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# Polyfluoroalkyl Compounds of Silicon. Part IX.<sup>1</sup> Silanes containing the Bis(trifluoromethyl)amino-group

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The silanes  $(CF_3)_2N \cdot CH_2 \cdot CH_2 \cdot SiX_3$  (X<sub>3</sub> = Me<sub>3</sub>, Cl<sub>3</sub>, or MeCl<sub>2</sub>) have been prepared by free-radical addition of the corresponding silanes to NN-bis(trifluoromethyl)vinylamine. The polymer [(CF<sub>3</sub>)<sub>2</sub>N·CH<sub>2</sub>CH<sub>2</sub>·Si·O<sub>1-5</sub>], and cyclic and linear siloxane polymers  $[(CF_3)_2N \cdot CH_2 \cdot CH_2 \cdot SiMe \cdot O]_n$  have been prepared and their thermal and hydrolytic stabilities compared with those of the model compounds (CF<sub>3</sub>)<sub>2</sub>N·CH<sub>2</sub>·SiMe<sub>3</sub> and (CF<sub>3</sub>)<sub>2</sub>N·CH<sub>2</sub>·CH<sub>2</sub>·SiF<sub>3</sub>. NN-Bis(trifluoromethyl)-2-bromoethane did not react with magnesium or lithium to give the corresponding metal derivatives. The reaction between mercury(II) bis(trifluoromethyl) amide and iodomethyl trimethyl silane gave perfluoro-(2-azapropene), its dimer perfluoro-(4-methyl-2,4-diazapent-2-ene) and, unexpectedly, fluoromethyltrimethylsilane, and ethylfluorodimethylsilane.

IN a continuation of a study of potentially thermallystable organosiloxane polymers,<sup>2</sup> compounds containing the NN-bis(trifluoromethyl)amino-group in the side chain have been prepared and investigated. The preparation and properties of the vinylamine starting materials have been reported recently.<sup>3</sup>

By analogy with fluoroalkyl-<sup>2</sup> and cyanoalkylsilanes,<sup>4</sup> it would be anticipated that satisfactory thermal and hydrolytic stability combined with solventresistance could be obtained in siloxane polymers with other electron-withdrawing substituents at the 2-position of an alkyl side-chain. In the present work organo-

<sup>1</sup> Part VIII, D. Cooper, R. N. Haszeldine, and M. J. Newlands, J. Chem. Soc. (A), 1967, 2098.
 <sup>2</sup> T. N. Bell, R. N. Haszeldine, M. J. Newlands, and J. B.

Plumb, J. Chem. Soc., 1965, 2107, and references cited therein.

silanes of formula  $(CF_3)_2$ N·CH<sub>2</sub>·CH<sub>2</sub>·SiR<sub>3</sub> [(IA; R<sub>3</sub> = Cl<sub>3</sub>); (IB;  $R_3 = MeCl_2$ ); (IC;  $R_3 = Me_3$ )] have therefore been prepared, and were obtained in almost quantitative yield by the rapid photochemical addition of the corresponding silane to NN-bis(trifluoromethyl)vinylamine:

$$\begin{array}{c} \text{HSiR}_{3} \xrightarrow{\text{u.v.}} \text{H} \cdot + \cdot \text{SiR}_{3} \\ \cdot \text{SiR}_{3} + (\text{CF}_{3})_{2} \text{N} \cdot \text{CH} \cdot \text{CH}_{2} \xrightarrow{} (\text{CF}_{3})_{2} \text{N} \cdot \mathring{\text{CH}} \cdot \text{CH}_{2} \cdot \text{SiR}_{3} \\ (\text{CF}_{3})_{2} \text{N} \cdot \mathring{\text{CH}} \cdot \text{CH}_{2} \cdot \text{SiR}_{3} + \text{HSiR}_{3} \xrightarrow{} \\ (\text{CF}_{3})_{2} \text{N} \cdot \text{CH}_{2} \cdot \text{CH}_{2} \cdot \text{SiR}_{3} + \cdot \text{SiR}_{3} \end{array}$$

<sup>3</sup> E. S. Alexander, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, J. Chem. Soc. (C), 1968, 796. <sup>4</sup> V. V. Korshak, 'Uspekhi v Oblasti Sinteza Elemento-

Organicheshkikh Polimerov,' Nauka, Moscow, 1966, pp. 40, 41.

Telomer formation, a problem in related studies,<sup>1,2</sup> was not observed.

The silane, (CF<sub>3</sub>)<sub>2</sub>N·CH<sub>2</sub>·CH<sub>2</sub>·SiF<sub>3</sub> (ID), was prepared in 52% yield by reaction of the trichlorosilane (IA) with antimony trifluoride; the other products, perfluoro-(2-azapropene) (43%), ethylene (47%), and silicon tetrafluoride (38%), are best explained on the basis of thermal decomposition of the silane possibly assisted by fluoride transfer from  $CF_3$  to antimony.

The silanes (IA) and (IB) readily hydrolysed in wet ether, but complete condensation of the silanols proved difficult. Electron-withdrawing groups in the alkyl side-chain have been reported 5 to hinder such condensations. However, the so-called 'non-equilibrating catalyst' of Merker et al.6 proved the most satisfactory method for giving a product free from Si-OH bonds (i.r.) from the silane (IA), and the white solid product sublimed in vacuo and had a molecular weight (1425) corresponding to a hexamer. These observations suggest, but do not prove, that the product has the prismatic structure (II), analogous to those reported previously.<sup>7</sup> A *liquid* polysilsesquioxane was obtained



from the silane (IA), by its treatment in toluene solution with aqueous hydrochloric acid with a final heat treatment of the crude polymer at 200°.

The hydrolytic stability of the polysilsesquioxane became apparent during attempts to achieve complete condensation by treatment with acids and bases at temperatures up to 160°.

The polysiloxane obtained by hydrolysis of silane (IB) was a mobile liquid which contained (i.r.) cyclic trimer, higher cyclic Si-O-Si compounds, and linear polymer.

Pyrolyses.—The results obtained from the static pyrolyses of the model silanes (IC) and (ID) and of the polymers  $[(CF_3)_2 N \cdot CH_2 \cdot CH_2 \cdot SiMeO]_n$ (III) and  $[(CF_3)_2 N \cdot CH_2 \cdot CH_2 \cdot Si \cdot O_{1 \cdot 5}]_n$  (IV) are summarised in Tables 1 and 2, respectively.

A series of intramolecular eliminations is postulated to account for the observed products from the silanes (IC) and (ID), by analogy with reported kinetic studies on the pyrolyses of fluoroalkylsilicon compounds.<sup>8</sup> In both cases perfluoro-(2-azapropene), ethylene, and silicon

Sci., 1964, 2, A, 31.

tetrafluoride or fluorotrimethylsilane, are considered to arise via a six-centred transition state, while the vinyl compounds (V) and (VI) are probably formed via a fourcentred transition state.

TABLE 1 Pyrolyses of the 2-[NN-bis(trifluoromethyl)amino]ethylsubstituted silanes

	(CF	°₃)₂N•CH CH₂•SiF	(CF <sub>3</sub> ) <sub>2</sub> N·CH <sub>2</sub> ·- CH <sub>2</sub> ·SiMe <sub>3</sub>		
Temp. (°)	290	350	390	360	380
Recovered reactant (%)	97	38	21	85	15
CE \ N.CH'CH				46	0
$Me_3SiF$				44	34 34
CE N'CE			*	$\uparrow$	
$CH_2$ :CH·SiF <sub>3</sub>		. <b>†</b> _	78		
CF₃•NCO	个 80	$\downarrow^{140}$	$\downarrow$	47†	1
SiF4	¥	67	73		1.55
сн сн		02	78		199
CHF.		25	28	¥	
HC:CH		20	Trace		¥
Product recovery	100	97	83	96	81
Charring	None	Slight	Exten- sive	Slight	Exten sive

\* Quoted as mmoles/100 mmoles of reactant decomposed for 6 hr. pyrolyses. † CH2:CH-SiF3 not observed.

## TABLE 2

Pyrolyses of 2-[NN-bis(trifluoromethyl)amino]ethylsubstituted siloxane polymers

	[(CF <sub>3</sub> )	$[(CF_3)_2N - CH_2 - C$			
$T_{1}$	$Si^{\bullet}O_{1^{\bullet}5}$			$SumeO_{n}^{\dagger}$	
Temp ()	300	400	435	380	420
Lime (nr.)	9	6	6	9	6
Recovered reactant (%)	83	69	0	82	77
Products ‡					
(CF.),N·CH.·CH.·SiF.	32	31			
CF.J.N.CH.CH.SiMeF					65
CH. CH.SiF.	2	Trace	17	٨	Ă
CE.N.CE.		11400	11	T	T
CF NCO				200 5	10#
	1	01	10	200 8	105
CH <sub>2</sub> .CH <sub>2</sub>	<u> </u>	31	19		
CO2	156	165	162	$\downarrow$	$\downarrow$
SiF	$\checkmark$	3	88	٠	•
CHF,	•	4	2		
HC <b>:</b> CH		Trace	10		
Product recovery (%)	97	83	60	99	99
Charring	Slight	Exten-	Verv	Slight	Slight
0	0	sive e	xtensive		80

\* Polymer prepared by method 2. † A mixture of trimer, higher cyclic, and linear polymer. ‡ Quoted as mmoles/100 mmoles of reactant decomposed. § Small amount of unidentified material also present.

Reaction of perfluoro-(2-azapropene) with the surface of the reaction tube gives trifluoromethyl isocyanate.9

The absence of the amine (VII) from the products of the pyrolyses of silane (ID) probably arises because of

<sup>7</sup> M. M. Sprung and F. O. Guenther, J. Amer. Chem. Soc., 1955, 77, 3990, 3996; A. Barry, W. Daudt, T. Domicone, and T. Gilkey, J. Amer. Chem. Soc., 1955, 77, 4248.
<sup>8</sup> R. N. Haszeldine, P. J. Robinson, and R. F. Simmons, J. Chem. Soc., 1964, 1890; G. Fishwick, R. N. Haszeldine, P. J. Robinson, and R. F. Simmons, Chem. Comm., 1965, 382.
<sup>9</sup> D. A. Barr and R. N. Haszeldine, J. Chem. Soc., 1955, 1881.

<sup>&</sup>lt;sup>5</sup> O. W. Steward and O. R. Pierce, J. Amer. Chem. Soc., 1959, **81**, 1983; J. Org. Chem., 1961, **26**, 2943; see also U.S.P., 2,915,544 (Chem. Abs., 1960, **54**, 7561). <sup>6</sup> R. L. Merker, M. J. Scott, and G. G. Haberland, J. Polymer

$$\begin{array}{c} H_{2} \\ CF_{3} \cdot N \xrightarrow{C} CH_{2} \\ F_{2}C \xrightarrow{F} Si \xrightarrow{L} CF_{3} \cdot N:CF_{2} + CH_{2}:CH_{2} + FSi \xrightarrow{L} CF_{3} \cdot N:CF_{2} + CH_{2}:CH_{2} + FSi \xrightarrow{L} CH_{2} + FSi \xrightarrow{L} CH_{2}:CH_{2} + FSi \xrightarrow{L} CH_{2} + FSi \xrightarrow{L$$

the known equilibrium of the amine with the azapropene and hydrogen fluoride; <sup>10</sup> further reaction of the hydrogen fluoride with the reaction vessel displaces the equilibrium to the right.

$$(CF_3)_2 NH \longrightarrow CF_3 \cdot N: CF_2 + HF \xrightarrow{SiO_2} SiF_4 + H_2O$$

The trifluoromethane observed at the higher temperatures indicates that either an elimination reaction of the type:

$$\begin{array}{c} CF_{3} \cdot N & \longrightarrow \\ F_{3}C & H & \longrightarrow \\ \end{array} CHF_{3} + CF_{3} \cdot N : CH \cdot CH_{2} \cdot Si \in \end{array}$$

is involved, or C-N fission is occurring to give trifluoromethyl radicals which then abstract hydrogen.

The pyrolyses of the polymers (III) and (IV) indicated that they had similar stability *in vacuo* to the **3,3,3**trifluoropropyl analogues, and this together with their resistance to acid and base suggests that they may merit technological investigation. The most significant feature of the pyrolyses was the formation of the fluorosilanes  $(CF_3)_2N\cdot CH_2\cdot CH_2\cdot SiMeF_2$  and (ID) from the polysiloxane (III) and polysilsesquioxane (IV), respectively. These and other products shown in Table 2 possibly arise as follows:

$$\begin{array}{c} H_2 \\ CF_3 \cdot N \\ I \\ F_2 C \\ F$$

$$4 [FSiO_{1:5}]_n \longrightarrow SiF_4 + 3SiO_2$$
  
CF<sub>3</sub>·N:CF<sub>2</sub> + H<sub>2</sub>O  $\longrightarrow$  CF<sub>3</sub>·NCO + 2HF  $\xrightarrow{SiO_2}$  SiF<sub>4</sub> + H<sub>2</sub>O  
CF<sub>3</sub>·NCO  $\xrightarrow{H_2O}$  CO<sub>2</sub> + NH<sub>4</sub>F + HF  $\xrightarrow{SiO_2}$  etc.

$$(CF_3)_2 N \cdot CH_2 \cdot CH_2 \cdot SiR \xrightarrow{O-} HF (CF_3)_2 N \cdot CH_2 \cdot CH_2 \cdot SiRF_2$$

$$O- (R = Me)$$
or (CF\_3)\_2 N · CH\_2 · CH\_2 · SiF\_3
$$(R = -O-)$$

<sup>10</sup> J. A. Young, R. D. Dresdner, and S. N. Tsoukalas, *J. Amer. Chem. Soc.*, 1958, **80**, 3604.

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The small amount of water required to initiate the sequence could arise from the condensation of small amounts of silanols present in the polymers.

Other Routes to  $(CF_3)_2N\cdot CH_2\cdot CH_2\cdot Si \leq Compounds.$ Substituted organosilanes may also be prepared by direct synthesis or via organometallic synthesis. Attempts to prepare organometallic compounds of the type  $(CF_3)_2$ - $N\cdot CH_2\cdot CH_2M$  (M = Li or MgX) from the corresponding bromo-compound have proved unsuccessful. With diethyl ether as solvent no reaction occurred even under reflux, whereas with tetrahydrofuran as solvent a vigorous reaction occurred to give ethylene, silicon tetrafluoride, and trifluoromethyl isocyanate, possibly via initial decomposition of the carbanion:

$$\overrightarrow{\mathsf{CH}_2} - \mathsf{CH}_2 - \mathsf{N}(\mathsf{CF}_3) - \mathsf{CF}_2 - \overrightarrow{\mathsf{F}} \longrightarrow \mathsf{CF}_3 \cdot \mathsf{N} \cdot \mathsf{CF}_2 + \mathsf{CH}_2 \cdot \mathsf{CH}_2 + \overrightarrow{\mathsf{F}}$$

A further possible route to the required silanes involves addition of NN-bis(trifluoromethyl)amine to a vinylsilane under basic conditions. A comparable reaction has been reported with ethylene imine,<sup>11</sup> but in

$$R_{3}Si \cdot CH:CH_{2} + CH_{2} \cdot CH_{2} \cdot N \xrightarrow{NH_{2}^{-}} R_{3}Si \cdot CH_{2} \cdot CH_{2} \cdot N \cdot CH_{2} \cdot CH_{2}$$

the present case no reaction occurred either in the silane as solvent or in liquid ammonia.

Attempted Preparation of [NN-Bis(trifluoromethyl)amino]methyltrimethylsilane.—The reaction of mercury(II) bis(trifluoromethyl)amide with iodomethyltrimethylsilane was expected to occur according to the equation:

$$[(CF_3)_2N]_2Hg + 2ICH_2 \cdot SiMe_3$$

 $2(CF_3)_2N\cdot CH_2\cdot SiMe_3 + HgI_2$ 

and this would provide a compound in which the electron-attracting  $(CF_3)_2N$  group is on the carbon  $\alpha$  to silicon for tests on thermal and chemical stability. No reaction was observed at room temperature, and although at 60° precipitation of mercury(II) iodide was observed, fractionation gave only perfluoro-(2-azapropene) (27%), perfluoro-(4-methyl-2,4-diazapent-2-ene) (21%), trifluoromethyl isocyanate (trace), and higher-boiling material. Attempted fractionation of the higherboiling material was accompanied by further precipitation of mercury(II) iodide (total yield 94%) and the isolation of the unexpected products fluoromethyltrimethylsilane (VIII) (58%), and dimethylethylfluorosilane (IX) (14%), together with further quantities of perfluoro(2-azapropene) and its dimer.

The silane (VIII) when heated alone or in the presence of mercury(II) iodide at 210° was recovered unchanged, which indicates that silane (IX) is unlikely to have been formed by rearrangement of silane (VIII) under the reaction conditions employed. These silanes are thought to arise by competitive nucleophilic attack by fluorine

<sup>11</sup> N. S. Nametkin, Doklady Akad. Nauk S.S.S.R., 1964, **158**, 898.

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on silicon or carbon. The suggested mechanism is analogous to the well-known rearrangements of chloromethylsilanes under the influence of such Lewis acids as aluminium chloride.<sup>12</sup>

The remaining product,  $CF_3 \cdot N \cdot CF \cdot N (CF_3)_2$ , is a dimer of perfluoro-(2-azapropene) from which it is produced by fluoride-ion catalysis.<sup>13</sup>

#### EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system to avoid contamination with air or moisture. Photochemical reactions were carried out at a distance of *ca*. 20 cm. from a Hanovia S.500 lamp. Products were separated either by repeated fractional distillation *in vacuo* or by preparative-scale g.l.c. (Perkin-Elmer 116, 154B, or 451 Fraktometers). The identities of products were established by molecular-weight determination (Regnault's method), elemental analysis, i.r. spectroscopy (Perkin-Elmer 21 instrument with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 spectrometer operating at 56.46 MHz for <sup>19</sup>F and 60.0 MHz for <sup>1</sup>H), mass spectrometry (A.E.I. MS/2H instrument with a resolution of 1 in 700), and g.l.c.

NN-Bis(trifluoromethyl)vinylamine was prepared as described previously.<sup>3</sup> Iodomethyltrimethylsilane was prepared in 67% yield by the reaction of sodium iodide with chloromethyltrimethylsilane in acetone as solvent,<sup>14</sup> and vinyltrimethylsilane was prepared in 72% yield by the reaction of methyl magnesium iodide in di-n-butyl ether with vinyltrichlorosilane.<sup>15</sup>

The Reaction of Silanes with NN-Bis(trifluoromethyl)vinylamine.—(a) Trimethylsilane. A mixture of the olefin (1.87 g., 10.45 mmoles) and the silane (1.44 g., 20.0 mmoles), sealed in a silica ampoule (300 ml.) and irradiated (48 hr.), gave unchanged silane (0.80 g., 10.3 mmoles, 51.5%recovered) (Found: M, 78. Calc. for  $C_3H_{10}Si: M$ , 74), shown by i.r. spectroscopy to be contaminated with a small amount of unchanged vinylamine, and 2-[NN-bis(trifluoromethyl)amino]ethyltrimethylsilane (2.50 g., 9.9 mmoles, 95%)

<sup>12</sup> M. Kumada and K. Tamao, Adv. Organometallic Chem. 1968, **6**, 72; V. Bažant, V. Chvalovský, and J. Rathousky, 'Organosilicon Compounds,' Czeckoslovak Academy of Sciences Press, Prague, 1965, vol. 1, (a) p. 326; (b) p. 434. (Found: C, 33.0; H, 5.0; F, 44.9; N, 5.6%; M, 252.  $C_7H_{13}F_6NSi$  requires C, 33.2; H, 5.1; F, 45.1; N, 5.5%; M, 253), b.p. 118°/770 mm. (Siwoloboff); main i.r. bands at 3.38m, 6.78m, 7.23s, 7.54s, 7.76s, 7.97s, 8.57, and 8.62vs (doublet), 9.25w, 9.86m, 10.29s, 11.11s, 11.76 and 11.91s (doublet), 12.72vs, 13.11m, 14.00s, and 14.52m  $\mu$ m.

(b) Dichloromethylsilane. A mixture of the olefin (4:40 g., 24.8 mmoles) and dichloromethylsilane (4:29 g., 37.3 mmoles), sealed in a silica ampoule (300 ml.) and irradiated (48 hr.) whilst being shaken, gave unchanged dichloromethylsilane (1:43 g., 12:4 mmoles, 33% recovered; M, 114) and 2-[NN-bis(trifluoromethyl)amino]ethyldichloromethylsilane (7:29 g., 24:8 mmoles, 100%) (Found: C, 20:5; H, 2:5; Cl, 23:9; N, 5:0. C<sub>5</sub>H<sub>7</sub>Cl<sub>2</sub>F<sub>6</sub>NSi requires C, 20:4; H, 2:4; Cl, 24:1; N, 4:8%), b.p. 142° (isoteniscope); main i.r. bands at 3:40w, 3:45w, 6:79m, 7:25s, 7:54s, 7:78s, 7:90s, 8:70s, 9:19m, 9:35m, 9:90m, 10:27s, 11:18s, 12:11s, 12:30s, 12:65s, 13:30m, 13:72m, and 14:35m  $\mu$ m.

(c) Trichlorosilane. A mixture of the olefin (3·47 g., 19·4 mmoles) and trichlorosilane (3·94 g., 29·1 mmoles), sealed in a silica ampoule (300 ml.) and irradiated (40 hr.) whilst being shaken, gave (i) unchanged vinylamine (0·19 g., 1·4 mmoles, 7% recovered), (ii) unchanged trichlorosilane (1·43 g., 10·6 mmoles), and (iii) 2-[NN-bis(trifluoromethyl)-amino]ethyltrichlorosilane (5·65 g., 18·0 mmoles, 100%) (Found: C, 15·3; H, 1·6; N, 4·5. C<sub>4</sub>H<sub>4</sub>Cl<sub>3</sub>F<sub>6</sub>NSi requires C, 15·6; H, 1·3; N, 4·5%), b.p. 134° (isoteniscope); main i.r. bands at 3·45w, 6·79m, 7·23s, 7·49s, 7·78s, 8·05w, 8·59s, 9·14m, 9·90w, 10·25m, 11·21m, 12·65m, 13·15w, and 13·87m µm.

The Preparation of 2-[NN-Bis(trifluoromethyl)amino]ethyltrifluorosilane. 2-[NN-Bis(trifluoromethyl)aminoethyltrichlorosilane (7.20 g., 23.0 mmoles) was passed, in vacuo, eight times through a tube containing excess of antimony trifluoride and a small amount of antimony pentachloride maintained at 20°. The products were (i) ethylene (0.30 g., 10.7 mmoles, 46.5%), (ii) silicon tetrafluoride (0.92 g., 8.8 mmoles), (iii) perfluoro-(2-azapropene) (1.30 g., 10.0 mmoles, 43%) (Found: *M*, 130. Calc. for C<sub>2</sub>F<sub>5</sub>N: *M*, 133), and (iv) 2-[NN-bis(trifluoromethyl)amino]ethyltrifluorosilane (3.18 g., 12.0 mmoles, 52%) (Found: C, 18.3; H, 1.7; N, 5·2%, M, 265. C<sub>4</sub>H<sub>4</sub>F<sub>9</sub>NSi requires C, 18·1; H, 1·5; N, 5.3%; M, 265), b.p. 78° (Siwoloboff); main i.r. bands at 3.30w, 3.38w, 6.77s, 7.18s, 7.43s, 7.74s, 8.03s, 8.50s, 9.05s, 10.32s, 11.23s, 12.10s, 12.60s, 13.24m, 13.50m, 14.27s, and 15·28m μm.

The Hydrolysis of 2-[NN-Bis(trifluoromethyl)amino]ethyltrichlorosilane.—(a) Method 1. Water (2.0 g.) was added to the silane (1.35 g., 4.3 mmoles) in diethyl ether (5 ml.) and the mixture was refluxed (1 hr.). The ether and water were then removed in vacuo to give a viscous liquid (0.95 g., 4.1 mmoles, 95% yield calculated as polysilsesquioxane) the i.r. spectrum of which indicated the presence of a considerable amount of silanol (broad band at 3.0  $\mu$ ). The liquid was then heated in vacuo as follows: 2 hr. at 100°; 2 hr. at 150°; 2 hr. at 200°; and 2 hr. at 350°. An i.r. spectrum was run after each 2 hr. period and only after the final 2 hr. at 350° were OH groups shown to be absent. The final product was a viscous liquid identified as poly-{2-[NNbis(trifluoromethyl)amino]ethylsilsesquioxane} (0.92 g., 4.0

<sup>13</sup> R. D. Dresdner, F. N. Tlumac, and J. A. Young, J. Org. Chem., 1965, 30, 3524.
 <sup>14</sup> F. C. Whitmore and L. H. Sommer, J. Amer. Chem. Soc.,

<sup>14</sup> F. C. Whitmore and L. H. Sommer, *J. Amer. Chem. Soc.*, 1946, **68**, 484.

<sup>15</sup> R. Nagel and H. W. Post, J. Org. Chem., 1952, 17, 1379.

mmoles, 92%) (Found: C, 20.6; H, 1.7; N, 5.9.  $C_4H_4F_6NO_{1.5}Si$  requires C, 20.7; H, 1.7; N, 6.0%).

(b) Method 2. The silane (2.80 g., 9.0 mmoles) dissolved in toluene (10 ml.) was treated with hydrochloric acid (3% w/v, 10 ml.) and the mixture was refluxed (5 hr.). The toluene and water were removed in vacuo and the liquid product was heated in vacuo at 200° (4 hr.) to give the polysilsesquioxane (1.90 g., 8.2 mmoles, 91%) the i.r. spectrum of which showed only a slight absorption at  $3.0 \mu$ but which otherwise was spectroscopically identical with the material prepared by Method 1.

(c) Method 3. Water (3.0 g.) was added to the silane (6.23 g., 19.8 mmoles) in diethyl ether (10 ml.) and the mixture was refluxed (1 hr.). The ether was displaced by toluene and the water was removed by azeotropic distillation with toluene. The resultant viscous liquid was treated with a 2:1 molar mixture of 2-ethylhexanoic acid and 1,1,3,3-tetramethylguanidine dissolved in an equimolar weight of toluene (0.047 g.) and the mixture was refluxed (5.5 hr.) by use of an azeotrope trap. The precipitated solid was washed several times with boiling toluene to remove any catalyst and the resultant product was then heated at 100° in vacuo (2 hr.) to give a crystalline solid (4.32 g., 18.6 mmoles, 94%), which, when purified by sublimation in vacuo, gave material (4.15 g., 17.8 mmoles, 90%) [Found: C, 20.7; H, 2.0; F, 48.8; N, 5.9%; M (by osmometry), 1425. Calc. for C<sub>24</sub>H<sub>24</sub>F<sub>36</sub>N<sub>6</sub>O<sub>9</sub>Si<sub>6</sub>: C, 20.7; H, 1.7; F, 49.1; N, 6.0%; M, 1392]; main i.r. bands at 6.78m, 7.23s, 7.50s, 7.76s, 8.40-9.20vs (br), 9.91m, 10.27m, 11.17m, 12.36m, 12.83w, and 14.42m (br) µm, possibly the cyclic hexamer (II).

Reaction of the Liquid Polysilsesquioxane with Acid and Base.—Treatment of the liquid polymer with (a) concentrated sulphuric acid at  $100^{\circ}$  (1 hr.), (b) syrupy phosphoric acid at  $160^{\circ}$  (1.5 hr.), (c) methanol and aqueous hydrochloric acid under reflux (4 hr.), (d) powdered, dry sodium hydroxide at  $100^{\circ}$  (0.5 hr.), or (e) 2M-sodium hydroxide at  $100^{\circ}$  (0.5 hr.) gave, in all cases, only unchanged polymer.

Slight charring was observed when the polymer was heated with concentrated sulphuric acid at  $150^{\circ}$  (1 hr.).

The Hydrolysis of 2-[NN-Bis(trifluoromethyl)amino]ethyldichloromethylsilane.—(a) Method 1. Diethyl ether (10 ml.) saturated with water was added to the silane (0.95 g., 3.23 mmoles) in diethyl ether (5 ml.) and the mixture was refluxed (2 hr.). The ether and water were removed by distillation and the liquid product was heated at 200° in vacuo (2 hr.) after which time OH groups were shown to be absent (i.r.). The resultant viscous oil was identified as poly-{2-[NN-bis(trifluoromethyl)amino]ethylmethylsiloxane} (0.75 g., 3.1 mmoles, 97%) (Found: C, 24.8; H, 2.9; N, 6.1. C<sub>5</sub>H<sub>7</sub>F<sub>6</sub>NOSi requires C, 25.1; H, 2.9; N, 5.9%);

main i.r. bands at 3·33m, 3·39w, 4·60w, 4·75w, 6·44w, 6·77s, 7·00s, 7·22vs, 7·50vs, 7·76vs, 7·87vs, 8·30s, 8·70s (br), 9·25—9·50s (br) (cyclic tetramer, higher cyclics, and linear polymer; Si-O-Si), 9·86vs (cyclic trimer; Si-O-Si), 10·25s, 11·13s, 12·46s (br), 13·08m, 13·80w, and 14·43s μm.

(b) Method 2. Diethyl ether (20 ml.) saturated with water was added to the silane (7.24 g., 24.6 mmoles) in diethyl ether (20 ml.) and the mixture was refluxed (2 hr.). The ether was distilled off and the water was removed by azeotropic distillation with toluene. The excess of toluene was then removed by distillation. The resultant polysiloxane (5.20 g., 21.4 mmoles, 87%) [Found: M (by osmometry), 962. Calc. for  $C_{20}H_{26}F_{24}N_4O_4Si_4$ : M, 956]

had a comparable i.r. spectrum to that of the material prepared by method 1 [except for the presence of a very strong band at  $9.28 \ \mu m$  (cyclic tetramer; Si-O-Si) rather than the broad absorption at 9.25— $9.50 \ \mu m$ ] and was more mobile. When distilled *in vacuo* the polysiloxane could not be separated into trimer, tetramer *etc.* fractions.

Pyrolysis of Polymers and Model Compounds.—In all cases the substance was sealed in vacuo in a dry silica ampoule (300 ml.) and the ampoule was heated at the requisite temperature (6 hr.). The resultant pyrolysate was fractionated in vacuo and the composition of mixtures of two known components was estimated from the molecular weight. The composition of more complex mixtures was estimated by molecular-weight determination both before and after hydrolysis with 2M-sodium hydroxide. Attempts to devise a g.l.c. method for estimating the compositions of the product mixtures were unsuccessful.

The results obtained from the pyrolyses of the model compounds (IC) and (ID) are shown in Table 1, and those obtained from the pyrolyses of the polysiloxane (prepared by method 2) and polysilsesquioxane (liquid polymer prepared by method 2) polymers are shown in Table 2.

The Reaction of Mercury(II) Bis(trifluoromethyl)amide with Iodomethyltrimethylsilane.—The mercurial (24.2 g., 48.1 mmoles) and the silane (22.8 g., 106.5 mmoles), sealed in a Pyrex ampoule (40 ml.) and shaken at room temperature (2 days), gave only unchanged reactants. The reactants were resealed in the ampoule, and the ampoule was shaken at  $60^{\circ}$  (5 days) to give (i) trifluoromethyl isocyanate (0.01 g., 0.1 mmole), (ii) perfluoro-(2-azapropene) (3.42 g., 25.9 mmoles, 27%), (iii) perfluoro-(4-methyl-2,4-diazapentene) (2.58 g., 10.0 mmoles, 21%) (Found: M, 259. Calc. for  $C_4F_{10}N_2$ : M, 266), (iv) a higher-boiling fraction (23 g.), and (v) a residue of mercury(II) iodide (16.5 g., 36.3 mmoles, 76%). The higher-boiling fraction, distilled at atmospheric pressure, gave perfluoro-(4-methyl-2,4-diazapent-2-ene) (0.62 g., 2.3 mmoles, 5%), b.p.  $<45^{\circ}$ , and a fraction (5.7 g.), b.p. 50-60°, but when the bath temperature reached ca. 125° mercury(II) iodide precipitated, low-boiling material was evolved [perfluoro-(2-azapropene) and its dimer], and a further quantity of material (2.9 g.), b.p. 50-60°, was obtained. A continuation of the distillation gave unchanged iodomethyltrimethylsilane (1.8 g., 8.4 mmoles, 8% recovered) and a residue of mercury(II) iodide (4.0 g., 8.8 mmoles, 18%).

The fraction, b.p. 50-60° (8.60 g.), was separated by g.l.c. (4 m. Silicone MS550 oil at 40°) into its four components identified as (i) perfluoro-(2-azapropene) (0.30 g., 2.25 mmoles, 2%), (ii) the azapropene dimer (1.01 g., 3.75mmoles, 8%), (iii) ethyldimethylfluorosilane (1.41 g., 13.3 mmoles, 14%) (Found: C, 44.8; H, 10.4%; M, 105. Calc. for C<sub>4</sub>H<sub>11</sub>FSi: C, 45·3; H, 10·4%; M, 106), b.p. 50° (lit., 16 50.5°); main i.r. bands at 3.40s, 3.49s, 6.85m, 7.06s, 7.95s, 9.86s, 9.95s, 10.35s, 11.30vs, 12.39s, 12.53vs, and 14.1-14.4s (br) µm, and (iv) fluoromethyltrimethylsilane (5.88 g., 55.5 mmoles, 58%) (Found: C, 45.6; H, 10.4%; M, 106.  $C_4H_{11}FSi$  requires C, 45.3; H, 10.4%; M, 106), b.p. 64°/752 mm. (Siwoloboff); main i.r. bands at 3.45m (triplet), 5.03w, 6.78w, 7.02s, 7.72m, 7.88vs, 7.98vs, 8.23m, 8.50w, 9.46m, 9.57m, 10.01vs (triplet), 11.57vs, 12.30-12.60m (br), 13.05s, and 14.23vs  $\mu m.$ 

The Attempted Rearrangement of Fluoromethyltrimethylsilane.—A sample of the silane, contained in an n.m.r. tube,

<sup>16</sup> C. Eaborn, J. Chem. Soc., 1953, 494.

was heated at 100° (2 hr.), 133° (2 hr.), 164° (2 hr.), 183° (2 hr.), and 211° (2 hr.) and the  $^{19}{\rm F}$  n.m.r. spectrum was recorded after the sample was heated to each temperature;

## TABLE 3

## Main mass-spectral bands

m e	Intensity	Assignment
(CF	<sub>3</sub> ) <sub>2</sub> N•CH <sub>2</sub> •CH <sub>2</sub> •Si	.Cl <sub>3</sub>
177, 175, 173, and		
171 166	4 100	$C_2H_4 \cdot S_1C_3^+$
149, 147, 145, and	200	(01 3/21, 0112
143	10	SiCl <sub>3</sub> +
78 69	19	CF <sub>2</sub> ·N·CH <sub>2</sub> <sup>+</sup>
28	5	$C_2H_4^+, CH_2N^+$
(C	F <sub>3</sub> ) <sub>2</sub> N·CH <sub>2</sub> ·CH <sub>2</sub> ·	SiMe <sub>3</sub>
166	1	$(CF_3)_2 N \cdot CH_2^+$
159	26	$C_2F_5 \cdot N \cdot C_2H_2^+$
147	6	$C_2F_5 \cdot N \cdot CH_2^+$ $C_2F_2 \cdot N^+$
105	13	$C_2H_4$ ·SiFMe+
77	100	Me <sub>2</sub> SiF+
73	90	Me <sub>3</sub> Si <sup>+</sup>
45	10	MeSiH.+
43	8	MeSi <sup>+</sup>
28	45	$C_2H_4^+, CH_2N^+$
	$Me_2EtSiF$	
106	8	M+ MoEtSiEt
91 77	100	Me_SiF+
63	51	MeSiHF+
49	15	SiH <sub>2</sub> F <sup>+</sup>
47		SIFT
(CF	$_{3}_{2}$ N·CH <sub>2</sub> ·CH <sub>2</sub> ·S	1MeCl <sub>2</sub>
166	32	$(CF_3)_2 N \cdot CH_2^+$ C H ·SFC1 +
117, 115, and 113	10	MeSiCl.+
99, 97	17	$MeSiFCl^+$
78	32	CF <sub>2</sub> ·N·CH <sub>2</sub> +
28	100 62	C <sub>a</sub> H <sub>a</sub> +.CH <sub>a</sub> N+
10	F.).N.CH. CH.	SiF
166	100	(CF <sub>2</sub> ) <sub>2</sub> N·CH <sub>2</sub> +
113	83	C <sub>2</sub> H <sub>4</sub> ·SiF <sub>3</sub> +
112	7	$C_2H_3 \cdot SiF_3^+$
93 85	18	$C_2H_3 \cdot 51F_2^+$ SiF.+
85 78	70	CF, N·CH,+
69	1	CF <sub>3</sub> +
28 27	$\frac{22}{26}$	$C_2H_4^+, CH_2N^+$ $C_2H_2^+, CHN^+$
2.	Mo Sich F	02113 ,0211
	Me <sub>3</sub> SPCH <sub>2</sub> F	M. CITL
77 73	12	Me <sub>2</sub> Si <sup>+</sup>
63	54	MeSiHF+
59	4	Me <sub>2</sub> SiH+
49	8 15	SIH <sub>2</sub> F <sup>+</sup> SiF <sup>+</sup>
45	30	MeSiH,+
43	14	MeSi+
29	7	SiH+

<sup>17</sup> J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, Oxford, 1966, vol. 2, p. 927.

there was no change in the spectrum. The sample was then heated at  $211^{\circ}$  (2 hr.) in the presence of mercury(II) iodide; again there was no change in the n.m.r. spectrum.

The Reaction of Vinyltrimethylsilane with NN-Bis(trifluoromethyl)amine.—Experiment 1. The vinylsilane (2·10 g., 20·0 mmoles), the amine (2·22 g., 14·5 mmoles), and sodamide (0·04 g., 1·0 mmole), sealed in a Pyrex ampoule (30 ml.) and the ampoule shaken at room temperature (7 days), gave unchanged reactants contaminated with perfluoro-(2-azapropene) (0·13 g., 1·0 mmole).

*Experiment* 2. The vinylsilane (1.99 g., 19.9 mmoles) and the amine (3.18 g., 20.7 mmoles) were condensed *in vacuo* into a stainless steel autoclave (16 ml.) containing sodamide (0.084 g., 2.20 mmoles), sodium (0.040 g., 1.70 mmoles), and ammonia (5.00 g., 0.29 mole), and the autoclave was shaken at room temperature (7 days) and then stood at room temperature (14 days). The products were unreacted vinylsilane (1.81 g., 18.1 mmoles, 91% recovered), unreacted ammonia (2.34 g., 0.13 mole, 47% recovered) (Found: M, 18. Calc. for NH<sub>3</sub>: M, 17) shown by i.r. spectroscopy to be contaminated with perfluoro-(2-aza-propene), and a residue which gave positive tests for ammonium and fluoride ions.

Mass-spectral Data.—The main mass-spectral bands of the compounds prepared in the present work are shown in Table 3.

The spectra of the silanes (IA—ID) showed that primary Si-C<sub>ethyl</sub> fission decreased as the groups attached to silicon changed from electron-donating to electron-withdrawing, while C-C fission changed in the opposite direction, *i.e.*, the silanes (IA) and (ID) showed a base peak at m/e 166 due to  $(CF_3)_2N\cdot CH_2^+$ . Certain rearrangement peaks were observed in which fluorine was transferred from carbon to silicon; such reactions have a favourable energy change  $(\Delta H \ ca. \ 20 \ kcal. \ mole^{-1})$  but only with silane (IC) was the peak of high intensity. A further interesting observation was the intensity of the peak at m/e 69 (CF<sub>3</sub><sup>+</sup>) which varied extensively; 100% (IB), 19% (IA), 6% (IC), *ca.* 1% (ID).

The fluorosilane (IX) showed a relatively weak parent peak in its spectrum at m/e 106 and the remaining major peaks all contained silicon and fluorine with the base peak corresponding to loss of methyl from the parent. The isomer (VIII) showed no parent peak in its spectrum and the base peak corresponded to loss of CH<sub>2</sub>F from the parent; the ion Me<sub>2</sub>Si·CH<sub>2</sub>F<sup>+</sup> was not observed. Strong rearrangement peaks due to transfer of both F and H from carbon to silicon were present, *e.g.*, m/e 77 (Me<sub>2</sub>SiF<sup>+</sup>), m/e 63 (MeSiHF<sup>+</sup>), and m/e 45 (MeSiH<sub>2</sub><sup>+</sup>).

*N.m.r. Spectra.*—The spectra of the compounds prepared are shown in Table 4, and were measured on neat liquids with trifluoroacetic acid as the external reference for  $^{19}$ F and tetramethylsilane as the internal reference for  $^{1}$ H, unless stated to the contrary.

The chemical shift of the  $(CF_3)_2N$  group  $(-19\cdot2 \text{ to} -20\cdot6 \text{ p.p.m.})$  agreed closely with values found previously for  $(CF_3)_2N$  groups bonded to carbon. The chemical shift  $(+86\cdot8 \text{ p.p.m.})$  of the fluorine atom in the silane Me<sub>2</sub>EtSiF is in the region expected <sup>17,18</sup> and both the chemical shift (+196 p.p.m.) and the coupling constant  $(J \ 46\cdot8 \text{ c./sec.})$ observed for the fluorine atom in the silane Me<sub>3</sub>Si·CH<sub>2</sub>F are typical of  $-CH_2F$  groups  $(cf. \ CH_3F; ^{19} \ 198\cdot1 \text{ p.p.m.}; J \ 46\cdot4 \text{ c./sec.})$ .

<sup>18</sup> J. Dyer and J. D. Lee, unpublished results.

19 Ref. 18, p. 883.

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		N.m.r9	spectral data				
	19F			1H			
$(CF_3)_2 N \cdot CH_2 \cdot CH_2 \cdot SiF_3$	Group a d	Type Complex Complex	Chemical shift (p.p.m.) -19.2 61.0	Group b* c*	Type Complex Complex	Chemical shift $(\tau)$ 5.84 7.76	Coupling constants J (Hz)
$(CF_3)_2 N \cdot CH_2 \cdot CH_2 \cdot SiCl_3$	a	t	-20.5	b* c*	Complex Complex	6·45 8·20	a–b, 1·4
$(CF_3)_2 N \cdot CH_2 \cdot CH_2 \cdot SiMeCl_2$ a b c d	a	t	-20.2	b * c * d	Complex Complex s	$6.46 \\ 8.45 \\ 9.25$	a−b, 1·3
$(CF_3)_2 N \cdot CH_2 \cdot CH_2 \cdot SiMe_3$ b c d	a	Complex	-20.6	b * c * d	Complex Complex s	6·72 9·00 10·00	
$[(\mathrm{CF}_3)_2\mathrm{N}^{\bullet}\mathrm{CH}_2^{\bullet}\mathrm{CH}_2^{\bullet}\mathrm{SiMeO}]_n^{\dagger}]_{\mathrm{d}}$	a	S	-20.4	b * c * d	Complex Complex s	$5.93 \\ 8.25 \\ 9.15$	
$\operatorname{CH}_{a} \cdot \operatorname{CH}_{2} \cdot \operatorname{SiMe}_{2} \operatorname{F}_{c}_{d}$	d	Complex	86.8	a, b c	$\begin{array}{c} \operatorname{Complex} \\ \operatorname{d} \end{array}$	8.65 - 9.45 9.65	cd, 7·2
FCH <sub>2</sub> ·SiMe <sub>3</sub>	a	t	196-0	b c	d d	5·47 9·69	a-b, 46·8 a-c, 0·7

TABLE 4

s = Singlet, d = doublet, t = triplet.\* Mid point of absorption.  $\dagger 60\%$  solution in acetone.

The <sup>1</sup>H spectra of the silanes were all as expected with the hydrogens of the substituted ethyl groups in the silanes (IA-ID) appearing as an AA'BB' pattern characteristic of most 2-substituted ethylsilanes.18

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