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Reaction of bis(trifluoromethyl)amino-oxyl with alkylchlorosilanes and allyldichloro(methyl)silane and of perfluoro-2,5-diazahexane 2,5-dioxyl with vinylsilanes and hydrolysis of the products

Anthony E. Tipping* and Rajendraprasad B. Yadav
Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD (UK)

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Abstract

Treatment of the silanes $MeSiHCl_2$, Me_2SiHCl and $EtSiMeCl_2$ with the oxyl $(CF_3)_2NO\cdot$ (**1**) gives the substitution products $(CF_3)_2NOSiMeCl_2$ (**4**) and $(CF_3)_2NOSiMe_2Cl$ (**5**), and a mixture of $(CF_3)_2NOCHMeSiMeCl_2$ (**8**) and $(CF_3)_2NOCH_2CH_2SiMeCl_2$ (**9**) (ratio 20:37), respectively, while the silane $EtSiMe_2Cl$ affords mainly the ester $(CF_3)_2NO_2CMe$ (**7**). Attack of oxyl **1** on the silane $CH_2{=}CHCH_2SiMeCl_2$ results in both allylic substitution and addition to give the compounds $CH_2{=}CHCH(SiMeCl_2)ON(CF_3)_2$ (**14**) and $(CF_3)_2NOCH_2CH(CH_2SiMeCl_2)ON(CF_3)_2$ (**15**) (ratio 56:40). Reaction of the dioxyl $\cdot ON(CF_3)CF_2CF_2N(CF_3)O\cdot$ (**2**) with the vinylsilanes $CH_2{=}CHSiX_3$ ($X_3 = Me_3$, Cl_3, $MeCl_2$) gives mainly 1:1 copolymers $[ON(CF_3)CF_2CF_2N(CF_3)OCH_2CH(SiX_3)]_n$ (**17**), although the cyclic 1:1 adduct $\overline{ON(CF_3)CF_2CF_2N(CF_3)OCH_2C}HSiMeCl_2$ (**18**) is also formed in low yield.

Hydrolysis of the silanes **15**, $(CF_3)_2NOCH_2CH(SiMeCl_2)ON(CF_3)_2$ (**19a**) and $(CF_3)_2NOCH_2CH(SiCl_3)ON(CF_3)_2$ (**19b**) affords the corresponding polysiloxanes **24** and **25**, and the polysilsesquioxane **26**, respectively; the polymers **25** and **26** undergo rearrangement of the type $-CH(Si\leqslant)ON(CF_3)_2 \rightarrow -CH(OSi\leqslant)N(CF_3)_2$ on storage. The 1:1 copolymers **17b** ($X_3 = MeCl_2$) and **17c** ($X_3 = Cl_3$) are also hydrolysed to the corresponding siloxane and silsesquioxane polymers. In contrast, hydrolysis of the compounds **4**, **5** and $(CF_3)_2NOCH_2CH(OSiX_3)N(CF_3)_2$ (**20a**; $X_3 = MeCl_2$) and (**20b**; $X_3 = Cl_3$) results in Si–O bond cleavage.

Introduction

It has been observed that the α-position of the alkyltrihalogenosilanes $RSiCl_3$ ($R = Et$, Pr^n, Pr^i and Bu^n) and $RSiF_3$ ($R = Et$ and Pr^n) is deactivated towards attack by the oxyl $(CF_3)_2NO\cdot$ (**1**) [1]. This deactivation is apparent in the attack on dialkyldichlorosilanes, e.g. attack on the silane $Pr^nSiMeCl_2$ occurs at the β-position of the propyl group [2]. The dichlorosilanes $(CF_3)_2NOCH_2CH_2SiEtCl_2$, $(CF_3)_2NOCHMeCH_2SiMeCl_2$ and $(CF_3)_2NO(CH_2)_3SiMeCl_2$ [from $(CF_3)_2NOCH_2CH{=}CH_2 + MeSiHCl_2/H_2PtCl_6$] have been hydrolysed to the corresponding polysiloxanes [2].

In the present work, further alkylchlorosilanes containing one or two $(CF_3)_2NO$ groups have been prepared and an initial study of the reaction of the dioxyl $\cdot ON(CF_3)CF_2CF_2N(CF_3)O\cdot$ (**2**) with vinylsilanes has been undertaken. The hydrolysis of certain of the products was then investigated.

Results and discussion

Reaction of the oxyl **1** with the silanes $MeSiHCl_2$ and Me_2SiHCl (2:1 molar ratio) gave the hydroxylamine $(CF_3)_2NOH$ (**3**) and the amino-oxysilanes **4** (85%) and **5** (83%), respectively, via abstraction of the Si–H hydrogen and trapping of the resulting silyl radicals with **1**, i.e.

$$\underset{(\mathbf{1})}{(CF_3)_2NO\cdot} + X_3SiH \longrightarrow$$

$$\underset{(\mathbf{3})}{(CF_3)_2NOH} + X_3Si\cdot \xrightarrow{1} (CF_3)_2NOSiX_3 \quad \begin{array}{l}(\mathbf{4})\ X_3 = MeCl_2 \\ (\mathbf{5})\ X_3 = Me_2Cl\end{array}$$

Compound **5** has been prepared previously by the same route, although spectral data were not reported [3] and compound **4** was formed as a byproduct in the reaction of oxyl **1** with the silane Me_2SiCl_2 [4].

The reactions of the silanes $EtSiMeCl_2$ and $EtSiMe_2Cl$ with oxyl **1** were then investigated to determine if the former substrate would afford $(CF_3)_2NO$-substituted silanes suitable for preliminary hydrolysis experiments

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*Author to whom correspondence should be addressed.

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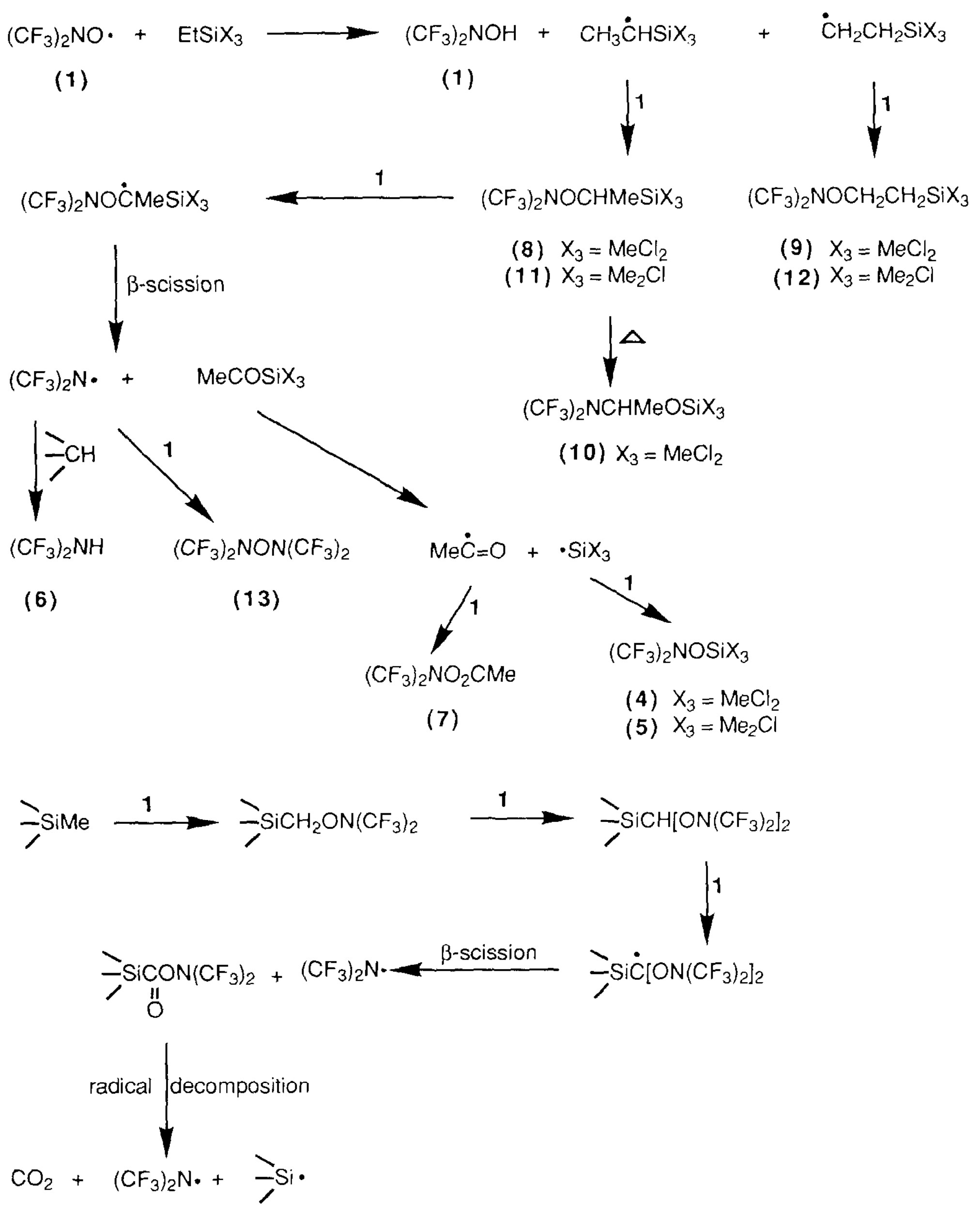


Scheme 1.

to be undertaken. The results obtained from the reaction of oxyl **1** with these silanes could also be compared with those reported for reaction of oxyl **1** with other dialkyldichlorosilanes [1, 2] and with alkyltrichlorosilanes [1].

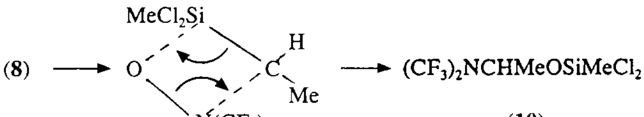
Treatment of the silane $EtSiMeCl_2$ with oxyl **1** (1:1 molar ratio) at room temperature gave unchanged silane (65% recovered), carbon dioxide (3%), bis(trifluoromethyl)amine (**6**) (11%), hydroxylamine **3** (32%), silane **4** (12%), *N,N*-bis(trifluoromethyl)-*O*-acetylhydroxylamine (**7**) (12%), the α-substituted silane **8** (7%) and the β-substituted silane **9** (13%), respectively.

$(CF_3)_2NH$ $(CF_3)_2NO_2CMe$
(**6**) (**7**)

$(CF_3)_2NOCHMeSiMeCl_2$
(**8**)

$(CF_3)_2NO(CH_2)_2SiMeCl_2$
(**9**)

Silanes **8** and **9** were distinguished by their ^1H NMR spectra, i.e. bands at δ_H 4.28 (q, 1H) and 1.62 (d, 3H) ppm for the O−CHMe−Si grouping in **8** and bands at δ_H 4.16 (t, 2H) and 1.45 (t, 2H) ppm for the $O-CH_2-CH_2-Si$ grouping in **9**, and by their ^{19}F NMR spectra, i.e. δ_F +9.8 ppm for α-$(CF_3)_2NO$ and +8.6 ppm for β-$(CF_3)_2NO$. As observed with other α-$(CF_3)_2NO$-substituted silanes [1, 2, 5, 6], compound **8** underwent thermal rearrangement (*c.* 20%) to compound **10** on GLC separation at 90 °C as shown by ^1H NMR spectral bands at δ_H 5.82 (q, 1H) and 1.58 (d, 3H) ppm for N−CHMe−O and a ^{19}F NMR spectral band at δ_F +22.0 [$(CF_3)_2N$] ppm, i.e.



(10)

The products are considered to have been formed as shown in Scheme 1 with the compounds **3**, **6** and **7** arising via further oxyl **1** attack on the α-substituted silane **8** at the α-carbon atom.

In contrast, from the reaction of oxyl **1** with the silane $EtSiMe_2Cl$ (2:1 molar ratio), the α- and β-substituted silanes **11** and **12**, respectively, analogous to **8** and **9**, were not detected in the products which were carbon dioxide (*c.* 3%), compounds **6** (8%), **3** (36%), **5** and **7**, and perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (**13**) together with a small amount of unidentified higher-boiling material which contained carbonyl groups (IR spectroscopy). The major products formed, i.e. **5** and **7**, indicate that oxyl **1** attack was favoured at the α-position of the ethyl group (Scheme 1).

The small amounts of carbon dioxide isolated from the two reactions can be explained by minor oxyl **1** attack occurring at methyl (Scheme 1).

When allowance is made for (i) the presence of three β-hydrogens and only two α-hydrogens in the ethyl group of the silane $EtSiMeCl_2$ and (ii) the products arising from further attack on the α-substituted silane **8**, the relative reactivity of the α- and β-positions towards oxyl **1** is *c.* 1.0:0.4, cf. *c.* 1.0:1.0 in $EtSiCl_3$ [1] and *c.* 1.0:0.8 in Et_2SiCl_2 [2]. With the silane $EtSiMe_2Cl$, the ratio is 1.0:0 since only products resulting from α-attack were detected.

Thus α-attack becomes more favoured (i) in the series $EtSiMe_2Cl > EtSiMeCl_2 > EtSiCl_3$, i.e., as chlorine on silicon is replaced by methyl, and (ii) when ethyl on silicon is replaced by methyl, i.e. $EtSiMeCl_2 > Et_2SiCl_2$. The factors involved (steric and electronic effects and hyperconjugative stabilisation of the intermediate radicals) have been discussed in detail previously [1, 2].

$(CF_3)_2NON(CF_3)_2$ **(13)**

$CH_2{=}CHCH(SiMeCl_2)ON(CF_3)_2$ **(14)**

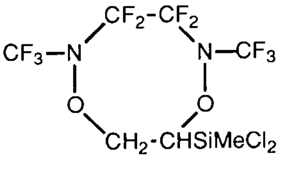
$(CF_3)_2NOCH_2CH(CH_2SiMeCl_2)ON(CF_3)_2$ **(15)**

Reaction of oxyl **1** with allyldichloro(methyl)silane (2:1 molar ratio) gave hydroxylamine **3** (28%), the allylic substitution compound **14** (28%) and the 2:1 adduct **15** (40%) (yields based on oxyl **1**). The surprising feature of the reaction was that the intermediate allyl radical **16**, which is resonance stabilised, i.e. $CH_2{=}CH-\dot{C}HSiMeCl_2 \leftrightarrow \dot{C}H_2-CH{=}CHSiMeCl_2$, underwent coupling with oxyl **1** exclusively at the more stabilised secondary carbon, the expected least reactive site. Compound **14** was identified by its ^1H NMR spectrum (three vinylic hydrogens and an allyl methine hydrogen bonded to oxygen). The products are considered to be formed as shown in Scheme 2.

The chemistry of dioxyl **2** has been studied in far less detail than that of oxyl **1**, but it has been observed that liquid-phase reaction with alkenes favours 1:1 copolymer formation while in the gas phase cyclic 1:1 adducts are favoured [7, 8]. Reaction of the vinylsilanes $CH_2{=}CHSiX_3$ ($X_3 = Me_3$, $MeCl_2$ and Cl_3) with dioxyl **2** in the liquid phase (*c.* 1:1 molar ratio) gave 1:1 copolymers **17a** ($X_3 = Me_3$) (89%), **17b** ($X_3 = MeCl_2$) (81%) and **17c** ($X_3 = Cl_3$) (91%); the copolymer **17a** was somewhat impure and did not give a correct elemental analysis. Copolymers **17** each showed a broad IR absorption at 3510–3330 cm^{-1} (O−H str.), indicating that some hydrogen abstraction had occurred and OH end-groups were present. From the reaction involving the silane $CH_2{=}CHSiMeCl_2$, the cyclic 1:1 adduct **18** (4%) was also isolated and all the products are considered to be formed via dioxyl **2** attack on the terminal CH_2 group of each vinylsilane.

$$H{-}\!\!\left[ON(CF_3)_2CF_2CF_2N(CF_3)OCH_2CH(SiX_3)\right]_{n}$$

(17) a; $X_3 = Me_3$
b; $X_3 = MeCl_2$
c; $X_3 = Cl_3$



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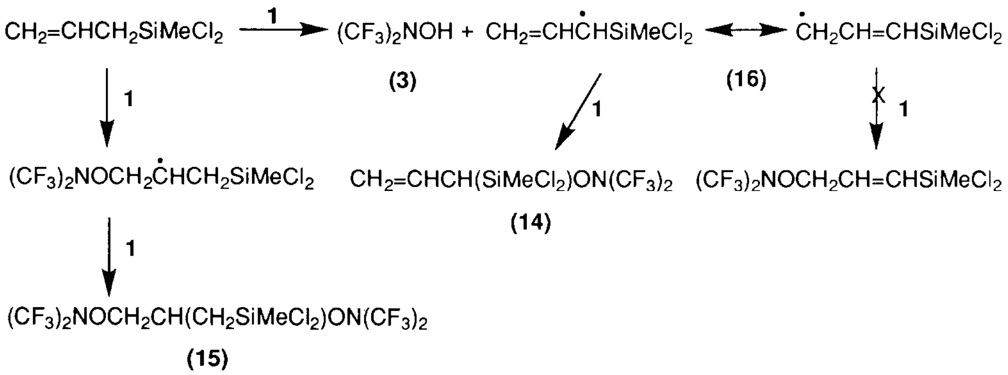


Scheme 2.

$(CF_3)_2NOCH_2CH(SiX_3)ON(CF_3)_2$

(19) a; $X_3 = MeCl_2$
b; $X_3 = Cl_3$

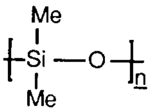
$(CF_3)_2NOCH_2CH(OSiX_3)N(CF_3)_2$

(20) a; $X_3 = MeCl_2$
b; $X_3 = Cl_3$

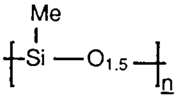
Hydrolysis of silanes to afford oligomers

A preliminary investigation of the hydrolyses of the dimethylchlorosilane **5**, the methyldichlorosilanes **4**, **15**, **17b**, **19a** and **20a**, and the trichlorosilanes **17c**, **19b** and **20b** was then undertaken.

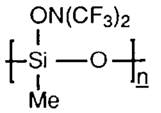
Treatment of the monochlorosilanes **5** with aqueous potassium hydroxide at 60 °C afforded the hydroxylamine **3** and poly(dimethylsiloxane) (**21**) (89%), while an ethereal solution of dichlorosilane **4** heated at 35 °C with water gave hydroxylamine **3** and a mixture (90%) of poly(methylsilsesquioxane) (**22**) and poly{[bis-(trifluoromethyl)amino-oxy]methylsiloxane} (**23**) in the ratio 85:15. Thus, facile cleavage of the Si–$ON(CF_3)_2$ bond occurred in both hydrolyses.


$[\mathrm{Si(Me)_2{-}O}]_n$

(21)

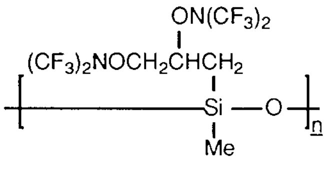

$[\mathrm{Si(Me){-}O_{1.5}}]_n$

(22)

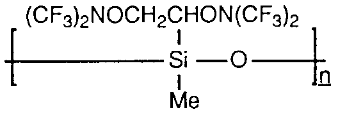

$[\mathrm{Si(Me)(ON(CF_3)_2){-}O}]_n$

(23)

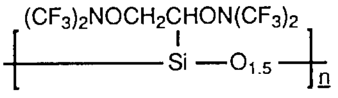
Hydrolysis of silane **15** with water at 90 °C gave a low molecular weight polysiloxane **24** (M, 1873; $n = c.$ 4) (92%) which contained a $(CF_3)_2NO$ group on the β-carbon and was stable on prolonged storage. In contrast, polymers **25** (93%) and **26** (97%), obtained by hydrolysis of chlorosilanes **19a** and **19b** with water at room temperature and which contain a $(CF_3)_2NO$ group on an α-carbon, were unstable and rearranged to the corresponding alkoxysilanes **27** (17% over 3 months) and **28** (100% in 5 d), respectively.


$[\mathrm{Si(Me)(CH_2CH(ON(CF_3)_2)CH_2ON(CF_3)_2){-}O}]_n$

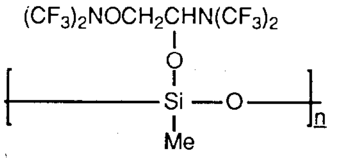
(24)


$[\mathrm{Si(Me)(CH(ON(CF_3)_2)CH_2ON(CF_3)_2){-}O}]_n$

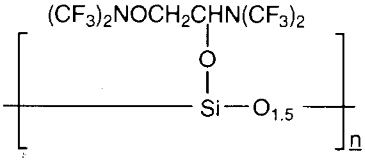
(25)


$[\mathrm{Si(CH(ON(CF_3)_2)CH_2ON(CF_3)_2){-}O_{1.5}}]_n$

(26)


$[\mathrm{Si(Me)(OCH(N(CF_3)_2)CH_2ON(CF_3)_2){-}O}]_n$

(27)


$[\mathrm{Si(OCH(N(CF_3)_2)CH_2ON(CF_3)_2){-}O_{1.5}}]_n$

(28)

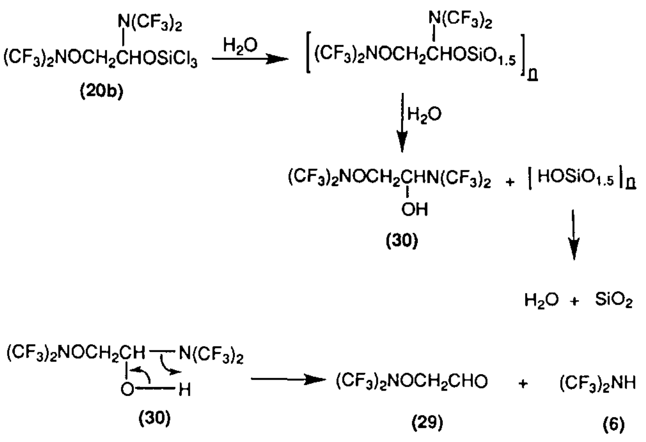
The rearranged polymers **27** and **28** were identified by their ^{19}F NMR spectra, i.e. replacement of the absorption at δ_F *c.* 10 ppm [α-$ON(CF_3)_2$] in polymers

25 and **26** by an absorption at 21 ppm [$N(CF_3)_2$]. An analogous rearrangement (at room or elevated temperature) has been observed previously with other alkylsilanes which contain a $(CF_3)_2NO$ group on an α-carbon atom [1, 2, 5, 6], and the chloroalkoxysilanes **20a** and **20b** were prepared in the present work by thermal rearrangement of the chloroalkylsilanes **19a** and **19b**, respectively [6]; it is probable that such rearrangement takes place via a four-centre transition state as shown earlier for the conversion of compound **8** into alkoxysilane **10**.

Hydrolysis of chloroalkoxysilane **20a** with water at room temperature afforded poly(methylsilsesquioxane) (**22**) (99%) and volatile material which was not examined. However, hydrolysis of the chloroalkoxysilane **20b** under comparable conditions gave, as volatile material, amine **6** (38%) and a mixture of the aldehyde **29** and alcohol **30** in the ratio 30:70 (NMR spectroscopy). Examination (coupled GLC/MS at 80 °C) of the al/ol mixture showed the presence of **6**, **29** and **30** in the ratio 39:57:4. This indicated that alcohol **30** underwent thermal decomposition at 80 °C to afford compounds **6** and **29** (Scheme 3). It is probable that hydrolysis of compound **20a** followed an analogous pathway.

Compounds **29** and **30** were identified from the NMR spectra of the mixture and the mass spectra of the individual components. Compound **29**: ^1H NMR δ: 9.36 (s, 1H, CH=O); 3.82 (s, 2H, CH_2O) ppm. ^{19}F NMR δ: +7.35 [s, $(CF_3)_2NO$] ppm. MS *m/z*: 211 (0.2%, M^+); 69 (84.6, CF_3^+); 43 (100.0, $C_2H_3O^+$). Compound **30**: ^1H NMR δ: 5.04 (mult., 1H, $\rangle$CHO); 4.02 (br., 1H, OH); 3.80 (d, 2H, CH_2O, $J = 7$ Hz) ppm. ^{19}F NMR δ: +21.2 [s, 6F, $(CF_3)_2N$]; +7.4 [s, 6F, $(CF_3)_2NO$] ppm. MS *m/z*: 364 (0.4%, M^+); 212 (1.2, $[M-(CF_3)_2N]^+$); 69 (100.0, CF_3^+).

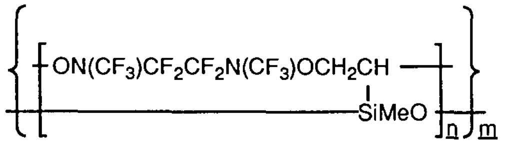
Thermolysis of the silsesquioxane **26** at 100 °C *in vacuo* gave a mixture of the compounds $CF_3N{=}CF_2$ (major component), CF_3NCO and SiF_4, amine **6** (2%) and a liquid mixture of two components in the ratio 68:32 (GLC) which showed a strong carbonyl absorption (1754 cm^{-1}) in its IR spectrum. The liquid mixture solidified on storage overnight and the solid, which did not show an IR absorption at 1754 cm^{-1}, gave a correct elemental analysis for $[(CF_3)_2NOCH_2CHO]_n$. It is probable that the liquid mixture consisted of aldehyde **29** and a polymer of **29**, and that the polymerisation was completed on storage overnight; the polymer is possibly the cyclic trimer **31**.



Scheme 3.

It has been reported previously that the silanes $RCH_2CH(SiXF_2)ON(CF_3)_2$ undergo decomposition (X=Me at 90 °C and X=F at 20 °C) via a six-centre transition state to afford the aldehyde RCH_2CHO, the azapropene $CF_3N{=}CF_2$ and the fluorosilane $SiXF_3$ [6]. Hence, it is possible that decomposition of silsesquioxane **26** follows a similar pathway, although initial rearrangement of **26** to **28** (which occurs quantitatively at 20 °C over 5 d), followed by decomposition via a five-centre transition state cannot be ruled out (Scheme 4).

Treatment of copolymer **17b**, formed from the vinylsilane $CH_2{=}CHSiMeCl_2$ and dioxyl **2**, with water gave a viscous mixture (91%) of the non-rearranged and rearranged polysiloxanes **32** and **33** in the ratio 33:67 (^{19}F NMR spectroscopy). Comparable hydrolysis of the corresponding trichlorosilyl copolymer **17c** gave an amorphous solid, which was insoluble in common organic solvents but analysed correctly for the silsesquioxane **34** or its isomer **35**. Since the polysilsesquioxane **26** rearranged at a much faster rate than did the polysiloxane **25**, it is probable that the product from copolymer **17c** is the rearranged polysilsesquioxane **35**.



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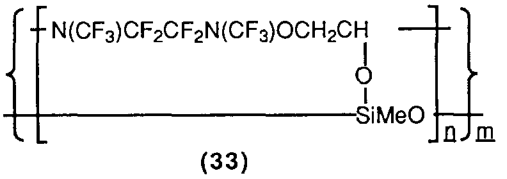

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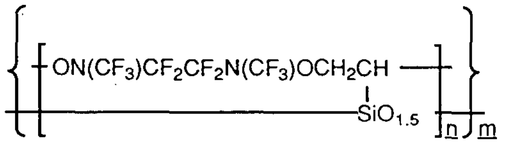

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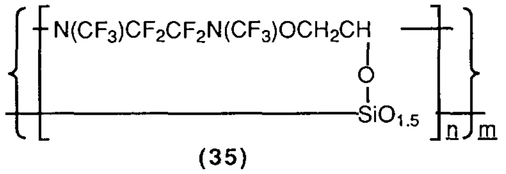

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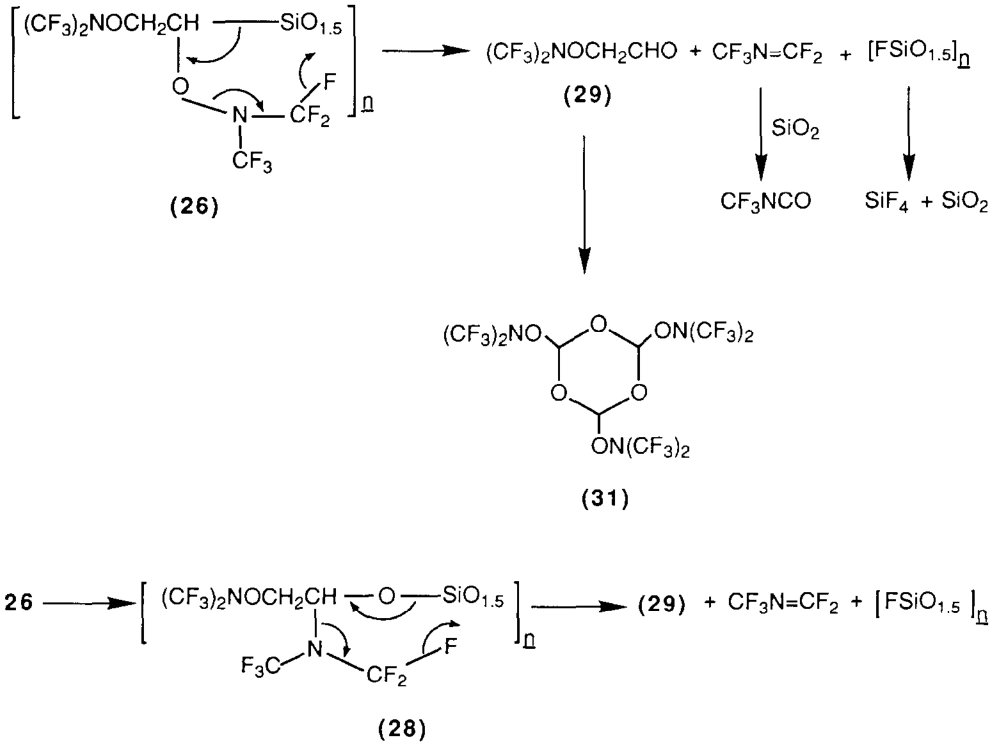

Scheme 4.

Experimental

Starting materials

The oxyl **1** and the dioxyl **2** were prepared by oxidation of the hydroxylamine $(CF_3)_2NOH$ (**3**) with silver(II) oxide [9] and the diol $HON(CF_3)CF_2CF_2N(CF_3)OH$ with potassium permanganate [7], respectively. The silanes $MeSiCl_3$, $MeSiHCl_2$, Me_2SiHCl and $CH_2{=}CHSiCl_3$ were commercial samples which were distilled before use and the remaining silanes were prepared as follows: (i) $MeSiCl_3 + EtMgBr \rightarrow MeEtSiCl_2$ (44%) [10]; (ii) $Me_2SiCl_2 + EtMgBr \rightarrow Me_2EtSiCl$ (47%) [11]; (iii) $MeSiHCl_2 + CH_2{=}CHCH_2Cl/H_2PtCl_6 \rightarrow Cl(CH_2)_3SiMeCl_2$ (37%) [12] $\xrightarrow[\text{heat}]{\text{quinoline}}$ $CH_2{=}CHCH_2SiMeCl_2$ (73%) [13]; (iv) $CH_2{=}CHSiCl_3 + MeMgBr \rightarrow CH_2{=}CHSiMeCl_2$ (71%) [14]; (v) $CH_2{=}CHSiCl_3 + 3MeMgBr \rightarrow CH_2{=}CHSiMe_3$ (49%) [15]; (vi) $CH_2{=}CHSiCl_3 + 2(CF_3)_2NO\cdot \rightarrow (CF_3)_2NOCH_2CH(SiCl_3)ON(CF_3)_2$ (**19b**) $\xrightarrow{220\ ^\circ\mathrm{C}}$ $(CF_3)_2NOCH_2CH(OSiCl_3)N(CF_3)_2$ (**20b**) (76%) [6]; and (vii) $CH_2{=}CHSiMeCl_2 + 2(CF_3)_2NO\cdot \rightarrow (CF_3)_2NOCH_2CH(SiMeCl_2)ON(CF_3)_2$ (**19a**) $\xrightarrow{150\ ^\circ\mathrm{C}}$ $(CF_3)_2NOCH_2CH(OSiMeCl_2)N(CF_3)_2$ (**20a**) (85%) [6].

General techniques

The reactions of oxyl **1** and dioxyl **2** were carried out *in vacuo* in Rotaflo tubes (*c.* 300 cm^3) at room temperature in the dark unless stated otherwise. Products were separated by fractional condensation *in vacuo* or by preparative-scale GLC [columns (2–6 m) packed with silicone SE30 oil, dinonyl phthalate (DNP) or Apiezon L grease (APL) (10%–20% w/w) on Celite] and were examined by IR spectroscopy (Perkin-Elmer 257 instrument), ^1H NMR spectroscopy [Perkin-Elmer R10 (60.0 MHz) or Varian Associates HA100 (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 (AEI MS902 instrument with an electron beam energy of 70 eV). The NMR spectra were recorded as solutions in $CDCl_3$, 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.

The IR spectra of products **4–7**, **8**, **9**, **14**, **15**, **17–20** and **24–32** containing $(CF_3)_2NO$ or $ON(CF_3)CF_2CF_2N(CF_3)O$ groups each showed bands ($\nu_{max.}$) at 2900–2950 (C–H str.); 1300–1150 (C–F str.); 1020–1070 (C–O–N str.); 950–980 (C–N str.); 700–750 (CF_3 def.) cm^{-1}.

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

(a) With dichloro(methyl)silane

A mixture of oxyl **1** (4.41 g, 26.12 mmol) and the silane (1.50 g, 13.03 mmol), stored (6 h), gave: (i) a

−196 °C fraction (0.12 g, 1.62 mmol; M, 78) shown (IR and mass spectrometry) to consist of hydrogen chloride (0.02 g, 0.54 mmol) and trifluoronitrosomethane (0.10 g, 1.08 mmol); (ii) *N,N*-bis(trifluoromethyl)-hydroxylamine (**3**) (2.20 g, 13.0 mmol, 50%) which condensed at −78 °C; and (iii) a −45 °C fraction which was identified as dichloro[bis(trifluoromethyl)amino-oxy]methylsilane (**4**) (3.10 g, 11.0 mmol, 85%). (Analysis: Found: C, 12.9; H, 1.0; N, 5.1%. $C_3H_3Cl_2F_6NOSi$ requires: C, 13.2; H, 1.1; N, 5.0%.) ^{1}H NMR (neat) δ: 9.15 (s, Si−Me) ppm. ^{19}F NMR δ: +8.5 [s, $(CF_3)_2NO$] ppm. IR ($\nu_{max.}$) (cm^{-1}): 1065 (s) (Si−O str.); 860 (m) (Si−O−N str.); 800 (m) (Si−Me def.).

(b) With chloro(dimethyl)silane

A mixture of oxyl **1** (5.87 g, 35.0 mmol) and the silane (1.60 g, 17.5 mmol), stored (8 h), gave: (i) a −196 °C fraction shown (IR spectroscopy and MS) to consist of hydrogen chloride (0.02 g, 0.39 mmol) and trifluoronitrosomethane (0.10 g, 1.05 mmol); (ii) a mixture of *N,N*-bis(trifluoromethyl)amine (**6**) and unidentified material (IR spectroscopy) which condensed at −120 °C; (iii) hydroxylamine **3** (2.80 g, 16.20 mmol, 46%) which condensed at −78 °C; and (iv) a −45 °C fraction which was identified as chloro[bis(trifluoromethyl)amino-oxy]dimethylsilane (**5**) (3.80 g, 13.70 mmol, 78%). ^{1}H NMR (neat) δ: 9.31 (s, Si−Me) ppm. ^{19}F NMR δ: +9.0 [s, $(CF_3)_2NO$] ppm. IR ($\nu_{max.}$) (cm^{-1}): 1072 (s) Si−O str.); 865 (m) (Si−O−N str.); 820 (m) (Si−Me def.).

(c) With dichloro(ethyl)methylsilane

A mixture consisting of oxyl **1** (4.76 g, 28.3 mmol) and the silane (4.05 g, 28.3 mmol), stored (22 h), gave: (i) a −196 °C fraction shown (IR spectroscopy) as consisting mainly of carbon dioxide (0.04 g, 0.91 mmol, *c.* 3%) (Analysis: Found: M, 47. Calc. for CO_2: M, 44); (ii) amine **6** (0.47 g, 3.07 mmol, 11%) which condensed at −120 °C; (iii) hydroxylamine **3** (1.53 g, 9.06 mmol, 32%) which condensed at −78 °C; and (iv) higher-boiling material (6.1 g) which was shown by GLC (6 m APL at 90 °C) to contain five components in the ratio 12:16:10:19:43. These components were separated by GLC (as before) to give: (i) *N,N*-bis(trifluoromethyl)-*O*-acetylhydroxylamine (**7**) (0.72 g, 3.40 mmol, 12%) identified by a comparison of its IR spectrum and its ^{1}H and ^{19}F NMR spectra with those reported [1]; (ii) dichloro[bis(trifluoromethyl)amino-oxy]methylsilane (**4**) (0.96 g, 3.40 mmol, 12%) identified by a comparison of its IR spectrum with that of an authentic sample; (iii) dichloro-{1-bis(trifluoromethyl)-amino-oxy]ethyl}methylsilane (**8**) (nc) (0.61 g, 1.98 mmol, 7%) (Analysis: Found: C, 19.6; H, 2.5; N, 4.4%. $C_5H_7Cl_2F_6NOSi$ requires: C, 19.4; H, 2.3; N, 4.5%) {^{1}H NMR ($CDCl_3$) δ: 4.28 (q, 1H, >CHO, $J=7$ Hz); 1.62 (d, 3H, CH_3, $J=7$ Hz); 0.72 (s, 3H, Si−Me) ppm. ^{19}F NMR δ: +9.8 [s, $(CF_3)_2NO$] ppm (the NMR spectra indicated that some rearrangement (*c.* 20%) to dichloro-{1-bis(trifluoromethyl)amino]ethoxy}methylsilane (**10**) had occurred during GLC separation as shown by bands at δ_H 5.52 [q, 1H, N−C*H*(Me)−O, $J=7$ Hz] and 1.68 (d, 3H, C*H*$_3$CH, $J=7$ Hz) ppm and at δ_F +22.0 [s, $(CF_3)_2N$] ppm)}; (iv) dichloro-{2-bis(trifluoromethyl) amino-oxy]ethyl}methylsilane (**9**) (nc) (1.14 g, 3.68 mmol, 13%) (Analysis: Found: C, 19.5; H, 2.4; N, 4.6%. $C_5H_7Cl_2F_6NOSi$ requires: C, 19.4; H, 2.3; N, 4.5%). {^{1}H NMR ($CDCl_3$) δ: 4.16 (t, 2H, CH_2−O, $J=7$ Hz); 1.45 (t, 2H, CH_2−Si, $J=7$ Hz); 0.67 (s, 3H, CH_3−Si) ppm. ^{19}F NMR δ: +8.6 [s, $(CF_3)_2NO$] ppm}; and (v) unchanged dichloro(ethyl)methylsilane (2.63 g, 18.4 mmol, 65% recovered).

(d) With chloro(ethyl)dimethylsilane

A mixture of oxyl **1** (3.61 g, 21.5 mmol) and the silane (1.32 g, 10.76 mmol), stored (15 h), gave: (i) carbon dioxide (0.026 g, 0.65 mmol, 3%) which condensed at −196 °C; (ii) the amine **6** (0.285 g, 1.83 mmol, 8%) (Analysis: Found: M, 156. Calc. for C_2HF_6N: M, 153) which condensed at −120 °C and was shown (IR spectroscopy) to be contaminated with a small amount of perfluoro-2-azapropene; (iii) hydroxylamine **3** (1.29 g, 7.65 mmol, 36%) which condensed at −78 °C; (iv) a −45 °C fraction (1.21 g) which was shown (NMR spectroscopy) to consist mainly of the *O*-acetylhydroxylamine **7**, perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (**13**) and chloro[bis(trifluoromethyl)-amino-oxy]dimethylsilane (**5**); (v) a −23 °C fraction (1.76 g) which was shown (NMR spectroscopy) to consist mainly of the *O*-acetylhydroxylamine **7** contaminated with an unidentified methylsilane (IR, 826 cm^{-1}); and (vi) a residue (0.42 g) which was not identified and showed IR bands ($\nu_{max.}$) at 1812, 1754 and 1718 (w) (C=O str.); 1266–1176 (s) (C−F str.); 1086–1020 (s) (N−O and Si−F str.); 980 (s) (C−N str.); and 709 (s) (CF_3 def.) cm^{-1}.

(e) With allyldichloro(methyl)silane

A mixture consisting of the oxyl **1** (3.79 g, 22.6 mmol) and the silane (1.76 g, 11.33 mmol), stored (6h), gave: (i) the hydroxylamine **3** (1.07 g, 6.38 mmol, 28%) which condensed at −78 °C; (ii) a −45 °C fraction (2.71 g) which was shown by GLC (2 m SE30 at 90 °C) to contain two components in the ratio 76:24 [these were identified as dichloro(methyl)-[1-bis(trifluoromethyl)-amino-oxy]prop-2-enylsilane (**14**) (2.06 g, 6.38 mmol, 28%) {^{1}H NMR ($CDCl_3$) δ: 5.64 (mult., 1H, =CH); 5.20 (mult., 2H, =CH_2); 4.30 (d, 1H, >CHO, $J=7$ Hz); 0.58 (s, 3H, Si−Me) ppm. ^{19}F NMR δ: +9.95 [s, $(CF_3)_2NO$] ppm} and dichloro(methyl)-{[2,3-bis-(trifluoromethyl)amino-oxy]propyl}silane (**15**) (0.65 g, 1.32 mmol, 12%)]; and (iii) a 0 °C fraction which consisted of dichloro(methyl)-{[2,3-bis(trifluoromethyl)-amino-oxy]propyl}silane (**15**) (nc) (1.57 g, 3.20 mmol, 28%) (Analysis: Found: C, 19.9; H, 1.9, N, 5.7%. $C_8H_8Cl_2F_{12}O_2N_2Si$ requires: C, 19.6; H, 1.65; N, 5.7%), b.p. 184–186 °C {^{1}H NMR ($CDCl_3$) δ: 4.40 (mult., 1H, $>$CHO); 4.20 (mult., 2H, CH_2O); 0.50 (s, 2H, CH_2-Si); 0.33 (s, 3H, CH_3-Si) ppm. ^{19}F NMR δ: + 9.8 [s, 6F, α-$(CF_3)_2NO$]; +8.8 [s, 6F, β-$(CF_3)_2NO$] ppm. MS *m/z*: 455/457 [0.1%, $(M-Cl)^+$]; 322/324/326 {5.5, $[M-(CF_3)_2NO]^+$}; 308/310/312 {4.5, $[M-CH_2ON(CF_3)_2]^+$}; 150 (10.9, $C_2HF_5NO^+$); 113/115/117 (39.1, $CH_3SiHCl_2^+$); 92/94 (23.6, $C_2H_5ClSi^+$); 69 (18.6, CF_3^+); 43 (15.8, CH_3Si^+); 41 (100.0, $C_3H_5^+$)}.

Reactions of perfluoro-2,5-diazahexane 2,5-dioxyl (2) with vinylsilanes

(a) With trimethylvinylsilane

A mixture of the dioxyl **2** (2.09 g, 7.0 mmol) and the vinylsilane (0.90 g, 9.0 mmol), stored (13 h), gave: (i) an unidentified alkene (0.03 g, 0.45 mmol) (Analysis: Found: M, 67) [IR ($\nu_{max.}$) (cm^{-1}): 1610 (C=C str.)] which condensed at −196 °C; (ii) a −120 °C fraction which was identified (IR spectroscopy) as mainly perfluoro-2-azapropene (0.16 g, 1.2 mmol, 9%); (iii) unchanged vinylsilane (0.24 g, 2.4 mmol, 27% recovered); and (iv) a residue identified as impure 1:1 copolymer **17a** of dioxyl **2** and trimethylsilane (2.20 g, 6.28 mmol, 89%) [Analysis: Found: C, 25.9; H, 2.5; F, 47.0%. $(C_8H_{12}F_{10}N_2O_2Si)_n$ requires: C, 27.1; H, 3.0; F, 47.7%] {^{1}H NMR ($CDCl_3$) δ: 5.27 (mult., 1H, $>$CHO); 4.27 (mult., 2H, CH_2O); 0.20 (s, 9H, $SiMe_3$) ppm. ^{19}F NMR δ: +25 to +23 (mult., 1F, CF_3N); +11.0 (mult., 5F, CF_3-N-O); −15.2, −30.1 (mult., 4F, CF_2CF_2) ppm}.

(b) With dichloro(methyl)vinylsilane

A mixture of dioxyl **2** (1.94 g, 6.50 mmol) and the vinylsilane (0.96 g, 6.81 mmol), stored (6 h), gave: (i) perfluoro-2-azapropene (0.10 g, 0.67 mmol, 5%) which condensed at −120 °C; (ii) a −78 °C fraction (0.26 g) which was shown by GLC (2 m SE30 at 50 °C) to be a mixture of four components in the ratio 1:1:2:6; (iii) a 0 °C fraction identified as 7-[dichloro(methyl)silyl]-3,3,4,4-tetrafluoro-2,5-bis(trifluoromethyl)-1,6-dioxa-2,5-diazacyclo-octane (**18**) (nc) (0.11 g, 0.25 mmol, 4%) {^{1}H NMR ($CDCl_3$) δ: 3.91 (br, 1H, $>$CHO); 5.72 (br, 2H, CH_2O); 0.83 (s, 3H, Si–Me) ppm. ^{19}F NMR δ: +12.1 (br, 3F, CF_3-N-O); +11.2 (br, 3F, CF_3-N-O); −27.0 (mult., 2F, CF_2N); −27.9 (mult., 2F, CF_2N) ppm. MS *m/z*: 309 (1.2%, $C_6H_3F_{10}N_2O^+$); 165 (10.2, $C_3HF_6N^+$); 134 (19.9, $C_2HF_5N^+$); 114 (31.8, $C_2F_4N^+$); 85 (13.9, $CH_2F_3N^+$); 69 (100.0, CF_3^+); 43 (10.9, CH_3Si^+); 42 (13.0, CH_2Si^+)}; and (iv) a liquid residue which was identified as a 1:1 copolymer of dioxyl **2** and dichloro(methyl)vinylsilane (**17b**) (nc) 2.36 g, 81%) [Analysis: Found: C, 18.8; H, 1.4; F, 43.4%. $(C_7H_6Cl_2F_{10}N_2O_2Si)_n$ requires: C, 19.1; H, 1.4; F, 43.3%] {^{1}H NMR ($CDCl_3$) δ: 4.44 (br, 1H, $>$CHO); 4.27 (br, 2H, CH_2O); 0.75 (s, 3H, Si–Me) ppm. ^{19}F NMR δ: +10 to +12 (complex, 6F, $2CF_3-N-O$); −20 to −28 (complex, 4F, CF_2CF_2) ppm. IR ($\nu_{max.}$) (cm^{-1}): 3510–3330 (w) (O–H str.)}.

(c) With trichlorovinylsilane

A mixture consisting of the dioxyl **2** (2.76 g, 9.07 mmol) and the vinylsilane (1.49 g, 9.70 mmol), stored (10 h), gave: (i) an unidentified compound (0.18 g, 0.43 mmol) (Analysis: Found: M, 42) which condensed at −196 °C; (ii) perfluoro-2-azapropene (0.02 g, 0.3 mmol, 1%) which condensed at −120 °C; (iii) an unidentified −78 °C fraction (0.13 g, 0.8 mmol) (Found: M, 172); and (iv) a viscous residue which was identified as a 1:1 copolymer of dioxyl **2** and trichlorovinylsilane (**17c**) (nc) (3.88 g, 91%) [Analysis: Found: C, 15.5; H, 0.8; N, 6.0; F, 41.4%. $(C_6H_3Cl_3F_{10}N_2O_2Si)_n$ requires: C, 15.7; H, 0.7; N, 6.1; F, 41.3%] {^{1}H NMR ($CDCl_3$) δ: 6.27–5.87 (complex, $>$CHO and CH_2O) ppm. ^{19}F NMR δ: +12.0 (mult., 6F, $2CF_3-N-O$); −23.1 (complex, 4F, CF_2CF_2) ppm. IR ($\nu_{max.}$) (cm^{-1}): 3510–3330 (w) (O–H str.)}.

Hydrolysis experiments

(a) Dichloro[bis(trifluoromethyl)amino-oxy]methylsilane (4)

A solution of silane **4** (2.0 g, 7.1 mmol) in anhydrous diethyl ether (5 cm^3) was added dropwise to stirred water (10 cm^3) and the mixture was then heated under reflux at 35 °C (1.5 h). The ethereal layer was separated, dried ($MgSO_4$) and the ether removed *in vacuo* to give a mixture (0.68 g) [Analysis: Found: C, 13.6; H, 2.9; N, 0.7; F, 7.5%. Calc. for a mixture of $(CH_3O_{1.5}Si)_n$ and $(C_3HF_6NO_2Si)_n$ in the ratio 85:15: c, 13.6; H, 3.0; N, 0.7; F, 7.5%] of poly(methylsilsesquioxane) (**22**) and poly{[bis(trifluoromethyl)amino-oxy]methylsiloxane} (**23**).

(b) Chloro[bis(trifluoromethyl)amino-oxy]dimethylsilane (5)

Silane **5** (6.63 g, 25.4 mmol) was added dropwise to stirred aqueous potassium hydroxide (1.5 M, 25 cm^3) and the mixture heated at 60 °C (2 h). The product was extracted with diethyl ether (3×10 cm^3), dried (molecular sieve) and a mixture of ether and *N,N*-bis(trifluoromethyl)hydroxylamine (**3**) (as shown by IR spectroscopy) was removed *in vacuo* to give viscous liquid poly(dimethylsiloxane) (**21**) (1.64 g, 89%) identified by IR spectroscopy.

(c) Dichloro(methyl)-{[2,3-bis(trifluoromethyl)amino-oxy]propyl}silane (15)

A mixture consisting of silane **15** (1.50 g, 3.06 mmol) and water (5 cm^3) was heated at 90 °C (0.5 h) and the resultant material extracted with diethyl ether (3×10 cm^3), dried ($MgSO_4$) and the ether removed *in vacuo* to give a viscous liquid polymer (1.31 g). This liquid polymer was heated under reflux with aqueous potassium hydroxide (1.5 M, 5 cm^3) for 1 h and the product extracted with ether (3×10 cm^3), dried ($MgSO_4$) and the ether removed *in vacuo* to give a more viscous polymer identified as poly{methyl-[2,3-bis(trifluoromethyl)amino-oxy]propylsiloxane} (**24**) (nc) (1.21 g, 92%) [Analysis: Found: C, 22.5; H, 2.2; N, 6.2%. $(C_8H_8F_{12}N_2O_3Si)_n$ requires: C, 22.0; H, 1.8; N, 6.4%] {^{1}H NMR ($CDCl_3$) δ: 5.06–4.60 (complex, 3H, $>$CHO and CH_2O); 1.66 (d, 2H, CH_2Si, $J = 7$ Hz); 0.70 (s, 3H, Si–Me) ppm. ^{19}F NMR δ: +9.9 [s, 6F, $(CF_3)_2NO$]; +8.6 [s, 6F, $(CF_3)_2NO$] ppm. IR ($\nu_{max.}$) (cm^{-1}): 1090–1030 (s) (N–O str. and Si–O str.)}.

*(d) Dichloro(methyl)-{1,2-bis[bis(trifluoromethyl)amino-oxy]ethyl}silane (**19a**)*

Silane **19a** (6.20 g, 13.2 mmol) was added dropwise to stirred water (15 cm^3) at room temperature and stirring was continued (0.5 h). The product was extracted with diethyl ether (3×10 cm^3), dried ($MgSO_4$) and the ether removed *in vacuo* to give a viscous polymer identified as poly{methyl-1,2-bis[bis(trifluoromethyl)-amino-oxy]ethylsiloxane} (**25**) (nc) (5.09 g, 93%) [Analysis: Found: C, 19.9; H, 1.7; F, 53.5%. $(C_7H_6F_{12}N_2O_3Si)_n$ requires: C, 19.9; H, 1.4; F, 54.0%] {^{1}H NMR ($CDCl_3$) δ: 5.2–4.2 (complex, 3H, $>$CHO and CH_2O); 0.77 (s, 3H, CH_3Si) ppm. ^{19}F NMR δ: +10.0 [s, 6F, α-$(CF_3)_2NO$]; +9.0 [s, 6F, β-$(CF_3)_2NO$] ppm. IR ($\nu_{max.}$) (cm^{-1}): 1110–1030 (s) (N–O str. and Si–O str.)}.

When the ^{19}F NMR spectrum was rerun after 3 months, additional bands (1:1 ratio) were present at δ+21.0 [s, $(CF_3)_2N$] and +9.5 [s, $(CF_3)_2NO$] ppm, indicating rearrangement to poly{methyl-[1-bis(trifluoromethyl)amino-2-bis(trifluoromethyl)amino-oxy]ethoxysiloxane} (**27**) had occurred to the extent of *c.* 17%.

*(e) Trichloro-{1,2-bis[bis(trifluoromethyl)amino-oxy]ethyl}silane (**19b**)*

Silane **19b** (6.01 g, 13.44 mmol) was added dropwise to stirred water (15 cm^3) at room temperature and stirring was continued (0.5 h). The resultant material was extracted with diethyl ether (3×10 cm^3), dried ($MgSO_4$) and the ether removed *in vacuo* to give a viscous polymer identified as poly{1,2-bis[bis(trifluoromethyl)amino-oxy]ethylsilsesquioxane} (**26**) (nc) (5.02 g, 97%) [Analysis: Found: C, 17.2; H, 0.9%. $(C_6H_3F_{12}N_2O_{3.5}Si)_n$ requires: C, 17.3; H, 0.7%] {^{1}H NMR ($CDCl_3$) δ: 5.27–4.50 (complex, $>$CHO and CH_2O) ppm. ^{19}F NMR δ: +10.2 [s, 6F, α-$(CF_3)_2NO$]; +9.5 [s, 6F, β-$(CF_3)_2NO$] ppm. IR ($\nu_{max.}$) (cm^{-1}): 1075–1050 (s) (N–O str. and Si–O str.)}.

When the ^{19}F NMR spectrum was rerun after 5 d, bands (1:1 ratio) were present at δ+21.0 [s, $(CF_3)_2N$] and +8.0 [s, $(CF_3)_2NO$] ppm, indicating complete rearrangement to poly{[1-bis(trifluoromethyl)amino-2-bis(trifluoromethyl)amino-oxy]ethoxysilsesquioxane} (**28**) had taken place.

*(f) Dichloro(methyl)-{[1-bis(trifluoromethyl)amino-2-bis(trifluoromethyl)amino-oxy]ethoxy}silane (**20a**)*

Silane **20a** (6.50 g, 13.64 mmol) was added dropwise to stirred water (25 cm^3) at room temperature and stirring was continued (0.5 h). Extraction of the resulting material with diethyl ether (3×10 cm^3), drying ($MgSO_4$) and removal of the ether *in vacuo* gave poly(methylsilsesquioxane) (**22**) (0.91 g, 99%) [Analysis: Found: C, 13.2; H, 3.5%. $(CH_3SiO_{1.5})_n$ requires: C, 13.2; H, 3.3%].

*(g) Trichloro-{[1-bis(trifluoromethyl)amino-2-bis(trifluoromethyl)amino-oxy]ethoxy}silane (**20b**)*

A mixture of silane **20b** (2.53 g, 5.08 mmol) and water (15 cm^3), sealed *in vacuo* in a Rotaflo tube (*c.* 200 cm^3) and kept at room temperature (0.5 h), gave as volatile material: (i) *N*,*N*-bis(trifluoromethyl)amine (**6**) (0.29 g, 1.92 mmol, 38%) which condensed at −120 °C; (ii) a −48 °C fraction (0.72 g) consisting mainly of water and which, after drying (P_2O_5), afforded a mixture (0.09 g) of amine **6** and a carbonyl compound [IR $\nu_{max.}$ (cm^{-1}): 1754 (C=O str.)]; and (iii) a −23 °C fraction (1.46 g) which was shown (NMR spectroscopy) to be a mixture of 2-[bis(trifluoromethyl)-amino-oxy]ethanal (**29**) (nc) {^{1}H NMR ($CDCl_3$) δ: 9.36 (s, 1H, CH=O); 3.82 (s, 2H, CH_2O) ppm. ^{19}F NMR δ: +7.35 [s, $(CF_3)_2NO$] ppm} and 1-bis(trifluoromethyl)-amino-2-[bis(trifluoromethyl)amino-oxy]ethanol (**30**) (nc) {^{1}H NMR ($CDCl_3$) δ: 5.04 (mult., 1H, $>$CHO); 4.02 (br., 1H, OH); 3.80 (d, 2H, CH_2O, $J = 7$ Hz) ppm. ^{19}F NMR δ: +21.2 [s, 6F, $(CF_3)_2N$]: +7.4 [s, 6F, $(CF_3)_2NO$] ppm} in the ratio 30:70. A coupled GLC (2 m SE30 at 80 °C)–mass spectrometry examination of the fraction showed the presence of three components (ratio 39:57:4) identified as amine **6** [*m*/*z*: 153 (2.9%, M^+); 133 (19.7, $C_2F_5N^+$); 114 (31.6, $C_2F_4N^+$); 69 (100.0, CF_3^+)], aldehyde **29** [*m*/*z*: 211 (0.2%, M^+); 150 (28.9, $C_2HF_5NO^+$); 81 (14.9, $C_2F_3^+$); 69 (84.6, CF_3^+); 43 (100.0, $C_2H_3O^+$); 42 (10.2, $C_2H_2O^+$)] and alcohol **30** [*m*/*z*: 364 (0.4%, M^+); 212 (1.2, $C_4H_4F_6NO_2^+$); 211 (0.3, $C_4H_3F_6NO_2^+$); 191 (1.5, $C_4H_2F_5NO_2^+$); 182 (1.8, $C_3H_2F_6NO^+$); 177 (2.0, $C_4H_3F_5NO^+$); 69 (100.0, CF_3^+)].

*(h) 1:1 Copolymer **17c** of dioxyl **2** and trichlorovinylsilane*

A solution consisting of copolymer **17c** (3.9 g) in 1,1,2-trichlorotrifluoroethane (15 cm^3) was added dropwise to stirred water (25 cm^3) at room temperature and stirring was continued (0.5 h). The organic layer was separated, dried ($MgSO_4$) and the solvent removed *in vacuo* to give a white amorphous solid polysilsesquioxane **34** and/or **35** (nc) (3.21 g, 97%) [Analysis: Found: C, 18.2; H, 0.9; F, 47.5%. $(C_6H_3F_{10}N_2SiO_{3.5})_n$ requires: C, 18.0; H, 0.75; F, 47.4%], which was insoluble in common organic solvents.

*(i) 1:1 Copolymer **17b** of dioxyl **2** and dichloro(methyl)vinylsilane*

A solution consisting of copolymer **17b** (2.0 g) in 1,1,2-trichlorotrifluoroethane (15 cm^3) was added dropwise to stirred water (20 cm^3) at room temperature and stirring was continued (0.5 h). The organic layer was separated, dried ($MgSO_4$) and the solvent removed *in vacuo* to give a viscous mixture (1.62 g, 91%) of polysiloxane **32** and the rearranged polysiloxane **33** in the approximate ratio 33:67. ^{19}F NMR ($CDCl_3$) δ: +21 to +19 (2F, CF_3-N-C); +12 to +9 (4F, CF_3-N-O); −21 to −26 (4F, CF_2CF_2) ppm.

*Thermolysis of poly{1,2-bis[bis(trifluoromethyl)amino-oxy]ethylsilsesquioxane} (**26**)*

Silsesquioxane **26** (6.80 g, 16.38 mmol), sealed *in vacuo* in a Rotaflo tube (*c.* 300 cm^3) and heated at 100 °C (15.5 h) gave: (i) a −196 °C fraction (1.25 g, 13.92 mmol) (Analysis: Found: M, 83) which was shown (IR spectroscopy) to be a mixture of perfluoro-2-azapropene, trifluoromethylisocyanate and tetrafluorosilane; (ii) amine **6** (0.09 g, 0.61 mmol, 2%) which condensed at −120 °C; and (iii) a −45 °C liquid fraction (1.12 g) which was shown (IR spectroscopy) to contain a carbonyl compound [IR ($\nu_{max.}$) (cm^{-1}): 1754 (C=O str.)]. GLC studies (2 m PEGA at 20 °C) of the latter fraction showed the presence of two components (ratio 68:32), but the liquid solidified before a GLC separation could be attempted [Analysis: Found: C, 23.1; H, 1.6; N, 6.3; F, 53.9%. $(C_4H_3F_6NO_2)_n$ requires: C, 22.8; H, 1.4; N, 6.6; F, 54.0%] [IR ($\nu_{max.}$) (cm^{-1}): 2950, 2910 (m) (C−H str.); 1300–1250 (s) (C−F str.); 965 (m) (N−O str. and/or C−O str.); 715 (s) (CF_3 def.)].

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