The synthesis of [bis(trifluoromethyl)amino-oxy]-substituted dialkyldichlorosilanes and their conversion into polysiloxanes

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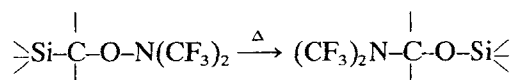
Abstract

Attack of the oxyl $(CF_3)_2NO\cdot$ (1) on an ethyl group of the silane Et_2SiCl_2 occurs at both the α- and β-positions relative to silicon (ratio 31:45), whereas with the silane $Pr^nSiMeCl_2$ attack takes place at the β-position of the propyl group. With the disilane $Me_3SiCH_2SiMe_3$, the major silicon-containing products formed from treatment with oxyl 1 are Me_3SiF, $(CF_3)_2NOSiMe_3$ and $Me_3SiSiMe_3$. Spcier-catalysed (H_2PtCl_6) addition of the silane $HSiCl_2X$ (X = Me and Cl) to the alkene $(CF_3)_2NOCH_2CH=CH_2$ gives the adducts $(CF_3)_2NOCH_2CH_2CH_2SiCl_2X$ (29, X = Me) and (28, X = Cl) in high yield. The substituted dichlorosilanes $(CF_3)_2NOCH_2CH_2SiEtCl_2$ (9), $(CF_3)_2NOCHMeCH_2SiMeCl_2$ (14) and $(CF_3)_2NOCH_2CH_2CH_2SiMeCl_2$ (29) are converted into the corresponding polysiloxanes ('prepolymers' of low molecular weight) by reaction with reagents including water, acid, base and metal oxides; equilibration of the polysiloxane 'prepolymer' 38, derived from dichlorosilane 29 by heating with powdered KOH, affords a solid rubbery polysiloxane.

Introduction

The major products from the reactions of the oxyl $(CF_3)_2NO\cdot$ (1) with the silanes Me_nSiCl_{4-n} were unstable silyl esters $(CF_3)_2NO_2CSiX_3$ ($X_3 = Cl_3$, $MeCl_2$, Me_2Cl and Me_3) which decomposed by elimination of carbon monoxide or carbon dioxide [1]. With the alkyltrihalogenosilanes $RSiCl_3$ (R = Et, Pr^n, Pr^i and Bu^n) and $RSiF_3$ (R = Et and Pr^n), the α-position of the alkyl group is deactivated towards attack by radical 1. This has been interpreted as being mainly steric in origin because the α-position is less deactivated in the alkyltrifluorosilanes than in the corresponding alkyltrichlorosilanes [2]. A number of the α-amino-oxy-substituted alkylsilanes isomerise on heating [2, 3], i.e.

$$\mathrm{\underset{|}{\overset{|}{>}Si-\underset{|}{\overset{|}{C}}-O-N(CF_3)_2} \overset{\Delta}{\longrightarrow} (CF_3)_2N-\underset{|}{\overset{|}{C}}-O-Si\underset{<}{\overset{<}{}}}$$
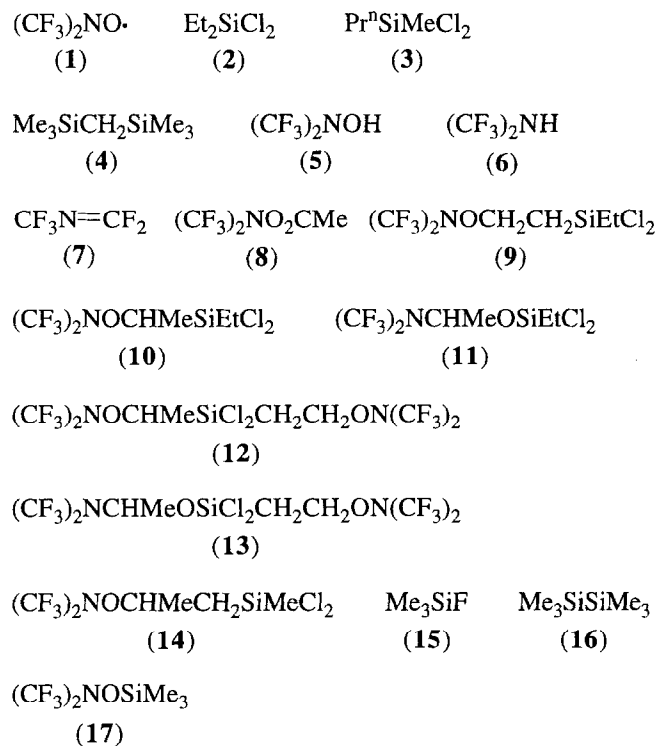
and the resultant alkoxysilanes are susceptible to hydrolysis [4] which precludes their use in the synthesis of polysiloxanes containing the $(CF_3)_2NO$ group.

In the present work, routes to dialkyldichlorosilanes containing the $(CF_3)_2NO$ group β or γ to silicon have been investigated with the object of using them to prepare the corresponding polysiloxanes.

Results and discussion

The results obtained from the reaction of oxyl 1 with the dialkyldichlorosilanes 2 and 3 and 2,2,4,4-tetramethyl-2,4-disilapentane (4) are summarised in Table 1.

$$(CF_3)_2NO\cdot \quad Et_2SiCl_2 \quad Pr^nSiMeCl_2$$
$$(1) \qquad\quad (2) \qquad\quad (3)$$

$$Me_3SiCH_2SiMe_3 \quad (CF_3)_2NOH \quad (CF_3)_2NH$$
$$(4) \qquad\qquad\quad (5) \qquad\qquad (6)$$

$$CF_3N{=}CF_2 \quad (CF_3)_2NO_2CMe \quad (CF_3)_2NOCH_2CH_2SiEtCl_2$$
$$(7) \qquad\qquad (8) \qquad\qquad\qquad (9)$$

$$(CF_3)_2NOCHMeSiEtCl_2 \qquad (CF_3)_2NCHMeOSiEtCl_2$$
$$(10) \qquad\qquad\qquad\qquad (11)$$

$$(CF_3)_2NOCHMeSiCl_2CH_2CH_2ON(CF_3)_2$$
$$(12)$$

$$(CF_3)_2NCHMeOSiCl_2CH_2CH_2ON(CF_3)_2$$
$$(13)$$

$$(CF_3)_2NOCHMeCH_2SiMeCl_2 \quad Me_3SiF \quad Me_3SiSiMe_3$$
$$(14) \qquad\qquad\qquad (15) \qquad\quad (16)$$

$$(CF_3)_2NOSiMe_3$$
$$(17)$$

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TABLE 1. Reaction of oxyl 1 with silanes at room temperature

Silane	Molar ratio silane/1	Recovered silane (%)	Products (%)[a]			
			5	6	7	Others
2	1:2	28	54	7	1	8, 7.5 (10); 9, 16 (45); 10, 11 (31)[b]; 12, 2 (3)[c]
3	1:1	58	50			14, 37 (87)[d]
4	1:1	77	33	23	31	CO$_2$, 25; 15 (40); 16 (15); 17, 10 (21)

[a]Based on oxyl 1; yields in parentheses are based on silane used, i.e. not recovered.
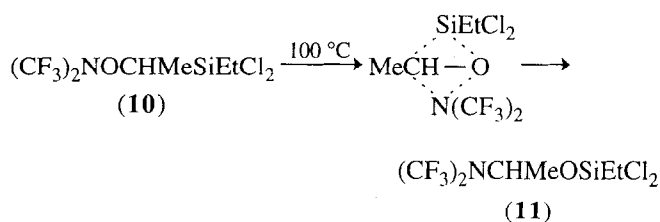[b]Underwent partial thermal rearrangement to 11 on GLC separation (100 °C).
[c]Underwent partial rearrangement to 13 on GLC separation (100 °C).
[d]Unidentified mixture (c. 2%) of bis- and/or poly-substituted silanes also formed.

Oxyl 1 attack on dichlorodiethylsilane 2 occurred both at the α- and β-positions relative to silicon in the ethyl group to give the monosubstituted silanes 10 and 9, respectively, with major attack taking place at the β-position; this is discussed later.

Compounds 9 and 10 were distinguished and identified from the NMR spectral data obtained, i.e. compound 9 contained a CH$_2$CH$_2$O group [δ_H 4.25 (t, 2H, CH$_2$-O, $J = 7$ Hz); 1.53 (t, 2H, Si-CH$_2$, $J = 7$ Hz) ppm] and a β-(CF$_3$)$_2$NO group (δ_F +8.85 ppm), while compound 10 contained an MeCHO group [δ_H 4.20 (q, 1H, MeCH-O, $J = 6.5$ Hz); 1.54 (d, 3H, CH$_3$CH, $J = 6.5$ Hz) ppm] and an α-(CF$_3$)$_2$NO group (δ_F +10.0 ppm). In general, (CF$_3$)$_2$NO groups α to silicon absorb to lower field than those β to silicon [2]. The NMR spectra of compound 10 (obtained by GLC separation at 100 °C) also contained bands for the rearranged isomer 11 {δ_H 5.60 [q, 1H, N-CH(Me)-O, $J = 6.5$ Hz] and 1.68 (d, 3H, CH$_3$CH, $J = 6.5$ Hz) ppm; δ_F +22.5 [s, (CF$_3$)$_2$N] ppm}. The relative NMR intensities for compounds 10 and 11 indicated that c. 15% rearrangement had occurred, i.e.

$$(CF_3)_2NOCHMeSiEtCl_2 \xrightarrow{100\ °C} \underset{\underset{N(CF_3)_2}{|}}{MeCH-O} \cdots SiEtCl_2 \longrightarrow$$
(10)

$$(CF_3)_2NCHMeOSiEtCl_2$$
(11)

The disubstituted compound 12 also rearranged partially on GLC separation at 100 °C and the NMR spectra indicated that compound 12 and its rearranged isomer 13 were present in a c. 1:1 ratio, i.e. ^{1}H NMR absorptions at δ_H 5.60 (q, 1H, N-CHMe-O in 13, $J = 6.5$ Hz); 4.25 (complex, c. 5H, CH-O in 12 and CH$_2$-O in 12 and 13); 1.60–1.20 (complex, c. 10H, SiCH$_2$ and CH$_3$ in 12 and 13) ppm and ^{19}F NMR absorptions at δ_F +22.5 [(CF$_3$)$_2$N in 13]; +10.0 [α-(CF$_3$)$_2$NO in 12];

+8.9 [β-(CF$_3$)$_2$NO in 12 and 13] ppm in the ratio c. 1:1:2.

The presence of the amine 6, the azapropene 7 and the O-acetylhydroxylamine 8 in the products can be explained by further oxyl 1 attack on the α-substituted silane 10 followed by decomposition of the resulting radical 18 and/or the α,α-disubstituted silane 19. All of the isolated products 5–13 are considered to be formed as shown in Scheme 1.

Two of the products required by Scheme 1, i.e. 20 and 21 were not isolated, but they would have been formed in low yield and could have been present in the minor unidentified products; compounds analogous to 20, i.e. (CF$_3$)$_2$NOSiX$_3$ (X = F and Cl) have been isolated in low yield from the reaction of oxyl 1 with the silanes EtSiCl$_3$ and EtSiF$_3$ [2].

Exclusive oxyl 1 attack on dichloromethyl-n-propyl-silane (3) occurred at the β-position of the n-propyl group to give the substituted silane 14, which was identified by its ^{1}H NMR [δ_H 4.50 (sextet, 1H, CH$_2$CH(Me)-O, $J = 7$ Hz); 1.50 (complex, 5H, SiCH$_2$ and CH$_3$); 0.79 (s, 3H, Si-CH$_3$) ppm] and ^{19}F NMR spectra [δ_F +10.55 ppm, (CF$_3$)$_2$NO].
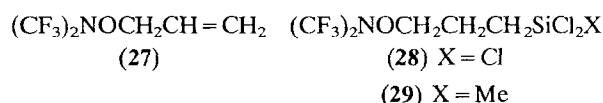
The relative reactivities of the C–H bonds in the dialkyldichlorosilanes 2 and 3 towards attack by oxyl 1 are compared in Table 2 with those reported previously for similar compounds. Table 2 has been compiled in terms of the mole fractions of products formed from attack in the various positions, with allowance made for the number of hydrogens available for abstraction in each position. The mole fraction of product resulting from attack at the most favoured position has been set equal to unity and the mole fractions of the other products are expressed relative to this.

The factors involved in the attack by oxyl 1 on C–H bonds in alkylchlorosilanes have been discussed in detail previously [2] and it was concluded that the following are important: (i) the ease of hydrogen abstraction, i.e. tertiary > secondary > primary; (ii) electrostatic re-

Et_2SiCl_2 $\xrightarrow{(1)}$ $(CF_3)_2NOH$ + $Me\overset{\cdot}{C}HSiEtCl_2$ + $\overset{\cdot}{C}H_2CH_2SiEtCl_2$

(2)   **(5)**

$(CF_3)_2NCHMeOSiEtCl_2$ $\xleftarrow{\;\triangle\;}$ $(CF_3)_2NOCHMeSiEtCl_2$ $(CF_3)_2NOCH_2CH_2SiEtCl_2$

(11)   **(10)**   **(9)**

$(CF_3)_2NO\overset{O-N(CF_3)_2}{\underset{Me}{\overset{|}{\underset{|}{C}}}}SiEtCl_2$ $\xleftarrow{(1)}$ $(CF_3)_2NO\overset{\cdot}{C}MeSiEtCl_2$ + **(5)**

(19)   **(18)**

         (5) + $(CF_3)_2NOCHMeSiCl_2CH_2CH_2ON(CF_3)_2$

             (12)

β– scission $\;\downarrow\;\triangle$

$MeCOSiEtCl_2$ + $(CF_3)_2N\cdot$ $(CF_3)_2NCHMeOSiCl_2CH_2CH_2ON(CF_3)_2$

            (13)

$\overset{>}{\underset{}{C}}$-H → $(CF_3)_2NH$

$Me\overset{\cdot}{C}=O$ + $\overset{\cdot}{S}iEtCl_2$ **(6)**

$(CF_3)_2NSiEtCl_2$ + $(CF_3)NO_2CMe$ $(CF_3)_2N\cdot$

         (8)

$(CF_3)_2NOSiEtCl_2$ $(CF_3)_2NSiEtCl_2$

   (20)

$CF_3-N\overset{CF_2}{\underset{SiEtCl_2}{\diagdown}}F$ $\longrightarrow$ $CF_3N=CF_2$ + $FSiEtCl_2$

         (7)   **(21)**

Scheme 1.

TABLE 2. Relative reactivities of C–H bonds towards attack by oxyl 1

Substrate									
–SiEt	$Cl_3Si–CH_2–CH_3$[a]			$MeCl_2Si–CH_2–CH_3$[b]			$EtCl_2Si–CH_2–CH_3$		
	1.0	1.0		0	1.0	0.39		1.0	0.77
–SiPr	$Cl_3Si–CH_2–CH_2–CH_3$[a]			$MeCl_2Si–CH_2–CH_2–CH_2$			$Cl_3Si–CH(CH_3)_2$[a]		
	0	1.0	0	0	0	1.0	0	1.0	0
–SiBu	$Cl_3Si–CH_2–CH_2–CH_2–CH_3$[a]								
	0	0.54	1.0	0					

[a]Ref. 2.
[b]Ref. 4.

pulsion between lone pairs on chlorine and oxyl 1 and steric hindrance which deactivate positions α to silicon; (iii) the inductive effect of the –Si group which will most affect the α-position; and (iv) hyperconjugative stabilisation of the intermediate radical, i.e. the greater the number of β-hydrogens the more stable the radical.

Scheme 2.

Deactivation of the α-position by the steric bulk of the groups on silicon is shown clearly by comparison of the results obtained with the silanes $EtSiMeCl_2$ and Et_2SiCl_2 for which replacement of methyl by ethyl considerably increased attack at the β-position. Exclusive attack at the β-position of the n-propyl groups was observed with the silanes Pr^nSiCl_3 and $Pr^nSiMeCl_2$, and so replacement of a chlorine by methyl did not result in any attack at the α-position in contrast to greater α-attack on the silane $EtSiMeCl_2$ as compared to $EtSiCl_3$. The much greater hyperconjugative stabilisation of the β-radical (five β-hydrogens) relative to that of the α-radical (two β-hydrogens) would appear to be the dominant factor in this case.

The reaction with the disilapentane 4 was investigated to determine whether the CH_2 group was activated or deactivated by the bulky but electron-releasing $SiMe_3$ groups towards attack by the weakly electrophilic $(CF_3)_2NO \cdot$ radical. Deactivation could result in oxyl 1 attack occurring at the methyl group.

Compounds containing $(CF_3)_2NO$ groups bonded to carbon were not detected and the products 5–7, 15–17 and CO_2 can all be rationalised as being formed via initial oxyl 1 attack at the CO_2 group leading to the monosubstituted compound 22 followed by abstraction of the methine hydrogen to give the radical 23, the precursor of the 3,3-disubstituted disilapentane 24, as shown in Scheme 2; evidence was not obtained for attack taking place at the methyl groups.

Decomposition of **23** and/or **24** via six-centre transition states led to the silyl ester **25**, further decomposition of which by a radical mechanism could account for all the observed products, although the fluorosilane **15** could have arisen, at least in part, by decomposition involving a six-centre transition state. Compounds analogous to **26**, containing a $(CF_3)_2N$ group bonded to silicon, have been observed previously to be unstable and to decompose via a four-centre transition state to give a fluorosilane and the azapropene **7** [5].

Synthesis of γ-substituted propylsilanes of the type $(CF_3)_2NOCH_2CH_2CH_2Si\underset{\sim}{\leqslant}$ was next investigated and it was considered that Speier-catalysed (H_2PtCl_6) addition of hydrosilanes $HSi\underset{\sim}{\leqslant}$ across the olefinic double bond of 3-[bis(trifluoromethyl)-amino-oxy]propene (**27**) was a reasonable route. The alkene **27** was prepared in 85% yield by reaction of the salt $(CF_3)_2NONa$ with allyl bromide in diglyme at 50 °C; it has been made previously by reaction of the complex $(CF_3)_2NOH–CsF$ with allyl chloride [6].

The Speier-catalysed additions of the hydrosilanes $HSiCl_2X$ (X = Cl or Me) to alkene **27** at 80 °C (1.1:1 molar ratio) went smoothly and gave the corresponding γ-substituted propylsilanes **28** (66%) and **29** (85%)

$(CF_3)_2NOCH_2CH=CH_2$ $(CF_3)_2NOCH_2CH_2CH_2SiCl_2X$
      (27)   **(28)** X = Cl

                                (29) X = Me

which were identified by their ^1H and ^{19}F NMR spectra as containing a $SiCH_2CH_2CH_2O$ grouping [δ_H c. 4.0 (t, 2H, $-CH_2-O$, J = 6 Hz); c. 1.8 (mult., 2H, $C-CH_2-C$); c. 1.3 (mult., 2H, CH_2Si) ppm] and a $(CF_3)_2NO$ group (δ_F c. 9 ppm).

The following minor products were also obtained from the two reactions: $MeCH=CH_2$ (trace and trace), $(CF_3)_2NOCH_2CH_2CH_3$ (**30**) (5% and 6%) and unchanged **27** (3% and 2%) recovered with yields based on **27** and $CH_3CH_2CH_2SiCl_2X$ (**31**) (X = Cl 7%) and **3** (X = Me, 6%), $(CF_3)_2NOSiCl_2X$ (**32**) (a, X = Cl, 8%; b, X = Me, 6%), $XCl_2SiSiCl_2X$ (**33**) (a, X = Cl, 2%; b, X = Me, 3%) and $XSiCl_3$ (**34**) (a, X = Cl, 3%); b, X = Me, 2%) with yields based on reactant hydrosilane.

The structures of the minor products, except **30**, were established by a comparison of their IR, NMR and mass spectra with those of authentic pure samples available in this Department. The propyl derivative **30** was identified in a mixture with unchanged alkene **27** via its ^1H NMR [δ_H 4.05 (t, 2H, CH_2-O, J = 6 Hz); 1.68 (sextet, 2H, $CH_3-CH_2-CH_2$, J = 6 Hz); 1.01 (t, 3H, CH_3, J = 6 Hz) ppm], ^{19}F NMR {δ_F +7.9 [s, $(CF_3)_2NO$] ppm} and mass spectra {band at m/z 43, 45%, $CH_3CH_2CH_2^+$, $[M-(CF_3)_2NO]^+$, which is not present in the mass spectrum of compound **27**}.

The Speier-catalysed reaction of trichlorosilane with allyl chloride gave, apart from the adduct

$(CF_3)_2NO\cdot\ +\ HSiCl_2X\ \longrightarrow$

(1)

$(CF_3)_2NOH\ +\ \overset{\cdot}{Si}Cl_2X\ \xrightarrow{\ x2\ }\ XCl_2SiSiCl_2X$

                                       (33)

$(CF_3)_2NOH\ +\ CH_2=CHCH_3\ \xrightarrow{H_2PtCl_6}$

$(CF_3)_2NOCH_2CH_2CH_3$

      (30)
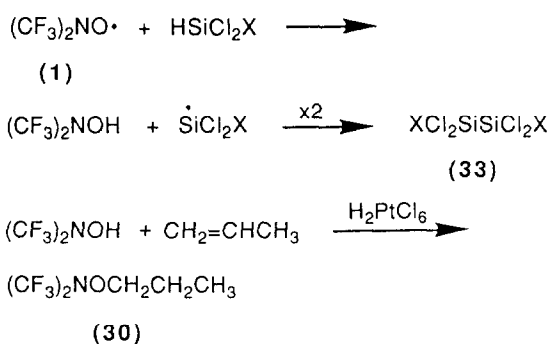
Scheme 3.

$ClCH_2CH_2CH_2SiCl_3$ (66%), propene (c. 3%), $CH_3CH_2CH_2SiCl_3$ (13%) and $SiCl_4$ (25%) [7], corresponding to the formation of propene and silanes **31** or **3**, **32** and **34** in the present reaction. However, products corresponding to the reduced alkene **30** and the disilanes **33** were not detected and it is possible that these compounds arise via the radical $(CF_3)_2NO\cdot$ which is formed in the reaction and abstracts a hydrogen atom from reactant hydrosilane (Scheme 3).

The formation of polysiloxanes from the β-substituted silanes $(CF_3)_2NOCHRCH_2SiR'Cl_2$ (**9**) (R = H, R' = Et) and (**14**) (R = R' = Me) and the γ-substituted silane $(CF_3)_2NO(CH_2)_3SiMeCl_2$ (**29**) was next investigated.

High molecular weight polysiloxanes are in general prepared by a two-stage process from dialkyldichlorosilanes. The first step involves conversion to a mixture of low molecular weight linear and cyclic polysiloxanes ('prepolymer') commonly by hydrolysis or reaction with a metal oxide. In the second step, the 'prepolymer' is further polymerised, e.g. by heat or reaction with acid, base or transition metal compounds. In the case of high molecular weight polymers containing strong electron-withdrawing groups, e.g. $[CF_3CH_2CH_2SiMeO]_n$, it has been found necessary to equilibrate the 'prepolymer' with base to form the cyclic trisiloxane which is then further polymerised [8].

The dichlorosilanes **9** and **14** underwent ready hydrolysis with water to give low molecular weight polysiloxanes **35** (n = c. 7) and **36** (n = c. 4), respectively, which contained OH end-groups as shown by their IR spectra (broad O-H str. centred on c. 3250 cm^{-1}).

Attempts to prepare high molecular weight polysiloxanes from these 'prepolymers' by heating with acid or base were unsuccessful.

A low molecular weight copolymer **37** (n = c. 1) was made by hydrolysis of a 4:1 molar mixture of dichlorodimethylsilane and dichlorosilane **9**. When this was heated with a catalytic amount of concentrated sulphuric acid, it discoloured but there was little apparent increase in viscosity.
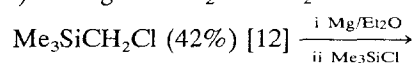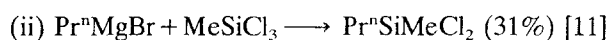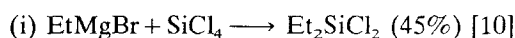
Attention was next turned to the polymerisation of the γ-substituted silane 29 and low molecular weight polysiloxane oils 38 were obtained by treatment of a solution of 29 (a) in diethyl ether with the reagents (i) H_2O at 0 °C ($n = 3.8$), (ii) $NaHCO_3$ at 35 °C ($n = 3.8$) and (iii) $CuSO_4 \cdot 5H_2O$ at 20 °C ($n = 4.5$) or (b) in acetonitrile at 80 °C with (i) $PbO_2/HgCl_2$ (catalytic amount) ($n = 5.2$) and (ii) $MgO/HgCl_2$ (catalytic amount) ($n = 5.7$) or by treatment with (i) 50% aqueous sulphuric acid at 0 °C ($n = 8.5$) and (ii) 30% aqueous KOH at 0 °C ($n = 10$). The IR spectra of all the samples of 'prepolymer' 38 showed that OH end-groups were present (broad band centred on c. 3250 cm^{-1}). Further polymerisation of 'prepolymer' 38 was investigated by heating with catalytic amounts of (a) concentrated H_2SO_4, (b) solid $FeCl_3$, (c) Et_3N and (d) solid KOH. In reactions (a)–(c) an increase in viscosity was noted, while reaction (d) gave a solid rubbery polymer for which a molecular weight was not determined because of its insolubility in suitable solvents, although it was soluble in trifluoroacetic acid. All of the polymers prepared by further treatment of 'prepolymer' 38 showed the absence of the O–H stretching band (c. 3250 cm^{-1}) in their IR spectra, i.e. they had structure 39.

(35)

(36)

(37)

(38)

(39)
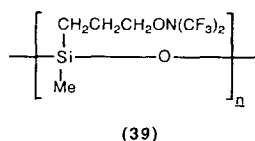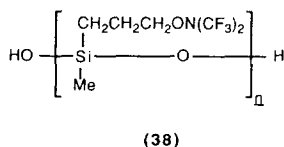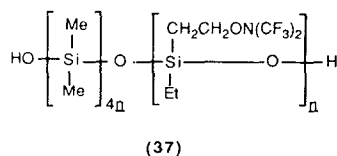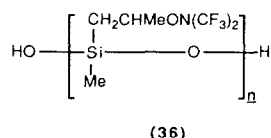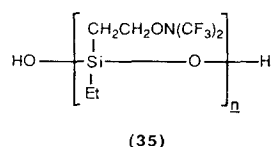
Experimental

Starting materials

The oxyl 1 was prepared by oxidation of the hydroxylamine $(CF_3)_2NOH$ (5) with silver(II) oxide [9]. Of the reactant silanes, $HSiCl_3$, $HSiMeCl_2$ and $Me_2SiClCH_2Cl$ were commercial samples which were distilled before use and the remaining silanes were prepared as follows (yields refer to pure compounds obtained by fractional distillation);

(i) $EtMgBr + SiCl_4 \longrightarrow Et_2SiCl_2$ (45%) [10]

(ii) $Pr^nMgBr + MeSiCl_3 \longrightarrow Pr^nSiMeCl_2$ (31%) [11]

(iii) $MeMgBr + Me_2SiClCH_2Cl \longrightarrow$

Me_3SiCH_2Cl (42%) [12] $\xrightarrow[\text{ii } Me_3SiCl]{\text{i } Mg/Et_2O}$

$Me_3SiCH_2SiMe_3$ (55%) [13]

General techniques

The reactions involving nitroxide 1 or the Speier catalyst H_2PtCl_6 were carried out in vacuo in Rotaflo tubes (c. 300 cm^3). Products were separated by fractional condensation in vacuo or GLC [Perkin-Elmer F21 or Aerograph Autoprep machines using columns (3.5–6 m) packed with silicone SE30 or OV1 oils (10%–20% w/w) on Celite as indicated in the text] and were examined by IR spectroscopy (Perkin-Elmer 257 instrument), ^1H NMR spectroscopy [Perkin-Elmer R10 (60.0 MHz), Hitachi R20A (60.0 MHz) or Varian Associates HA 100 (100.0 MHz) spectrometers; internal reference tetramethylsilane], ^{19}F NMR spectroscopy [Perkin-Elmer R10 (56.46 MHz) or Varian Associates HA100 (94.12 MHz) instruments; external reference trifluoroacetic acid] and mass spectrometry (A.E.I. MS902 instrument with an electron beam energy of 70 eV). The NMR spectra were recorded using neat liquids or solutions in $CDCl_3$ (as stated in the text); chemical shifts to low field of reference are designated positive.

Molecular weights of polymers were determined by vapour phase osmometry (Hitachi Perkin-Elmer 115 instrument) and boiling points were measured using Siwoloboff's method.

Reactions of bis(trifluoromethyl)amino-oxyl (1) with silanes

(a) Dichlorodiethylsilane (2)

A mixture of oxyl 1 (13.44 g, 80.0 mmol) and silane 2 (6.28 g, 40.0 mmol) kept at room temperature (4 h) gave a volatile material (15.37 g) which on fractional condensation in vacuo afforded (i) a −196 °C fraction (1.18 g) identified [IR spectroscopy and GLC (3.5 m SE30 at 30 °C)] as a mixture of N,N-bis(trifluoromethyl)amine (6) (0.87 g, 5.6 mmol, 7%) and perfluoro-2-azapropene (7) (0.14 g, 1.1 mmol, 1%); (ii) N,N-bis(trifluoromethyl)hydroxylamine (5) (7.01 g, 41.4 mmol, 51%) which condensed at − 78 °C; (iii) a −45 °C fraction (1.0 g) shown by IR spectroscopy and GLC (3.5 m SE30 at 50 °C) to consist of hydroxylamine 5 (0.36 g, 2.1 mmol, 3%) and N,N-bis(trifluoromethyl)-O-acetylhydroxylamine (8) (0.64 g, 3.0 mmol, 10%); and (iv) a combined − 23 °C and 0 °C fraction (6.17 g) which was shown by GLC (6 m OV1 at 90 °C) to consist of three components (A–C). A colourless liquid

residue (3.67 g) was also obtained, which contained four components (A–D) as shown by GLC (6 m OV1 at 90 °C), and this was combined with the −23 °C and 0 °C fraction and the components separated by preparative-scale GLC (6 m OV1 at 100 °C).

Component A was identified as unchanged silane 2 (1.79 g, 11.4 mmol, 28% recovered).

Component B was identified as {2-[bis(trifluoromethyl)amino-oxy]ethyl}dichloroethylsilane (9) (nc) (4.22 g, 13.0 mmol, 45%) (Analysis: Found: C, 22.5; H, 2.6%. $C_6H_9Cl_2F_6NOSi$ requires: C, 22.2; H, 2.8%), b.p. 184 °C. ^1H NMR (neat) δ: 4.25 (t, 2H, CH_2O, $J=7$ Hz); 1.53 (t, 2H, CH_2Si, $J=7$ Hz); 1.15 (mult., 5H, Et) ppm. ^{19}F NMR δ: +8.85 [s, $(CF_3)_2NO$)] ppm. MS m/z: 308/310/312 [2.2%, $(M-CH_3)^+$]; 294/296/298 [4.9, $(M-C_2H_5)^+$]; 155/157/159 {25.3, $[M-(CF_3)_2-NO]^+$}; 114 (1.6, $C_2F_4N^+$); 99/101/103 (55.5, $SiHCl_2^+$); 69 (100.0, CF_3^+); 63/65 (24.2, $SiCl^+$).

Component C was identified as {1-[bis(trifluoromethyl)amino-oxy]ethyl}dichloroethylsilane (10) (nc) (2.87 g, 8.9 mmol, 31%) (Analysis: Found: C, 22.4; H, 2.9%. $C_6H_9Cl_2F_6NOSi$ requires: C, 22.2; H, 2.8%). ^1H NMR (neat) δ: 4.20 (q, 1H, $\rangle$CHO, $J=6.5$ Hz); 1.54 (d, 3H, CH_3, $J=6.5$ Hz); 1.16 (mult., 5H, Et) ppm. ^{19}F NMR δ: +10.0 [s, $(CF_3)_2NO$] ppm; the ^1H and ^{19}F NMR spectra indicated that some rearrangement (c. 15%) to {1-[bis(trifluoromethyl)amino]ethoxy}ethyldichlorosilane (11) had taken place during GLC separation.

Component D (0.42 g, 0.86 mmol, 3%) was tentatively identified as a mixture of {1-[bis(trifluoromethyl)amino]ethoxy}-{2'-[bis(trifluoromethyl)amino-oxy]-ethyl}dichlorosilane (13) and {1,2'-bis(trifluoromethyl)amino-oxy]ethyl}dichlorosilane (12). ^1H NMR (neat) δ: 5.60 (q, 1H, CHOSi, $J=6.5$ Hz); 4.25 (complex, c. 5H, $\rangle$CHO and CH_2O); 1.60 (complex, c. 10H, CH_2Si and CH_3) ppm. ^{19}F NMR δ: +22.5 (s, c. 3F, $(CF_3)_2N$]; +10.0 [s, c. 6F, β-$(CF_3)_2NO$]; +8.9 [s, c. 3F, α-$(CF_3)_2NO$] ppm. MS m/z: 310/312/314 {14.2%, $[M-(CF_3)_2NCHMe]^+$}; 294/296/298 {15.9 $[M-(CF_3)_2NOCHMe]^+$}; 180 [69.0, $(CF_3)_2NCHMe^+$]; 169 [22.3, $(CF_3)_2NOH^+$]; 161/163/165 (32.0, $C_2H_4Cl_2FOSi^+$); 69 (100.0, CF_3^+).

(b) Dichloromethyl-n-propylsilane (3)

A mixture of oxyl 1 (3.33 g, 19.82 mmol) and silane 3 (3.32 g, 21.2 mmol), kept at room temperature (2 h), gave a volatile material (3.68 g) which on fractional condensation in vacuo afforded a −78 °C fraction, identified as a mixture of hydroxylamine 5 (1.66 g, 9.8 mmol, 50%) and unchanged silane 3 (0.60 g, 3.8 mmol, 18% recovered) by GLC (3.5 m SE30 at 50 °C) and a −45 °C fraction, identified as unchanged silane 3 (1.42 g, 9.0 mmol, 43% recovered). The colourless non-volatile liquid residue (3.10 g) was separated into its

two components by preparative-scale GLC (6 m OV1 at 80 °C) to give (i) {2-[bis(trifluoromethyl)amino-oxy]propyl}dichloromethylsilane (14) (nc) (2.36 g, 7.28 mmol, 87%) (Analysis: Found: C, 22.4; H, 2.9; F, 35.4%. $C_6H_9Cl_2F_6NOSi$ requires: C, 22.2; H, 2.8; F, 35.2%), b.p. 179 °C. ^1H NMR (neat) δ: 4.50 (sextet, 1H, $\rangle$CHO, $J=7$ Hz); 1.50 (complex, 5H, CH_2Si and CH_3); 0.79 (s, 3H, CH_3Si) ppm. ^{19}F NMR δ: +10.55 [s, β-$(CF_3)_2NO$] ppm. MS m/z: 196 [2.1%, $(M-CH_2SiMeCl_2)^+$]; 155/157/159 (26.1, $C_4H_9Cl_2Si^+$); 150 (9.1, $C_2HF_5NO^+$); 113/115/117 (100.0, $CH_3SiCl_2^+$); 69 (21.9, CF_3^+); 63/65 (11.7, $ClSi^+$); 43 (12.1, CH_3Si^+); and (ii) an unidentified liquid (0.44 g) which was shown (IR, NMR spectroscopy and mass spectrometry) to be a complex mixture of bis- and poly-[N,N-bis(trifluoromethyl)amino-oxy]-substituted derivatives of the reactant silane.

(c) 2,2,4,4,-Tetramethyl-2,4-disilapentane (4)

A mixture of oxyl 1 (3.36 g, 20.0 mmol) and the disilapentane 4 (3.20 g, 20.0 mmol), kept at room temperature (4 h), gave a volatile material (6.39 g), which on fractional condensation in vacuo afforded (i) a −196 °C fraction, identified (IR spectroscopy) as carbon dioxide (0.22 g, 5.0 mmol, 25%) (Analysis: Found: M, 44); (ii) a −123 °C fraction (1.52 g), shown by IR spectroscopy and GLC (3.5 m SE30 at 30 °C) to consist of amine 6 (0.70 g, 4.6 mmol, 23%) and azapropene 7 (0.82 g, 6.2 mmol, 31%); (iii) a −78 °C fraction (2.19 g) which was separated by preparative-scale GLC (3.5 m SE30 at 40 °C) into its components hydroxylamine 5 (1.12 g, 6.6 mmol, 33%), trimethylfluorosilane 15 (0.38 g, 4.1 mmol, 44%), [bis(trifluoromethyl)amino-oxy]trimethylsilane (17) (0.47 g, 1.95 mmol, 21%) and hexamethyldisilane 16 (0.11 g, 0.73 mmol, 15%); and (iv) unchanged 4 (2.46 g, 15.4 mmol, 77% recovered) which condensed at −23 °C. The colourless non-volatile residue (0.11 g) which remained in the tube was shown (NMR spectroscopy) to be a multicomponent mixture and it was not examined further.

Preparation of 3-[bis(trifluoromethyl)amino-oxy]propene (27)

A solution of sodium bis(trifluoromethyl)amino-oxyl [prepared from N,N-bis(trifluoromethyl)hydroxylamine (5) (8.8 g, 52.0 mmol) and sodium hydride (1.29 g, 50.0 mmol)] in diglyme (25 cm^3) was added dropwise to a stirred solution of allyl bromide (6.2 g, 50.0 mmol) in diglyme (15 cm^3) at 50 °C and the solution was then further stirred (1 h) at 50 °C. Fractional distillation of the volatile material gave 3-[bis(trifluoromethyl)amino-oxy]propene (27) (8.9 g, 42.5 mmol, 85%).

Speier-catalysed additions of silanes to 3-[bis(trifluoromethyl)amino-oxy]propene (27)

(a) Dichloromethylsilane

A mixture of propene 27 (4.18 g, 20.0 mmol), dichloromethylsilane (2.50 g, 22.0 mmol) and hexachloroplatinic acid (0.1 g), heated at 80 °C (20 h), gave a volatile material (1.14 g), which on fractional condensation *in vacuo* afforded (i) a -196 °C fraction shown (IR spectroscopy) to be propene (0.1 g, 0.3 mmol, 1.5%); (ii) a -78 °C fraction (0.84 g) which was separated by preparative-scale GLC (6 m OV1 at 40 °C) into a mixture of 1-[bis(trifluoromethyl)amino-oxy]propane (30) (0.25 g, 1.2 mmol, 6%) and unchanged propene 27 (0.05 g, 0.24 mmol, 1% recovered), 2,2,3,3-tetrachloro-2,3-disilabutane (33b) (0.08 g, 0.33 mmol, 3%), trichloromethylsilane (34b) (0.07 g, 0.44 mmol, 2%) and [bis(trifluoromethyl)amino-oxy]dichloromethylsilane (32b) (0.34 g, 1.2 mmol, 6%); and (iii) dichloromethyl-n-propylsilane (3) (0.20 g, 1.3 mmol, 6%) which condensed at -23 °C.

The non-volatile liquid residue was distilled to give {3-[bis(trifluoromethyl)amino-oxy]propyl}dichloromethylsilane (29) (nc) (5.50 g, 17.0 mmol, 85%) (Analysis: Found: C, 22.3; H, 3.0; F, 35.0%. $C_6H_9Cl_2F_6NOSi$ requires: C, 22.2; H, 2.8; F, 35.2%), b.p. 170 °C. ^1H NMR (neat) δ: 4.07 (t, 2H, CH_2O, $J=6$ Hz); 1.81 (complex, 2H, CH_2); 1.16 (complex, 2H, CH_2Si); 0.99 (s, 3H, CH_3) ppm. ^{19}F NMR δ: $+8.5$ [s, $(CF_3)_2NO$] ppm. MS m/z: 155/157/159 {21.9% [M $-$ $(CF_3)_2NO$]$^+$}; 113/115/117 (100.0, $CH_3Cl_2Si^+$); 69 (10.3, $CF_3{}^+$); 63/65 (6.4 ClSi$^+$).

(b) Trichlorosilane

A mixture of propene 27 (4.18 g, 20.0 mmol), trichlorosilane (2.71 g, 22.0 mmol) and hexachloroplatinic acid (0.1 g), heated at 80 °C (20 h), gave a volatile material (1.36 g) which on fractional condensation *in vacuo* afforded (i) a -196 °C fraction identified (IR spectroscopy) as propene (0.08 g, 0.2 mmol, 1%); (ii) a -78 °C fraction (1.01 g) which was separated by preparative-scale GLC (6 m OV1 at 50 °C) into a mixture of 1-[bis(trifluoromethyl)amino-oxy]propane (30) (0.21 g, 1.0 mmol, 5%) and unchanged propene 27 (0.07 g, 0.3 mmol, 2% recovered), hexachlorodisilane (33a) (0.06 g, 0.2 mmol, 2%), tetrachlorosilane (34a) (0.12 g, 0.7 mmol, 3%) and [bis(trifluoromethyl)amino-oxy]trichlorosilane (32a) (0.53 g, 1.76 mmol, 8%); and (iii) trichloro-n-propylsilane (31) (0.27 g, 1.5 mmol, 7%) which condensed at -23 °C.

The non-volatile residue was distilled to give {3-[bis(trifluoromethyl)amino-oxy]propyl}trichlorosilane (28) (nc) (4.50 g, 13.2 mmol, 66%) (Analysis: Found: C, 17.7; H, 1.8; F, 32.8%. $C_5H_6Cl_3F_6NOSi$ requires: C, 17.4; H, 1.8; F, 33.1%), b.p. 187 °C. ^1H NMR (neat) δ: 3.97 (t, 2H, CH_2O, $J=6$ Hz); 1.84 (complex, 2H,

CH_2); 1.40 (t, 2H, CH_2Si, $J=6$ Hz) ppm. ^{19}F NMR δ: $+9.2$ [s, $(CF_3)_2NO$] ppm. MS m/z: 175/177/179/181 {79.2%, [M $-$ $(CF_3)_2NO$]$^+$}; 150 (7.1, $C_2HF_5NO^+$); 133/135/137/139 (100.0, Cl_3Si^+); 99/101/103 (7.2, HCl_2Si^+); 98/100/102 (7.4, Cl_2Si^+); 69 (38.3, $CF_3{}^+$); 63/65 (12.9, ClSi$^+$); 41 (30.6, $C_3H_5{}^+$).

Polysiloxane formation from {2-[bis(trifluoromethyl)-amino-oxy]ethyl}dichloroethylsilane (9)

(a) Hydrolysis

A small flask fitted with a condenser, magnetic stirrer and septum cap was charged with a solution of silane 9 (0.50 g, 1.6 mmol) in diethyl ether (0.5 cm^3) and cooled to 0 °C. Water (0.45 g, 25.0 mmol) was added dropwise to the stirred solution from a syringe via the septum cap and the mixture was heated under reflux (0.5 h). The resulting material was extracted with ether (3 $\times$ 5 cm^3), the extracts dried (MgSO$_4$) and the ether removed *in vacuo* to give a colourless oil identified as poly-{2-[bis(trifluoromethyl)amino-oxy]ethyl} siloxane (35) (nc) (0.41 g, 87%). [Analysis: Found: C, 26.5; H, 3.3; F, 41.6%; M, 1850. $(C_6H_9F_6NO_2Si)_7 \cdot H_2O$ requires: C, 26.5; H, 3.3; F, 41.9%; M, 1901.] IR $\nu_{max.}$ (cm^{-1}): 3320 (m, O–H str.); 3000–2900 (m, C–H str.); 1300–1205 (vs, C–F str.); 1100–1005 (s, Si–O, C–O and N–O str.); 968 (s, C–N str.); 708 (s, CF$_3$ def.). ^1H NMR (CDCl$_3$) δ: 4.43 (complex, 2H, CH$_2$O); *c*. 1.3 (complex, 7H, CH$_2$Si and CH$_3$CH$_2$Si) ppm. ^{19}F NMR δ: $+8.25$ [s, $(CF_3)_2NO$] ppm.

Attempted equilibration of siloxane 35 (0.3 g) with potassium hydroxide (trace) at 80 °C (18 h) *in vacuo* gave a polymer which had identical physical characteristics to that of the starting material. Heating with concentrated sulphuric acid (trace) was also unsuccessful.

(b) Cohydrolysis with dichlorodimethylsilane

A stirred mixture of silane 9 (1.10 g, 3.3 mmol) and dichloromethylsilane (1.70 g, 13.2 mmol) in diethyl ether (2 cm^3) at 0 °C was treated dropwise with water (0.75 g, 42.0 mmol) as in the previous experiment and the mixture heated under reflux (1 h). The resulting material was extracted with ether (3 $\times$ 5 cm^3), the extracts dried (MgSO$_4$) and the ether removed *in vacuo* to give a colourless oil identified as a copolymer of poly-{2-[bis(trifluoromethyl)amino-oxy]ethyl}ethylsiloxane and polydimethylsiloxane (37) (nc) (1.90 g, 100%) {Analysis: Found: C, 29.7; H, 5.8; F, 20.6%; M, 570. $[C_6H_9F_6NO_2Si(C_2H_6OSi)_4 \cdot H_2O]$ requires: C, 29.7; H, 5.8; F, 20.2%; M, 583}.

Polysiloxane formation from {3-[bis(trifluoromethyl)-amino-oxy]propyl}dichloromethylsilane (29)

(a) Hydrolysis with water

A stirred solution of silane **29** (1.66 g, 5.1 mmol) in diethyl ether (4 cm³) was treated dropwise with water (0.18 g, 10.0 mmol) at 0 °C and the mixture heated under reflux (1 h). Work-up as in the previous experiments gave a colourless oil identified as poly-{3-[bis(trifluoromethyl)amino-oxy]propyl}methylsiloxane **(38)** (nc) (1.3 g, 93%) [Analysis: Found: C, 26.7; H, 3.6; F, 40.9%; M, 1030. $(C_6H_9F_6NO_2Si)_4 \cdot H_2O$ requires: C, 26.3; H, 3.5; F, 41.6%; M, 1094]. IR ν_{max} (cm⁻¹): 3280 (m, O–H str.); 2960 and 2900 (m, C–H str.); 1298–1170 (vs, C–F str.); 1110–1036 (s, Si–O, C–O and N–O str.); 966 (s, C–N str.); 709 (s, CF_3 def.). ¹H NMR ($CDCl_3$) δ: 4.28 (t, 2H, CH_2O, $J = 6$ Hz); 1.90 (mult., 2H, CH_2); 0.86 (complex, 2H, CH_2Si); 0.39 (s, 3H, CH_3Si) ppm. ¹⁹F NMR δ: +8.5 [s, $(CF_3)_2NO$] ppm. MS m/z: 364 (46.8%, $C_7H_{13}F_7NO_4Si^+$); 298 (14.6, $C_7H_{11}F_6NO_3Si^+$); 286 (17.9, $C_6H_{10}F_6NO_3Si^+$); 237 (84.6, $C_5H_5F_6NOSi^+$); 215 (86.6, $C_2F_7NOSi^+$); 197 (28.6, $C_4H_4F_6NO^+$) 150 (27.0, $C_2HF_5NO^+$); 114 (16.0, $C_2F_4N^+$); 91 (56.9, $C_3H_8FSi^+$); 77 (22.1, $C_2H_6FSi^+$); 69 (100.0, CF_3^+); 44 (30.9, OSi^+); 41 (66.5, $C_3H_5^+$).

(b) Hydrolysis with copper(II) sulphate pentahydrate

A stirred suspension of powdered copper(II) sulphate pentahydrate (0.26 g, 1.0 mmol) in diethyl ether (2 cm³) was treated dropwise with silane **29** (1.50 g, 4.6 mmol) at room temperature and the mixture heated under reflux (1 h). Ether (5 cm³) was added to the resulting material which was then filtered, washed with water (2 cm³), dried (MgSO₄) and the ether removed *in vacuo* to give a colourless oil identified (IR and NMR spectroscopy) as polysiloxane **38** (1.22 g, 97%) (Analysis: Found: M, 1210).

(c) Treatment with sodium bicarbonate

Silane **29** (1.50 g, 4.6 mmol) was added to a stirred suspension of sodium bicarbonate (0.43 g, 5.1 mmol) in diethyl ether (2 cm³) and heated under reflux (1 h). Work-up as in the previous experiment (b) gave a colourless oil which was identified (IR and NMR spectroscopy) as polysiloxane **38** (1.10 g, 87%) (Analysis: Found: M, 1030).

(d) Treatment with lead(IV) oxide

Silane **29** (1.50 g, 4.6 mmol), lead(IV) oxide (1.10 g, 4.6 mmol), mercury(II) chloride (0.01 g) and acetonitrile solvent (1.5 cm³) were sealed *in vacuo* in a Rotaflo tube (c. 50 cm³) and heated at 80 °C (18 h). The contents of the tube were washed out with diethyl ether (4 cm³) and after filtration the filtrate was washed with water (2×3 cm³), dried (MgSO₄) and the solvent removed *in vacuo* to afford a colourless oil which was

identified (IR and NMR spectroscopy) as polysiloxane **38** (1.25 g, 100%) (Analysis: Found: M, 1410).

(e) Treatment with magnesium(II) oxide

Silane **29** (1.50 g, 4.6 mmol), magnesium(II) oxide (0.20 g, 5.1 mmol), mercury(II) chloride (0.01 g) and acetonitrile solvent (1.5 cm³) were sealed *in vacuo* in a Rotaflo tube (c. 50 cm³) and heated at 80 °C (18 h). Work-up as in the previous experiment (d) gave a colourless oil which was identified (IR and NMR spectroscopy) as polysiloxane **38** (1.25 g, 100%) (Analysis: Found: M, 1520).

(f) Treatment with aqueous sulphuric acid

Silane **29** (1.50 g, 4.6 mmol) was added dropwise to a stirred aqueous solution of sulphuric acid (2 cm³, 50% v/v) at 0 °C and the mixture heated at 60 °C (1 h). After cooling to room temperature, diethyl ether (4 cm³) was added and the ethereal layer washed with a saturated solution of sodium bicarbonate (2×3 cm³) then with water (2×3 cm³) and dried (MgSO₄). Removal of the ether *in vacuo* gave a colourless oil which was identified (IR and NMR spectroscopy) as polysiloxane **38** (1.12 g, 85%) (Analysis: Found: M, 2270).

(g) Treatment with aqueous potassium hydroxide

Silane **29** (1.50 g, 4.6 mmol) was added dropwise to a stirred aqueous solution of potassium hydroxide (2 cm³, 30% w/w) at 0 °C and the mixture heated at 50 °C (1 h). The mixture was then cooled, diethyl ether (4 cm³) added and the ethereal layer separated. This was washed with dilute hydrochloric acid (0.1 M, 2×3 cm³) then water (2×3 cm³), dried (MgSO₄) and the ether removed *in vacuo* to give a colourless oil which was identified (IR and NMR spectroscopy) as poly-siloxane **38** (1.21 g, 96%) (Analysis: Found: M, 2700).

Equilibration reactions of the polysiloxane 'prepolymer' 38

(a) With aqueous sodium hydroxide

A sample of the 'prepolymer' **38** (1.6 g) was dissolved in a mixture of toluene and ethanol (1:1 v/v, 5 cm³) and treated with a saturated solution of aqueous sodium hydroxide (3 drops) and heated at 100 °C (12 h) *in vacuo* in a Rotaflo tube (c. 50 cm³). The resulting material was washed with water (2× 3 cm³), then the solvent was removed *in vacuo* and the residue dried *in vacuo* to give a colourless viscous oil **(39)** (1.48 g) [Analysis: Found: C, 27.0; H, 3.5%. $(C_6H_9F_6NO_2Si)_n$ requires: C, 26.8; H, 3.3%] which was only partially soluble in common organic solvents. The IR and NMR spectra were almost identical to those of the reactant 'prepolymer' except for the absence of a band at c. 3260 cm⁻¹ (O–H str.).

(b) With solid potassium hydroxide

The 'prepolymer' **38** (0.5 g) and powdered potassium hydroxide (0.001 g) were added *in vacuo* in a Rotaflo tube (*c.* 5 cm^3) and heated at 80 °C (24 h) to give a rubbery solid (**39**) (0.47 g) [Analysis: Found: C, 26.9; H, 3.3%. (C$_6$H$_9$F$_6$NO$_2$Si)$_n$ requires: C, 26.8; H, 3.3%] with IR and NMR spectral properties almost identical to those of the reactant 'prepolymer' except for the absence of an IR band at *c.* 3260 cm^{-1} (O–H str.) and which was insoluble in common organic solvents but soluble in trifluoroacetic acid.

(c) With other reagents

Samples of the 'prepolymer' **39** (0.5 g) were sealed *in vacuo* in Rotaflo tubes (*c.* 5 cm^3) with (i) concentrated sulphuric acid (0.001 g), (ii) iron(III) chloride (0.001 g) and (iii) triethylamine (0.001 g) and heated at 80 °C (24 h). Viscous oils (**39**) (*c.* 0.46 g) were obtained in each case (some darkening was observed in the first two reactions) and the IR and NMR spectral properties were identical to those of the reactant prepolymer apart from the absence of an IR band at *c.* 3260 cm^{-1} (O–H str.).

Polysiloxane formation from {2-[bis(trifluoromethyl)-amino-oxy]propyl}dichloromethylsilane (14)

A solution of silane **14** (0.50 g, 1.5 mmol) in diethyl ether (1 cm^3) was added dropwise to water (1 cm^3), then heated under reflux (0.5 h) and cooled. The resulting material was extracted with ether (3×2 cm^3), dried (MgSO$_4$) and the ether removed *in vacuo* to give a colourless oil which was identified as poly-{2-[bis(trifluoromethyl)amino-oxy]propyl}methylsiloxane (**36**) (0.34 g, 83%) [Analysis: Found: C, 26.2; H, 3.4%; M, 1100. (C$_6$H$_9$F$_6$NO$_2$Si)$_4$·H$_2$O requires: C, 26.3; H, 3.5%; M, 1094]. IR ν_{max} (cm^{-1}): 3270 (br., O–H str.); 2960 and 2900 (w, C–H str.); 1298–1170 (s, C–F str.);

1090 and 1049 (s, Si–O, C–O and N–O str.); 969 (s, C–N str.); 704 (m, CF$_3$ def.). ^{1}H NMR (CDCl$_3$) δ: 4.80 (mult., 1H, CHO); 1.83 (mult., 5H, CH$_2$–Si and CH$_3$); 0.74 (s, 3H, CH$_3$–Si) ppm. ^{19}F NMR δ: +9.80 [s, (CF$_3$)$_2$NO] ppm. MS *m/z*: 513 (16.3%, C$_9$H$_{13}$F$_{12}$-N$_2$O$_4$Si$_2$$^+$); 364 (100.0, C$_7H_{13}F_7NO_4Si_2$$^+$); 298 (22.6, C$_7H_{10}F_6NO_3Si^+$); 286 (34.0, C$_6H_{10}F_6NO_3Si^+$); 237 (43.7, C$_4HF_6NO_2Si^+$); 215 (74.2, C$_2F_7$NOSi$^+$); 197 (19.5, C$_4H_5F_6NO^+$); 69 (49.3, CF$_3$$^+$).

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