Polyfluoroalkyl Compounds of Silicon. Part X.[1] Further Silanes containing the Bis(trifluoromethyl)amino-group

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The silanes $[(CF_3)_2N]_2C{:}CH{\cdot}SiX_3$ (X_3 = Me_3 or $MeCl_2$) have been prepared by free-radical reaction of the corresponding silanes with 1,1-di[bis(trifluoromethyl)amino]ethylene. The reaction of *NN*-bis(trifluoromethyl)prop-2-enylamine with trimethylsilane or dichloro(methyl)silane in the presence of hexachloroplatinic(IV) acid as catalyst gives the corresponding 1 : 1 compounds $(CF_3)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SiX_3$ (X_3 = Me_3 or $MeCl_2$) in high yield; a similar reaction between *NN*-bis(trifluoromethyl)vinylamine and dichloro(methyl)silane gives {2-[*NN*-bis(trifluoromethyl)amino]ethyl}dichloro(methyl)silane. A relatively high molecular-weight polysiloxane $\{(CF_3)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}SiMe{\cdot}O\}_n$ has been prepared from {2-[*NN*-bis(trifluoromethyl)amino]ethyl}dichloro(methyl)silane *via* the cyclic trisiloxane $\{(CF_3)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}SiMe{\cdot}O\}_3$.

IN the previous paper in this series,[1] preparations of the silanes $(CF_3)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}SiX_3$ [(I); $X_3 = Me_3$, (II); $X_3 = Cl_3$, and (III); $X_3 = MeCl_2$], by free-radical additions of corresponding hydrosilanes to *NN*-bis(trifluoromethyl)vinylamine, were reported. Silanes (II) and (III) were hydrolysed and the former gave a compound believed to be the cyclic hexamer $\{(CF_3)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}Si{\cdot}O_{1{\cdot}5}\}_6$, while the latter afforded a low molecular-weight liquid polysiloxane $\{(CF_3)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}SiMe{\cdot}O\}_n$. Pyrolyses of these polymers indicated that they had similar thermal stability *in vacuo* to the 3,3,3-trifluoropropyl analogues and this, together with their resistance to acid or base, suggested that the preparation and properties of a high molecular-weight polysiloxane would merit technological investigation.

With this in view silane (III) has been prepared by an improved method and the conversion of it into a high molecular-weight polysiloxane has been investigated. The preparation of potentially useful silane monomers $(CF_3)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SiX_3$ and the reactions of hydrosilanes with 1,1-di[bis(trifluoromethyl)amino]ethylene under various conditions have also been carried out.

RESULTS AND DISCUSSION

Preparation of the Silanes $(CF_3)_2N{\cdot}(CH_2)_n{\cdot}SiX_3$.—Of a number of catalysts which promote the addition of hydrosilanes to olefins, one of the most active and convenient to use is the Speier catalyst, hexachloroplatinic(IV) acid.[2] This catalyst has been found to be efficient with electron-rich terminal olefins in affording the 1 : 1 compound in which the silicon atom is bonded to the terminal carbon atom of what was the original olefin. Non-terminal olefins generally rearrange to give the same 1 : 1 compound as formed from the corresponding terminal olefin. In contrast electron-deficient olefins react more slowly than electron-rich olefins (in some cases reaction does not take place), although olefins containing only one electron-

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[1] Part IX, E. S. Alexander, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J. Chem. Soc.* (*A*), 1970, 2285.

[2] J. L. Speier, J. A. Webster, and G. H. Barns, *J. Amer. Chem. Soc.*, 1965, **87**, 16.

withdrawing group generally give reasonable yields of 1 : 1 compounds, *e.g.* $CF_3{\cdot}CH{:}CH_2$.[3]

In the present work, Speier-catalysed additions of dichloro(methyl)silane to the olefins $(CF_3)_2N{\cdot}CH{:}CH_2$ and $(CF_3)_2N{\cdot}CH_2{\cdot}CH{:}CH_2$ and of trimethylsilane to the latter olefin proceeded at 80—100 °C and gave high yields of the 1 : 1 compounds {2-[*NN*-bis(trifluoromethyl)amino]ethyl}dichloro(methyl)silane (III) (97%), {3-[*NN*-bis(trifluoromethyl)amino]propyl}dichloro(methyl)silane (IV) (96%), and {3-[*NN*-bis(trifluoromethyl)amino]propyl}trimethylsilane (V) (98%), respectively. This method of formation of compound (III)

$$(CF_3)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}Si(Me)X_2$$
$$\text{(IV) } X = Cl$$
$$\text{(V) } X = Me$$

is superior to the previously reported preparation by photochemically initiated addition of the hydrosilane.[1] Compound (IV) is a potential monomer for preparation of the polysiloxane $\{(CF_3)_2N{\cdot}(CH_2)_3{\cdot}SiMe{\cdot}O\}_n$.

Reaction of Silanes with 1,1-*Di*[*bis*(*trifluoromethyl*)*amino*]*ethylene*.—Attempted Speier-catalysed additions of trimethylsilane and dichloro(methyl)silane to 1,1-di[bis(trifluoromethyl)amino]ethylene at elevated temperature gave only unchanged reactants. It has been reported[4] previously that attempted ionic addition to this olefin of hydrogen bromide, both alone and in the presence of aluminium bromide, was unsuccessful. The lack of reaction was suggested as being due to interactions between the bulky geminal bis(trifluoromethyl)amino-groups which forced them out of coplanarity with the rest of the molecule. This would result in a reduced contribution from a mesomeric effect (overlap of the nitrogen lone-pair with the olefinic π-cloud) and enable the strong $-I$ inductive effect of the bis(trifluoromethyl)amino-groups to render the olefin electron deficient and so not susceptible to electrophilic attack.

Under photochemical conditions the two silanes reacted with the olefin to give high yields, albeit in low conversions, of the corresponding ethenylsilanes (VI) (95%) and (VII) (93%), together with hydrogen. These

$$[(CF_3)_2N]_2C{:}CH{\cdot}Si(Me)X_2$$
$$\text{(VI) } X = Me$$
$$\text{(VII) } X = Cl$$

products can be accounted for by equations (1)—(4) (X = Me or Cl). Formation of the unsaturated compounds was unexpected, since radical addition of hydrogen bromide to the olefin had been observed[4] previously to give saturated $[(CF_3)_2N]_2CH{\cdot}CH_2Br$ (100%). The intermediate radicals (VIII) and $[(CF_3)_2N]_2{\cdot}\dot{C}{\cdot}CH_2Br$ (IX), formed by addition of a bromine atom, are expected to be of comparable stability, and so the differences in type of product from the silane and hydrogen bromide reactions are probably caused by differences in the ease of chain transfer in the two reactions. Bond energies of the H–Br and $H{-}Si{\lessdot}$ bonds are comparable and so it is suggested that the apparent difference in ease of chain transfer with compound (VIII) as compared with (IX) is steric in origin. The former intermediate radical (VIII) contains a $-CH_2{\cdot}Si{\lessdot}$ group which is more bulky than the CH_2Br group in (IX) and also the chain-transfer agent $HSi{\lessdot}$ is more bulky than HBr.

$$HSi(Me)X_2 \xrightarrow{\text{u.v.}} {}^{\bullet}SiMeX_2 + H^{\bullet} \qquad (1)$$

$$[(CF_3)_2N]_2C{:}CH_2 + {}^{\bullet}SiMeX_2 \longrightarrow [(CF_3)_2N]_2\dot{C}{\cdot}CH_2{\cdot}Si(Me)X_2 \qquad (2)$$
$$\text{(VIII)}$$

$$\text{(VIII)} + {}^{\bullet}SiMeX_2 \text{ or } H^{\bullet} \longrightarrow [(CF_3)_2N]_2C{:}CH{\cdot}Si(Me)X_2 + HSi(Me)X_2 \text{ or } H_2 \qquad (3)$$

$$H^{\bullet} + HSi(Me)X_2 \longrightarrow H_2 + {}^{\bullet}Si(Me)X_2 \qquad (4)$$

Preparation of Poly{2-[NN-*bis*(*trifluoromethyl*)*amino*]*ethyl*}*methylsiloxane*.—High molecular-weight polysiloxanes are prepared by equilibration of cyclic siloxanes, usually trimers, in the presence of a catalyst. The trimers can, in certain cases, be separated directly by distillation from the crude hydrolysate formed by hydrolysis of the corresponding dichlorosilane.[5] Much higher yields are obtained[6] by first equilibrating the higher molecular-weight linear and cyclic polysiloxanes present in the crude hydrolysate by heating in the presence of a basic catalyst, usually a metal hydroxide. When equilibration and distillation are carried out simultaneously, formation of the more volatile cyclics is favoured, because they are continuously removed from the mixture. This method, when applied to the hydrolysate from the silane $CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}Si(Me)Cl_2$ using potassium hydroxide as catalyst, afforded a high yield of the cyclic trimer $\{CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}SiMe{\cdot}O\}_3$.[7]

The crude hydrolysate from the previously reported[1] hydrolysis of silane (III) was shown by i.r. spectroscopy to contain the cyclic trimer, but no attempt was made to isolate it. In the present work silane (III) was hydrolysed with aqueous potassium hydroxide to afford a liquid polysiloxane mixture (82%). This was dried and then distilled under reduced pressure from potassium hydroxide (1%) in a spinning-band column to afford a relatively constant-boiling fraction (b.p. 175 °C, 60 mmHg; 55%). This fraction was shown by i.r. (strong band at 9·82 μm) to contain a high proportion of the cyclic trimer (X). A lower-boiling fraction (*ca.* 33%) was also obtained, and this was shown by i.r. and n.m.r. spectroscopy to contain mainly the difluorosilane $(CF_3)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}Si(Me)F_2$,

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[3] R. N. Haszeldine and R. J. Marklow, *J. Chem. Soc.*, 1957, 3925.

[4] E. S. Alexander, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J. Chem. Soc.* (*C*), 1968, 796.

[5] M. J. Hunter and E. L. Warwick, *J. Amer. Chem. Soc.*, 1946, **68**, 667.

[6] W. I. Patnode and F. C. Schmidt, *J. Amer. Chem. Soc.*, 1946, **68**, 358.

[7] B.P. 832,487/1957 and 832,488/1957; Canad. P. 570,988/1959; O. R. Pierce, G. W. Holbrook, O. K. Johannson, J. C. Saylor, and E. D. Brown, *Chem. and Ind.*, 1960, **52**, 783.

(XI). Considerable decomposition had thus taken place. The previously prepared low molecular-weight polysiloxane polymer partially decomposed on static pyrolysis *in vacuo* at *ca.* 420 °C to afford the difluorosilane (XI) as one of the products.[1] The trimer fraction on g.l.c. examination was found to contain *ca.* 70% of trimer (X), three more volatile components [all of which were present in the lower-boiling fraction, and the major one of which (*ca.* 25%) was the difluorosilane (XI)], and the cyclic tetramer (XII). The trimer was thus formed in *ca.* 38% overall yield.

In a second experiment the liquid polysiloxane mixture was distilled as quickly as possible under reduced pressure from potassium hydroxide to afford the difluorosilane (XI) (5%) and a mixture (*ca.* 60%) comprised of the difluorosilane (XI), the cyclic trimer (X), and the cyclic tetramer (XII) in the ratio 37 : 53 : 10. Redistillation of the trimer fraction twice in the absence of potassium hydroxide gave pure trimer (X) (*ca.* 11%), b.p. 184 °C at 60 mmHg. When treated at 150 °C *in vacuo* with anhydrous potassium hydroxide flour (*ca.* 1% by weight) the trimer (X) underwent almost immediate polymerisation and the product poly{2-[*NN*-bis(trifluoromethyl)amino]ethyl}methylsiloxane (90%) was formed as a highly viscous gum. A small amount (<10%) of unchanged trimer was recovered. The trimer (X) was also polymerised by treatment with anhydrous potassium hydroxide flour (1·5% by weight) at 150 °C at atmospheric pressure under nitrogen; this gave a polysiloxane gum $\{(CF_3)_2N\cdot CH_2\cdot CH_2\cdot SiMe\cdot O\}_n$ (96%) of average molecular weight 3 990 ($n = 16$). Other catalysts including caesium hydroxide and the dipotassium salt of tetramethyldisiloxane-1,3-diol were also successful in polymerising the cyclic trimer (X) to low molecular-weight polysiloxane oils. Whilst the polymers have good thermal and oxidative stability and good resistance to acid or base, it has not proved possible to prepare a polymer of high molecular weight, and at present therefore no advantage is shown over the analogous and commercially useful 3,3,3-trifluoropropyl elastomer.

$$\{(CF_3)_2N\cdot CH_2\cdot CH_2\cdot SiMe\cdot O\}_n$$

$$\text{(X)}\ n = 3$$

$$\text{(XII)}\ n = 4$$

EXPERIMENTAL

Techniques used were as described previously;[1] n.m.r. spectra were run on neat liquids using internal tetramethylsilane and external trifluoroacetic acid as the respective ^1H and ^{19}F references. 1,1-Di[*NN*-bis(trifluoromethyl)amino]ethylene and *NN*-bis(trifluoromethyl)vinylamine were prepared as reported[4] previously, and *NN*-bis(trifluoromethyl)prop-2-enylamine was made by dehalogenation of the major adduct from the reaction of *N*-bromobis(trifluoromethyl)amine with allyl chloride.[8] I.r., n.m.r., and mass spectral data for compounds marked with an asterisk are to be found in Supplementary Publication No. SUP 21026 (6 pp.).†

Reaction of Dichloro(methyl)silane with NN-*Bis(trifluoromethyl)vinylamine.*—The silane (22·80 g, 0·200 mol), the olefin (25·10 g, 0·140 mol), and hexachloroplatinic(IV) acid (0·10 g), sealed in a Pyrex ampoule (*ca.* 300 cm^3) and heated at 100 °C (48 h), gave (*i*) unchanged olefin (1·61 g, 9·0 mmol, 6% recovered), (*ii*) unchanged dichloro(methyl)silane (8·09 g, 0·071 mol, 35% recovered), and (*iii*) {2-[*NN*-bis(trifluoromethyl)amino]ethyl}dichloro(methyl)silane (37·2 g, 0·127 mol, 97%) which was identified by a comparison of its i.r. and n.m.r. spectra with those reported.[1]

Reaction of Silanes with NN-*Bis(trifluoromethyl)prop-2-enylamine.*—(a) *Trimethylsilane.* The silane (0·80 g, 10·81 mmol), the olefin (1·30 g, 6·73 mmol), and hexachloroplatinic(IV) acid (0·01 g), sealed in a Pyrex ampoule (*ca.* 20 cm^3) and heated at 80 °C (15 h), gave (*i*) unchanged trimethylsilane (0·33 g, 4·49 mmol, 41% recovered), (*ii*) unchanged olefin (0·19 g, 0·97 mmol, 17% recovered), and (*iii*) {*3-[*NN-*bis(trifluoromethyl)amino]propyl}trimethylsilane* * (1·52 g, 5·69 mmol, 98%) (Found: C, 36·4; H, 5·8; N, 5·2. Calc. for $C_8H_{15}F_6NSi$: C, 36·0; H, 5·7; N, 5·3%), b.p. 137 °C (Siwoloboff).

(b) *Dichloro(methyl)silane.* The silane (1·77 g, 15·54 mmol), the olefin (1·50 g, 7·77 mmol), and hexachloroplatinic(IV) acid (0·01 g), sealed in a Pyrex ampoule (*ca.* 20 cm) and heated at 80 °C (24 h), gave (*i*) unchanged olefin (0·18 g, 0·92 mmol, 11% recovered), (*ii*) unchanged dichloro(methyl)silane (1·02 g, 8·84 mmol, 56% recovered), and (*iii*) {*3-[*NN-*bis(trifluoromethyl)amino]propyl}dichloro(methyl)silane* * (2·03 g, 6·61 mmol, 96%) (Found: C, 23·6; H, 3·1; N, 4·7. Calc. for $C_6H_9Cl_2F_6NSi$: C, 23·5; H, 2·9; N, 4·6%), b.p. 163 °C (Siwoloboff).

Photochemical Reaction of Silanes with 1,1-*Di*[NN-*bis(trifluoromethyl)amino]ethylene.*—(a) *Trimethylsilane.* The silane (0·89 g, 12·02 mmol) and the olefin (2·00 g, 6·06 mmol), sealed in a silica tube (*ca.* 300 cm^3) and irradiated with a Hanovia S500 medium-pressure lamp at a distance of *ca.* 10 cm (7 days), gave (*i*) hydrogen (0·004 g, 1·75 mmol, 94%) (Found: *M*, 2·3), (*ii*) unchanged trimethylsilane (0·71 g, 9·64 mmol, 80% recovered), (*iii*) unchanged olefin (1·32 g, 3·99 mmol, 65% recovered), and (*iv*) {*2,2-di*[NN-*bis(trifluoromethyl)amino]ethenyl}trimethylsilane* * (0·72 g, 1·81 mmol, 95%) (Found: C, 27·2; H, 2·7; N, 6·9. Calc. for $C_9H_{10}F_{12}N_2Si$: C, 27·4; H, 2·5; N, 7·0%), b.p. 145 °C (Siwoloboff).

(b) *Dichloro(methyl)silane.* The silane (3·48 g, 30·30 mmol) and the olefin (5·00 g, 15·15 mmol), treated as in the previous experiment (7 days), gave (*i*) hydrogen (0·009 g, 4·69 mmol, 91%) (Found: *M*, 2·1), (*ii*) unchanged dichloro(methyl)silane (2·87 g, 24·98 mmol, 82% recovered), (*iii*) unchanged olefin (3·01 g, 9·10 mmol, 60% recovered), and (*iv*) *dichloro{2,2-di*[NN-*bis(trifluoromethyl)amino]ethenyl}methylsilane* * (2·23 g, 5·04 mmol, 93%) (Found: C, 19·2; H, 1·2; N, 6·1. Calc. for $C_7H_4Cl_2F_{12}N_2Si$: C, 18·9; H, 0·9; N, 6·3%), b.p. 148 °C (Siwoloboff).

Attempted Reaction of Silanes with 1,1-*Di*[NN-*bis(trifluoromethyl)amino]ethylene in the Presence of a Speier Catalyst.*—Reaction of a 2 : 1 molar ratio of trimethylsilane or dichloro(methyl)silane and the olefin in the presence of hexachloroplatinic(IV) acid (*a*) at 80 °C (24 h) and (*b*) at 160 °C (72 h) resulted in unchanged reactants only being obtained.

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† For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full size copies).

[8] D. H. Coy, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J.C.S. Perkin I*, 1973, 1062.

Hydrolysis of {2-[NN-*Bis(trifluoromethyl)amino*]*ethyl*}*dichloro(methyl)silane*.—The silane (30·00 g, 0·101 mol) was slowly added (30 min) to a stirred aqueous solution of potassium hydroxide (4M, 100 cm^3) at a rate sufficient to maintain a reaction temperature of 50—60 °C. After addition of the silane was complete, the mixture was stirred at 60 °C (2 h) and the organic material extracted with diethyl ether (2 × 50 cm^3). The ethereal solution was washed with water, dried (MgSO$_4$), and the ether removed *in vacuo* to afford poly{2-[*NN*-bis(trifluoromethyl)amino]-ethyl}methylsiloxane (19·60 g, 82%).

Preparation of 2,4,6-*Tri*{2-[NN-*bis(trifluoromethyl)amino*]-*ethyl*}-2,4,6-*trimethylcyclotrisiloxane*.—*Experiment* (1). The crude polysiloxane mixture (36·0 g), prepared as in the previous experiment, was distilled from dry powdered potassium hydroxide (1% by weight) under reduced pressure (60 mmHg) using an Ernst Haage spinning-band still (100 cm, 6 mm i.d.) fitted with a heated jacket maintained at *ca.* 165 °C, to afford (*i*) a fraction (11·8 g, 33%), b.p. 100—175 °C, 60 mmHg, which was shown by i.r. and n.m.r. spectroscopy to be mainly {2-[*NN*-bis(trifluoromethyl)amino]ethyl}difluoro(methyl)silane,[1] (*ii*) a trimer fraction (19·81 g, 28·1 mmol, 55%) (Found: C, 24·6; H, 3·2; N, 6·5. *M*, 705. Calc. for $C_{15}H_{21}F_{18}N_3O_3Si_3$: C, 25·1; H, 2·9; N, 5·9%. *M*, 717), b.p. *ca.* 175 °C, 60 mmHg, and (*iii*) a stillpot residue (*ca.* 4 g), b.p. >175 °C, 60 mmHg.

G.l.c. examination of the trimer fraction showed it to contain five components: one major (*ca.* 70% of the fraction); one of shorter retention time (*ca.* 25% of the fraction); and three minor components (*ca.* 5%), two of shorter and one of longer retention time than the major component. The major component was separated by g.l.c. (2m silicone SE30 oil at 170 °C) and was identified as 2,4,6-*tri*{2-[NN-*bis(trifluoromethyl)amino*]*ethyl*-2,4,6-*trimethylcyclotrisiloxane* * (*ca.* 13·5 g, *ca.* 19·7 mmol, *ca.* 38%) (Found: C, 25·1; H, 3·1; F, 47·7; N, 5·8. Calc. for $C_{15}H_{21}F_{18}N_3O_3Si_3$: C, 25·1; H, 2·9; F, 47·7; N, 5·9%), b.p. 184 °C at 60 mmHg.

Experiment (2). The polysiloxane mixture (36·0 g) was distilled as quickly as possible from dry powdered potassium hydroxide (1% by weight), as in the previous experiment, to afford (*i*) a mixture (21·6 g, 60%), b.p. 175—190 °C at 60 mmHg, which was shown by g.l.c. (as before) to contain the difluorosilane, the cyclic trimer, and the cyclic tetramer in the ratio 37 : 53 : 10, (*ii*) a stillpot residue (7·8 g, 20%), b.p. >190 °C at 60 mmHg, which was identified by i.r. spectroscopy as a mixture of siloxanes with the cyclic tetramer as the major component, and (*iii*) {2-[*NN*-bis(trifluoromethyl)amino]ethyl}difluoro(methyl)silane [1] (1·8 g, 6·9 mmol, 5%) (Found: C, 23·1; H, 2·6; N, 5·2. Calc. for $C_5H_7F_8NSi$: C, 22·9; H, 2·6; N, 5·3%) which passed through the receiver and was collected in a cold trap (−196 °C).

The cyclic trimer fractions from two runs (42 g) were combined and redistilled through the spinning-band column in the absence of potassium hydroxide to give (*i*) a mixture (15 g), b.p. 130—150 °C at 60 mmHg, which was shown by g.l.c. (as before) to contain the difluorosilane (3·96 g, 15·1 mmol) and the cyclic trisiloxane (11·04 g, 15·1 mmol), (*ii*) a mixture (15·5 g), b.p. 179—181 °C at 60 mmHg, which was shown by g.l.c. (as before) to contain the difluorosilane and the cyclic trisiloxane in the ratio 7 : 93, and (*iii*) a stillpot residue (10 g), b.p. >181 °C at 60 mmHg. Final redistillation of the 179—181 °C fraction (15·5 g) on the Haage column gave pure cyclic trisiloxane (8·6 g), b.p. 184 °C at 60 mmHg.

Polymerisation of 2,4,6-*Tri*{2-[NN-*bis(trifluoromethyl)*-*amino*]*ethyl*}-2,4,6-*trimethylcyclotrisiloxane*.— A stirred sample (0·30 g, 0·42 mmol) of the cyclic trimer was heated to 150 °C *in vacuo* and anhydrous potassium hydroxide flour (1% by weight) added. After *ca.* 70 s the viscosity of the sample had increased markedly and the product was cooled quickly to 10 °C. Traces of unconverted trimer were removed by heating the sample *in vacuo* to afford poly{2-[*NN*-bis(trifluoromethyl)amino]ethyl}methylsiloxane * (0·27 g, 90%) as a highly viscous slightly opaque gum.

In a second experiment a mixture of the cyclic trimer (5·0 g, 7·1 mmol) and dry potassium hydroxide flour (1·5% by weight) was stirred at 150 °C (6 h) under a nitrogen atmosphere. The viscous product was then cooled and traces of unreacted trimer removed *in vacuo* to afford poly{2-[*NN*-bis(trifluoromethyl)amino]ethyl}methylsiloxane (4·8 g, 96%) [Found: *M*, 3 990. Calc. for $(C_5H_7F_6NOSi)_{16}$: *M*, 3 956].

Mass-spectral Data.—The spectra were all in agreement with the proposed structures. Strong rearrangement peaks were observed for compounds of type R_FSiMe_3 at *m/e* 85 (Me_2SiF^+) and for compounds of type $R_FSi(Me)Cl_2$ at *m/e* 97 and 99 [$MeSi(F)Cl^+$]. The base peak in the spectra of the $SiMe_3$ compounds was at *m/e* 73 (Me_3Si^+) and similarly $(CF_3)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}Si(Me)Cl_2$ showed a base peak at *m/e* 113, 115, and 117 ($MeSiCl_2^+$), but in contrast the base peak for $[(CF_3)_2N]_2C{:}CH{\cdot}Si(Me)Cl_2$ was at *m/e* 69 (CF_3^+).

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