube was then opened to the system, GeF_4 was removed and measured, and a colourless solid 1 : 2 adduct remained. The adduct was resealed with an excess of GeF_4 and heated at 130 °C for 5 h; only starting materials were recovered.

TABLE 1

Physical properties of some aminofluorosilanes

Compound	M.p./°C	B.p. (extrap.) / °C	ΔH_{vap} / kcal mol^{-1}	ΔS_{vap} / cal mol^{-1} K^{-1}	d / g cm^{-3}	Ref.
$SiF_3{\cdot}NMe_2$	−108 [a]	17·5 [b]	7·1	24·2	—	*c*
$SiF_3{\cdot}NEt_2$	−98	79	6·77	19·2	1·08/23·5 °C	*d*
$SiF_3{\cdot}NC_5H_{10}$	—	103	8·5	22·6	1·36/24·5 °C	*d*
$SiF_3{\cdot}NHBu^t$	−80	73	8·1	23·2	—	*d*
$(SiF_3)_2NBu^s$	−120	53	6·22	19·1	—	*d*

[a] Lit., −111·7 °C; J. J. Moscony and A. G. MacDiarmid, *Chem. Comm.*, 1965, 307. [b] Lit., 21·0 °C; H. Grosse-Ruyken and, R. Kleesaat, *Z. anorg. Chem.*, 1961, **308**, 122; 21·7 °C; J. J. Moscony and A. G. MacDiarmid, *Chem. Comm.*, 1965, 307. [c] M. Allan, B. J. Aylett, and I. A. Ellis, (*a*) *Inorg. Nuclear Chem. Letters*, 1966, **2**, 261; (*b*) unpublished results. [d] This work.

Analysis.—Reaction of a known amount of aminofluorosilane with a known excess of anhydrous hydrogen chloride gave SiF_3Cl and a substituted ammonium chloride according to reaction (2). The products were separated by fractionation and weighed directly.

$$SiF_3NR_2 + 2HCl \longrightarrow SiF_3Cl + NH_2R_2Cl \qquad (2)$$

Physical Properties of Aminofluorosilanes.—Values of m.p., b.p., ΔH_{vap}, ΔS_{vap}, and density are in Table 1. Other information is given below.

SiF_3NEt_2. Vapour-pressure equation (208—274 K): $\log p/\text{mmHg} = 6{\cdot}900 - 1433/T$. I.r. spectrum (gas): 2990s, 2950m, 2895m, 1460mw, 1385m, 1360sh, 1297w, 1221s, 1172s, 1105w, 1051s, 977vs, 951vs, 851s, 788w, 655w, 495m, and 438s cm^{-1}.

$SiF_3NPr^n_2$. V.p. 5·5 mmHg at 0 °C; m.p. −90 °C. I.r. spectrum (gas): 2980s, 2955s, 2885s, 1460ms, 1365s, 1294w, 1267w, 1202m, 1169s, 1108m, 1063s, 1030s, (?SiF_4); 981vs, 953vs, 908s, 872m, 850m, 785w, 749w, 522w, and 454s cm^{-1}. N.m.r. spectrum: α-CH_2 (triplet), τ 7·17; β-CH_2 (sextet), τ 8·48; γ-CH_3, τ 9·11; $^3J(H_\alpha \cdots H_\beta) = {}^3J(H_\beta \cdots H_\gamma) = 7$ Hz.

$SiF_3NBu^n_2$. V.p. 1·5 mmHg at 0 °C. I.r. spectrum (gas): 2980s, 2945s, 2885s, 2850sh, 1460ms, 1375ms, 1285w, 1170s, 1065s, 1035m (?SiF_4), 980vs, 952vs, 905s, 875m, 840m, 665w, 540w, and 435m cm^{-1}.

$SiF_3NC_5H_{10}$. V.p. equation: $\log p/\text{mmHg} = 7{\cdot}561 - 1777/T$ (250—282 K). I.r. spectrum (gas): 2970s, 2930vs, 2860vs, 2705w, 1455m, 1390s, 1360m, 1341m, 1280w, 1208m, 1174s, 1121m, 1082vs, 1030w (?SiF_4), 979vs, 953vs, 871sh, 868s, 850sh, 822w, 537w, and 430m,br cm^{-1}.

SiF_3NHBu^t. V.p. equation: $\log p/\text{mmHg} = 7{\cdot}947 - 1757/T$ (208—250 K). I.r. spectrum (gas): 3430m, 2980s, 2890s, 1765w, 1480m, 1410sh, 1375m, 1231s, 1060s, 1030m (?SiF_4); 966vs, br, 900s, 797m, 700w, 512m, 485sh, and 429s cm^{-1}.

$(SiF_3)_2NPr^n$. I.r. spectrum (gas): 2985s, 2950sh, 2908m, 1485sh, 1468mw, 1390mw, 1323m, 1180s, 1095m, 1071m, 1032sh (?SiF_4) 1026vs, 984s, 915m, 886w, 853m, 838sh, 820m, 701w, 502w, 440m, and 415m cm^{-1}. N.m.r. spectrum: α-CH_2 (sextet), τ 7·05; β-CH_2, τ 8·50; γ-CH_3, τ 9·07.

$(SiF_3)_2NBu^n$. I.r. spectrum (gas): 2980s, 2945sh, 2910m, 2890m, 1470mw, 1385mw, 1328m, 1245w, sh, 1180s, 1072s, 1044sh, 1033sh (?SiF_4), 1028vs, 985s, 940m, 914m, 854m, 822m, 700w, 672w, 644w, 609w, 503w, 440m, and 415m cm^{-1}.

$(SiF_3)_2NBu^s$. V.p. equation: $\log p/\text{mmHg} = 7{\cdot}014 - 1347/T$ (193—223 K). I.r. spectrum (gas): 2980s, 2940m, 2890m, 1460m, 1405m, 1380m, 1270w, 1178m, 1144s, 1123s, 1040vs, 1030sh (?SiF_4), 1020s, 982vs, 898m, 820s, 641w, 597w, 528w, 490m, 440m, and 400m,br cm^{-1}. N.m.r. spectrum: α-CH_2, τ *ca.* 6·8 (broad), also a complex multiplet τ *ca.* 8·8 (β,γ).

RESULTS AND DISCUSSION

The volatile products obtained from the pyrolysis of tetrafluorosilane and some primary and secondary amines are shown in Table 2. Several points may be noted. (i) Primary amines with a given substituent R react less readily than the corresponding secondary amines NHR_2, particularly when R is not large. (ii) The effect of differing phase is clearly seen in the case of diethylamine: reaction is slow in a solid–gas system, rapid in a liquid–gas system, and negligible in an entirely gaseous system. Since adducts of primary amines studied here were all solid below 200 °C,* while adducts of secondary amines melted below this temperature,† the effect in (i) may be primarily a consequence of the phases present under the conditions used.

(iii) Adducts of secondary amines gave rise to *NN*-dialkyltrifluorosilylamines, SiF_3NR_2. Yields ranged from moderate to excellent as R increased in size from Me to Bu^n, but were poor in the case of derivatives of cyclic secondary amines, $SiF_3N(CH_2)_n$ ($n = 4$ or 5). As the tying back of attached groups in the last class reduces their effective size, all these observations are

---

* The m.p. of $SiF_4{,}2NH_2Ph$ has been recently reported [9] as 137—140 °C. We are unable at present to explain this discrepancy.

† It has been argued on other grounds that the lattice energy of primary amine adducts is greater than that of secondary amine adducts.[10]

consistent with steric assistance (*via* weakening of the adduct).

(iv) Adducts of primary amines gave low to moderate yields of *N*-alkylhexafluorodisilazanes, $(SiF_3)_2NR$, when $R = Pr^n$, Bu^n, and Bu^s (but not Me or Et); the yield increased with the steric demands of R. However, when $R = Bu^t$, a good yield of *N*-t-butyltrifluorosilylamine, SiF_3NHBu^t, was obtained. Some evidence had been found earlier for the derivatives SiF_3NHMe (from amine exchange between SiF_3NMe_2 and methylamine[15]) and SiF_3NHEt (from the pyrolysis of tetrafluorosilane, ethylamine, and sodium tetrahydroborate[16]), but these very unstable compounds could not be fully characterised. The corresponding trichloro-compounds $SiCl_3$-NHR have also been reported when R = Me,[17] Et,[17] and Bu^t.[18,19]

It was also found that 1 : 1 adducts with the diamines $NHR{\cdot}[CH_2]_2{\cdot}NHR$ (R = Me or Et) were unchanged after being heated at 190 °C for 7 h. The corresponding adduct with *NN'*-dimethylpropylenediamine, however, reacted under similar conditions to give as chief product a yellow resinous solid. This melted at 45 °C to form a red-brown liquid, and was rapidly hydrolysed in air, giving the parent amine and silica. The resinous solid appeared similar to that resulting from the spontaneous oligomerisation of the cyclic compound (I),[20] which apparently undergoes ring-opening in a similar fashion to (II)[21] and (III).[22] The solid reaction products comprised alkylammonium hexafluorosilicate (>80% with $NHEt_2$, $NHPr^i_2$, and NH_2Bu^t) and some fluoride. There was no evidence for pentafluorosilicates.[9,23,24] Formation of $(SiF_3)_2O$ and etching of the reaction vessel indicated that tetrafluorosilane and hydrogen fluoride had reacted to some extent with the glass.

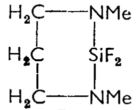
TABLE 2

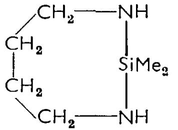
Pyrolysis of adducts of tetrafluorosilane

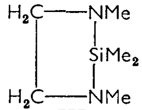
Adduct pyrolysed[a]	Reaction temp. °C	Reaction time h	Aminofluorosilane product	Yield (%)
$SiF_4,2NH_2Me$ (g)	220	2·5	—	0[b]
$SiF_4,2NH_2Et$ (s)	190—200	10	—	0[b]
$SiF_4,2NH_2Pr^n$ (s)	200	8·2	$(SiF_3)_2NPr^n$	3[c]
$SiF_4,2NH_2Pr^n$ (g)	190—200	10	—	0
$SiF_4,2NH_2Bu^n$ (s)	190—200	8·2	$(SiF_3)_2NBu^n$	6[c]
$SiF_4,2NH_2Bu^s$ (s)	190—200	8	$(SiF_3)_2NBu^s$	30[c]
$SiF_4,2NH_2Bu^s$ (l)	220—240	24	$(SiF_3)_2NBu^s$	75[c]
$SiF_4,2NH_2Bu^t$ (s)	190—200	8	SiF_3NHBu^t[g]	60[d]
$SiF_4,2NH_2Bu^t$ (l)	220—240	24	SiF_3NHBu^t[g]	86[d]
$SiF_4,2NH_2Ph$ (s)	180—200	12	—	0
$SiF_4,2NHMe_2$ (l)	175	1·5	SiF_3NMe_2	52[e,f]
$SiF_4,2NHEt_2$ (s)	40	21·5	SiF_3NEt_2[h]	10[e]
$SiF_4,2NHEt_2$ (l)	110—120	4·5	SiF_3NEt_2[h]	100[e,f]
$SiF_4,2NHEt_2$ (g)	175—190	7·5	—	0
$SiF_4,2NHPr^n_2$ (s)	100	3	$SiF_3NPr^n_2$[i]	100[e]
$SiF_4,2NHBu^n_2$ (s)	120	3·5	$SiF_3NBu^n_2$	100[e]
$SiF_4,2NHC_4H_8$ (l)	145	6	$SiF_3NC_4H_8$	1[e]
$SiF_4,2NHC_5H_{10}$ (s)	120	8	$SiF_3NC_5H_{10}$	Trace
$SiF_4,2NHC_5H_{10}$ (l)	175—185	3·8	$SiF_3NC_5H_{10}$[j]	16[e]
$SiF_4,NHMe{\cdot}[CH_2]_3{\cdot}NHMe$ (l)	150—160	3·5	See text	—

[a] Excess of SiF_4 present in all cases (*ca.* 5-fold). [b] I.r. spectrum of adduct unchanged after heating. [c] Based on equations (7) and (8). [d] Based on equation (7). [e] Based on equation (3). [f] *Ca.* 2 moles of SiF_4 consumed per mole of product. [g] Found: SiF_3, 54·2; NBu^t, 44·9. $SiF_3{\cdot}NHBu^t$ requires SiF_3, 54·1; NBu^t, 45·2%. [h] Found: SiF_3, 54·4; NEt_2, 45·3. $SiF_3{\cdot}NEt_2$ requires SiF_3, 54·1; NEt_2, 45·9%. [i] Found: SiF_3, 46·0; NPr^n_2, 53·7. $SiF_3NPr^n_2$ requires SiF_3, 46·0; NPr^n_2, 54·0%. [j] Found: SiF_3, 49·5; NC_5H_{10}, 49·4. $SiF_3{\cdot}NC_5H_{10}$ requires SiF_3, 50·3; NC_5H_{10}, 49·7%.

Several studies[23,25,26] have shown that organotrifluorosilanes and amines react together to give organofluorosilicates such as $(NH_2Pr^n_2)^+SiF_4Ph^-$ or $(NH_3Et)^+_2$-SiF_5Et^{2-}. In each case, attention was concentrated on the silicate product, and concomitant aminofluorosilanes were not definitely characterised, although evidence was obtained for their presence.[25] There seems a clear parallel with the present study, in which reactions however go more nearly to completion.


(I)


(II)


(III)

The facts above suggest that reactions with secondary amines can be represented by equilibria (3) and (4). The

$$SiF_4,2NHR_2 \rightleftharpoons SiF_3{\cdot}NR_2 + NH_2R_2F \quad (3)$$

$$2NH_2R_2F + SiF_4 \rightleftharpoons (NH_2R_2)_2SiF_6 \quad (4)$$

---

[15] I. A. Ellis, Ph.D. Thesis, University of Aberdeen, 1962.

[16] M. Allan, Ph.D. Thesis, University of London, 1966.

[17] J. E. Drake and N. P. C. Westwood, *J. Chem. Soc. (C)*, 1971, 3617.

[18] H. Breederveld and H. I. Waterman, *Research*, 1953, **6**, 43.

[19] U.S.P. 2,807,635/1957.

[20] B. J. Aylett, I. A. Ellis, and C. J. Porritt, unpublished results.

[21] F. A. Henglein and K. Lienhard, *Makromol. Chem.*, 1959, **32**, 218.

[22] C. H. Yoder and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1966, **88**, 4831.

[23] F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, 1968, **7**, 155.

[24] H. C. Clark, K. R. Dixon, and J. G. Nicolson, *Inorg. Chem.*, 1969, **8**, 450.

[25] L. Tansjö, *Acta Chem. Scand.*, 1964, **18**, 456, 465.

[26] N. Ishikawa and K. Kuroda, *J. Chem. Soc. Japan*, 1968, **89**, 421.

reversible nature of (3) was shown by experiments with tetrafluorosilane and diethylamine or piperidine. In both cases, the adduct was pyrolysed (in the liquid phase) for 15 min, yielding the appropriate trifluorosilylamine. The products were then sealed together at room temperature for several days; all silylamine was consumed and the original adduct remained.

Other significant equilibria are doubtless (5)—(7).

$$\mathrm{SiF_4,2NHR_2 \rightleftharpoons SiF_4 + 2NHR_2} \quad (5)$$

$$\mathrm{NH_2R_2F \rightleftharpoons NHR_2 + HF} \quad (6)$$

$$\mathrm{SiF_3{\cdot}NR_2 + HF \rightleftharpoons SiF_4 + NHR_2} \quad (7)$$

Equilibrium (7) is thought to lie well to the right,[27] so efficient removal of HF is essential. The large excess of tetrafluorosilane used in these experiments, primarily in order to lessen disproportionation of products, no doubt helped to lower the m.p.s of the adducts and to shift equilibria (5) and (7).

The course of reactions with primary amines is less easy to establish. The simplest interpretation is a stepwise replacement of hydrogen on nitrogen by SiF_3 groups [equations (8) and (9)]. This is supported by the

$$\mathrm{SiF_4,2NH_2R \longrightarrow SiF_3{\cdot}NHR + NH_3RF} \quad (8)$$

$$\mathrm{SiF_4 + 2SiF_3{\cdot}NHR + SiF_4,2NH_2R \longrightarrow 2(SiF_3)_2NR + 2NH_3RF} \quad (9)$$

formation of SiF_3NHBu^t when $R = Bu^t$; presumably steric factors inhibit further substitution in this case. With s-butylamine, not only was the disilazane $(SiF_3)_2$-NBu^s produced, but also an oligomeric oil similar to that obtained by disproportionation[28] of $(SiF_3)_2NBu^s$ alone [equation (10)]. It seems likely, although not fully

$$\mathrm{(SiF_3)_2NBu^s \longrightarrow SiF_4 + \frac{1}{n}(SiF_2NBu^s)_n} \quad (10)$$

$$\mathrm{SiF_3NHR \longrightarrow \frac{1}{n}(SiF_2NR)_n + HF} \quad (11)$$

established, that reaction (10) is reversible, and this suggests an alternative route to hexafluorodisilazanes *via* loss of hydrogen fluoride from SiF_3NHR [reaction (11)] and addition of tetrafluorosilane to $(SiF_2NR)_n$. However, the analogous loss of hydrogen from SiH_3NHR compounds has been shown to make only a minor contribution to their decomposition,[1,29] and it has not yet proved possible to elucidate the complex decomposition of the *N*-monoalkyltrifluorosilylamines and demonstrate the feasibility of the first step.

In an attempt to prepare volatile GeF_3–N compounds, diethylamine and an excess of tetrafluorogermane were heated together under similar conditions to those described for tetrafluorosilane. Apart from adduct formation, there was no reaction. This difference can probably be attributed to the generally greater strength of adducts of GeF_4 than of SiF_4, as measured by their enthalpies of formation.[30]

I.r Spectra.—There is little published information on trifluorosilyl compounds, and any assignments of such complex molecules as those discussed here must be tentative. Strong bands in the region 800—1000 cm^{-1} arise from Si–F stretching vibrations;[31] Si–N stretching in substituted aminosilanes, $R^1{}_3Si{\cdot}NR^2R^3$, gives rise to absorptions that, although sometimes found at the lower end of this region,* are often of low intensity.[32-34]

On the other hand, the asymmetric SiNSi stretching mode in disilazanes[32,35,36] is usually associated with a strong band between 900 and 1000 cm^{-1}. Skeletal modes of alkyl groups give rise only to weak bands in this region and can probably be disregarded.

It thus seems likely that absorption near 850 and 960 cm^{-1} in $SiF_3{\cdot}NR_2$ derivatives can chiefly be associated with symmetric and asymmetric ν(Si–F) modes respectively. In SiF_4 (T_d), these occur at 801 (A_1) and 1032 (T_2) cm^{-1}, while in SiF_3I (C_{3v}) they are closer[37] at 857 (A_1) and 996 (E) cm^{-1}. Further lowering of symmetry in $SiF_3{\cdot}NR_2$ might arise by restriction of rotation about the Si–N bond or by loss of planarity at nitrogen (or both these effects); it is expected to remove the degeneracy of the E mode and produce B_1 and B_2 components.

In accordance with these ideas, $SiF_3{\cdot}NMe_2$ exhibits a strong band at 879 cm^{-1} (A_1), and a pair of very strong bands at 958 and 980 cm^{-1} which we assign to B_1 and B_2 ν(Si–F).† Since $SiF_3{\cdot}NMe_2$ is known to be planar about nitrogen in the gas phase,[38] it seems likely that some rotational restriction exists in the Si–N bond. Bands occur in very similar positions in $SiF_3{\cdot}NEt_2$ (851, 951, and 970 cm^{-1}) and $SiF_3{\cdot}NC_5H_{10}$ (868, 953, and 979 cm^{-1}), and the suggested B_1—B_2 separation is essentially constant. Additional bands appear with $SiF_3{\cdot}NPr^n{}_3$ and $SiF_3{\cdot}NBu^n{}_2$, and we suggest that these may be associated with loss of planarity at nitrogen; models indicate that steric repulsions can thus be minimised.

This kind of analysis is more difficult with disilazanes, $(SiF_3)_2NR$, but it is suggested that the band near 820 cm^{-1}

---

* Literature assignments range from 480 to 900 cm^{-1}; mixing appears to be extensive.

† Very similar frequencies are found in $SiF_3{\cdot}N(CD_3)_2$: B. J. Aylett, I. A. Ellis, and D. C. McKean, unpublished results.

[27] U. Wannagat, H. Bürger, and F. Höfler, *Monatsh.*, 1968, **99**, 1198.

[28] M. Allan, B. J. Aylett, and I. A. Ellis, *Chem. and Ind.*, 1966, 1417.

[29] B. J. Aylett and M. J. Hakim, *J. Chem. Soc.* (*A*), 1969, 800.

[30] J. E. Fergusson, D. K. Grant, R. H. Hickford, and C. J. Wilkins, *J. Chem. Soc.*, 1959, 99; J. M. Miller and M. Onyszchuk, *J. Chem. Soc.* (*A*), 1967, 1132; G. Vandrish and M. Onyszchuk, *ibid.*, 1970, 3327.

[31] A. L. Smith, *Spectrochim. Acta*, 1960, **16**, 87.

[32] L. W. Breed, R. L. Elliott, and J. C. Wiley, *J. Organometallic Chem.*, 1971, **31**, 179.

[33] H. Bürger and W. Sawodny, *Spectrochim. Acta*, 1967, **23**, *A*, 2827; H. Bürger and U. Goetze, *Monatsh.*, 1968, **99**, 155; E. W. Randall and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1968, **90**, 3167.

[34] M. J. Buttler and D. C. McKean, *Spectrochim. Acta*, 1965, **21**, 485.

[35] M. J. Buttler, D. C. McKean, R. Taylor, and L. A. Woodward, *Spectrochim. Acta*, 1965, **21**, 1379.

[36] H. Bürger, *Monatsh.*, 1966, **97**, 869; U. Wannagat, F. Höfler, and H. Bürger, *ibid.*, 1968, **99**, 1186.

[37] B. J. Aylett and J. R. Richmond, unpublished data.

[38] W. Airey, C. Glidewell, A. G. Robiette, G. M. Sheldrick, and J. M. Freeman, *J. Mol. Structure*, 1971, **8**, 423.

be assigned to ν_s(Si–F) and bands usually near 915, 985, and 1020 cm^{-1} be assigned to coupled ν_{as}(Si–F) and ν_{as}(SiNSi).*

In the region 1000—1300 cm^{-1}, strong bands are expected for $SiF_3{\cdot}NR_2$ derivatives arising from mixed CNC stretching and alkyl rocking vibrations.† Specifically the strong bands appearing at 1051, 1172, and 1221 cm^{-1} for $SiF_3{\cdot}NEt_2$ are thought to derive thus; they correspond closely to bands reported earlier[27] for $SiF_2(NEt_2)_2$.

N.m.r. Spectra.—The parameters given here for $SiF_3{\cdot}NPr^n_2$ and $(SiF_3)_2NR$ (R = Pr^n, Bu^s) complement and support those already reported[39] for $SiF_3{\cdot}NR_2$ (R = Me, Et; $R_2 = C_5H_{10}$), SiF_3NHBu^t, and $(SiF_3)_2NMe$. It is interesting to compare the chemical-shift differences between some of these fluorosilyl derivatives and the corresponding amines.‡ The effect of the SiF_3 group is only weakly evidenced beyond the α-carbon atoms, and disilazanes are generally rather more effective than monosilylamines.

When the proton spectrum of SiF_3NEt_2 alone (rather than in dilute solution) was recorded, each member of the CH_2 quartet split into eight components 0·7 Hz apart, while no comparable splitting was observed for the CH_3 triplet. It seems possible that intermolecular N–Si interactions may reduce the SiNC bond angles:[40] consequent twisting and/or hindrance to free rotation then destroys the equivalence of methylene protons.[41]

Mass Spectra.—The low-resolution data ‡ show that, for SiF_3NEt_2, cleavage of Me and Et groups is a major decomposition route. The combined α–β loss[42] to give $SiF_3{\cdot}NCH_2^+$ (113) produces the second most intense peak, while other significant peaks correspond to $SiF_3{\cdot}N(Et)CH_2^+$ (142), $SiF_3{\cdot}NEt^+$ (128), and $SiF_3{\cdot}NC^+$ (111) (but not SiF_3N^+). Direct cleavage of the Si–N bond may give rise to the abundant species SiF_3^+ (85), while the many ions observed at and below *m*/*e* 58 result from decomposition of the other fragment. Direct loss of fluorine from the parent is not very important: $SiF_2{\cdot}NEt_2^+$ (138) is observed, but not $SiF{\cdot}MEt_2^+$. However, ions corresponding to $SiF_2{\cdot}NEt^+$ (109) and $SiF_2{\cdot}NCH_2^+$ (94) are present, and may be compared with an ion observed previously[29] in the mass spectrum of $SiH_3{\cdot}NHPh$ and provisionally formulated as $SiH_2{=}NPh^+$.

In the case of $SiF_3{\cdot}NC_5H_{10}$, SiF_3^+ again provides the most intense peak above *m*/*e* 30. A range of ions corresponding approximately to loss of one to four CH_2 groups from the molecular ion are observed, especially $SiF_3{\cdot}NC_2H_5^+$ (128) and $SiF_3{\cdot}NCH_n^+$ (n = 0—3; *m*/*e* 111—114). Correspondingly a large number of ions $C_nH_x^+$ or $C_{n-1}NH_{x-2}$ are observed, where n = 2—5 and $x \geqslant 2$.

We thank the Ministry of Technology for support, Dr. M. N. Lilly for assistance with mass spectra, and Drs. J. J. Harris, D. C. McKean, and G. Sheldrick for discussion and correspondence.

[2/1192 *Received*, 25*th May*, 1972]

---

* Corresponding bands in $(SiF_3)_2NMe$ are centred at 822s, 911s, 997vs, and 1016vs cm^{-1}; B. J. Aylett and I. A. Ellis, unpublished observations.

† For a discussion of this effect in SiH_3NMe_2, see ref. 34.

‡ A Table of such comparisons and mass spectral data for SiF_3NEt_2 and $SiF_3NC_5H_{10}$ have been deposited in Supplementary Publication No. SUP 20556 (3 pp.). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[39] W. Airey, G. M. Sheldrick, B. J. Aylett, and I. A. Ellis, *Spectrochim. Acta*, 1971, **27**, *A*, 1505.

[40] B. J. Aylett, *Adv. Inorg. Chem. Radiochem.*, 1968, **11**, 249.

[41] M. van Gorkom and G. E. Hall, *Quart. Rev.*, 1968, **22**, 14.

[42] J. H. Beynon, ' Mass Spectrometry and Its Applications to Organic Chemistry,' Elsevier, Amsterdam, 1960.