The synthesis of [bis(trifluoromethyl)amino-oxy]silacyclobutanes

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Abstract

The silacyclobutanes $\overbrace{CH_2CH_2CH_2}SiClX$ (**2**), X = Cl, and (**3**), X = Me, are attacked by the oxyl $(CF_3)_2NO\cdot$ (**1**) at the 3-position leading to the monosubstituted products $(CF_3)_2N\overbrace{OCHCH_2SiClXCH_2}$ (**8**), X = Cl, and (**9**), X = Me, and a minor amount of the disubstituted product $(CF_3)_2N\overbrace{OCHCH_2SiMeClCHON(CF_3)_2}$ (**10**) which arises via the silacyclobutene $\overbrace{CH_2CH=CHSiMeCl}$ (**17**). With the disilacyclobutane $\overbrace{CH_2SiMe_2CH_2SiMe_2}$ (**4**), the only silicon-containing products isolated are $(CF_3)_2NOSiMe_2CH_2SiMe_2F$ (**13**) and $FSiMe_2CH_2SiMe_2F$ (**12**), which are formed via attack of oxyl **1** at a ring CH_2 group. The 1-substituted 1-silacyclobutanes $\overbrace{CH_2CH_2CH_2}SiRR^1$ (**28**), R = Cl, $R^1 = ON(CF_3)_2$ (**29**), $R = R^1 = ON(CF_3)_2$, and (**27**), R = Me, $R^1 = ON(CF_3)_2$, are conveniently prepared by reaction of the mercurial $[(CF_3)_2NO]_2Hg$ (**26**) with the silacyclobutanes **2** and **3**. Reaction of the 3-substituted silacyclobutane **9** with anhydrous hydrogen chloride gives the open-chain, substituted dialkyldichlorosilane $(CF_3)_2NOCHMeCH_2SiMeCl_2$ (**14**), while treatment with hydrochloric acid affords a low molecular weight polysiloxane (**15**) derived from dichlorosilane **14**.

Introduction

It has been reported that attack of the oxyl $(CF_3)_2NO\cdot$ (**1**) on the methylsilanes Me_nCl_{4-n} gave unstable silyl esters $X_3SiCO_2N(CF_3)_2$ ($X_3 = Cl_3$, $MeCl_2$, Me_2Cl and Me_3) [1] whilst attack on the alkyltrihalogenosilanes $RSiX_3$ (X = Cl and F) [2] and the dialkyldichlorosilane RR^1SiCl_2 [2, 3] resulted in replacement of the alkyl hydrogen by the $(CF_3)_2NO$ group. With the silanes $RSiX_3$ and R_2SiCl_2, positions α to silicon are deactivated towards attack and the α-substitution products $(CF_3)_2NOCHR^1Si\lesssim$ are thermally unstable and rearrange to α-aminoalkoxysilanes $(CF_3)_2NCHR^1OSi\lesssim$ [2, 4].

In a continuation of a study into the preparation and reactions of silanes containing the $(CF_3)_2NO$ group, methods for the introduction of the $(CF_3)_2NO$ group into silacyclobutanes have been investigated.

Experimental

Starting materials

The oxyl **1** was prepared by oxidation of the hydroxylamine $(CF_3)_2NOH$ **5** with silver(II) oxide [5] and this was converted into the mercurial $[(CF_3)_2NO]_2Hg$ **26** by reaction with an excess of mercury *in vacuo* [6].

The reactant silacyclobutanes were prepared by standard methods (yields refer to pure compounds obtained by fractional distillation), i.e. (i)

$$ClCH_2CH{=}CH_2 + HSiCl_2X \xrightarrow{H_2PtCl_6} ClCH_2CH_2CH_2SiCl_2X$$

(X = Cl, 30%; X = Me, 34%) [7]

$$\xrightarrow[Et_2O]{Mg} \overbrace{CH_2CH_2CH_2}SiClX \text{ (2)}$$

(X = Cl, 55%), (**3**) (X = Me, 33%) [8]

and (ii)

$$Me_2SiClCH_2Cl \xrightarrow[THF]{Mg} \overbrace{CH_2SiMe_2CH_2}SiMe_2 \text{ (4) (38\%) [9].}$$

General techniques

The reactions involving oxyl **1** and mercurial **26** were carried out *in vacuo* in Rotaflo tubes (*c.* 300 cm^3 and *c.* 100 cm^3, respectively). Products were separated by fractional condensation *in vacuo* or by GLC methods [Perkin-Elmer F21 or Aerograph Autoprep machines using columns (3.5–10 m) packed with Silicone SE30 or OVI oils (10%–20% w/w) on Celite as stated in the text] and were examined by IR spectroscopy (Perkin-Elmer 257 instrument), ^1H NMR spectroscopy [Perkin-Elmer R10 (60.0 MHz) or Varian Associates HA100

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(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 using neat liquids or solutions in $CDCl_3$ (as stated in the text); chemical shifts to low field of reference are designated positive.

The molecular weight of polysiloxane **15** was determined by vapour-phase osmometry (Hitachi Perkin-Elmer 115 instrument) and boiling points were determined by Siwoloboff's method.

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

(a) 1,1-Dichloro-1-silacyclobutane (2)

A mixture of oxyl **1** (3.36 g, 20.0 mmol) and silane **2** (2.82 g, 20.0 mmol), kept at room temperature (3 h), gave only volatile material (5.99 g) which on fractional condensation *in vacuo* afforded (i) a −196 °C fraction (0.21 g), identified (IR spectroscopy) as a mixture of *N,N*-bis(trifluoromethyl)amine (**6**) and perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane); (ii) *N,N*-bis(trifluoromethyl)hydroxylamine (**5**) (1.66 g, 9.82 mmol, 49%) which condensed at −78% °C; and (iii) a combined −23 °C and 0 °C fraction (4.12 g) which was separated by preparative-scale GLC (6 m OVI at 95 °C) into its two components, i.e. unchanged silacyclobutane **2** (1.57 g, 11.13 mmol, 56.6% recovered) and 3-[bis(trifluoromethyl)amino-oxy]-1,1-dichloro-1-silacyclobutane (**8**) (nc) (2.38 g, 7.7 mmol, 87%) (Analysis: Found: C, 19.8; H, 1.8; F, 37.1%. $C_5H_5Cl_2F_6NOSi$ requires: C, 19.5; H, 1.6; F, 37.0%), b.p. 173 °C. ^1H NMR (neat) δ: 4.89 (pentet, 1H, CHO, $J=7$ Hz); 2.20 (d, 4H, $2CH_2Si$) ppm. ^{19}F NMR δ: +9.80 [s, β-$ON(CF_3)_2$] ppm. MS *m/z*: 266/268/270 [1.0%, $(M-C_3H_5]^+$; 150 (4.5, $C_2HF_5NO^+$); 139/141/143 (90.8, $C_3H_5Cl_2Si^+$); 117/119/121 (7.3, Cl_2FSi^+); 112/114/116 (53.9, $CH_2Cl_2Si^+$); 99/101/103 (15.0, HCl_2Si^+); 69 (56.7, CF_3^+); 63/65 (32.1, $ClSi^+$); 41 (100.0, $C_3H_5^+$).

(b) 1-Chloro-1-methyl-1-silacyclobutane (3)

A mixture of oxyl **1** (3.36 g, 20.0 mmol) and silane **3** (2.41 g, 20.0 mmol), kept at room temperature (1.5 h), gave only volatile material (5.75 g) which on separation by fractional condensation *in vacuo* afforded (i) a −196 °C fraction (0.15 g), which was shown (IR spectroscopy) to be a mixture of amine **6** and perfluoro-2-azapropene (**7**); (ii) a −78 °C fraction (2.27 g), which was shown [IR spectroscopy and GLC methods (3.5 m SE30 at 50 °C)] to consist of hydroxylamine **5** (1.65 g, 9.8 mmol, 49%) and unchanged silane **3** (0.62 g, 5.1 mmol, 25% recovered); (iii) a colourless liquid (1.89 g) which condensed at −23 °C and was separated by preparative-scale GLC (6 m OVI at 90 °C) into its two components, i.e. unchanged silane **3** (0.62 g, 5.2 mmol, 26% recovered) and 3-[bis(trifluoromethyl)amino-oxy]-1-chloro-1-methyl-1-silacyclobutane (**9**) (nc) (1.23 g, 4.3 mmol, 44%) (Analysis: Found: C, 25.2; H, 2.9; F, 39.5%. $C_6H_8ClF_6NOSi$ requires: C, 25.0; H, 2.8; F, 39.7%), b.p. 159 °C. ^1H NMR (neat) δ: 4.65 (pentet, 1H, CHO, $J=7$ Hz); 1.80 (complex, 4H, $2CH_2Si$); 0.70 and 0.61 (s, 3H, CH_3Si) ppm. ^{19}F NMR δ: +9.9 [s, β-$(CF_3)_2NO$] ppm. MS *m/z*: 246/248 (17.4%, $C_3H_3ClF_6NOSi^+$); 158/160 (7.9, $C_5H_8ClF_3NOSi^+$); 130 (9.9, $C_2F_4NO^+$); 119/121 (100.0, $C_4H_8ClSi^+$); 97/99 (26.2, CH_3ClFSi^+); 92/94 (96.1, $C_2H_5ClSi^+$); 79/81 (68.3, CH_4ClSi^+); 69 (68.3, CF_3^+); 63/65 (75.8, $ClSi^+$); 43 (59.4, CH_3Si^+); and (iv) a colourless liquid (1.44 g) which was separated by preparative-scale GLC (6 m OVI at 90 °C) into its two components, i.e. compound **9** (1.08 g, 3.7 mmol, 38%) and a mixture of 2,3-bis[bis(trifluoromethyl)amino-oxy]-1-chloro-1-methyl-1-silacyclobutane (**10**) and 5-bis(trifluoromethyl)amino-4-bis(trifluoromethyl)amino-oxy-2-chloro-2-methyl-2-silatetrahydrofuran (**11**) (0.36 g, 0.8 mmol, 8%) (Analysis: Found: C, 21.0; H, 1.6%. Calc. for $C_8H_7ClF_{12}N_2O_2Si$: C, 21.1; H, 1.5%). ^1H NMR (neat) δ: 6.20 (complex, 0.33H, ring O−CH); 4.05 (complex, 1.67H, CHO); 1.20 (complex, 2H, CH_2Si); 0.38 (s, 3H, CH_3Si) ppm. ^{19}F NMR δ: +20.5 [s, 1F, $(CF_3)_2N$]; +8.5 [s, 3F, β-$(CF_3)_2NO$]; +7.8 [s, 2F, α-$(CF_3)_3NO$] ppm. MS *m/z*: 302/304 {1.3%, $[M-(CF_3)_2N]^+$}; 286/288 {3.9, $[M-(CF_3)_2NO]^+$}; 246/248 (41.3, $C_3H_3ClF_6NOSi^+$); 107/109 (2.8, $C_2H_4ClOSi^+$); 94/96 (3.1, CH_3ClOSi^+); 69 (100.0, CF_3^+).

(c) 1,1,3,3-Tetramethyl-1,3-disilacyclobutane (4)

A mixture of oxyl **1** (3.36 g, 20.0 mmol) and silacyclobutane **4** (5.76 g, 40.0 mmol), kept at room temperature (5 h), gave volatile material (8.40 g) which on fractional condensation *in vacuo* afforded (i) a −196 °C fraction identified (IR spectroscopy) as carbon dioxide (0.16 g, 3.6 mmol, 18%) (Analysis: Found: M, 44. Calc. for CO_2: M, 44); (ii) a −120 °C fraction (1.48 g), shown by IR spectroscopy and GLC methods (4 m SE30 at 30 °C) to contain mainly amine **6** (0.52 g, 3.4 mmol, 17%) and azapropene **7** (0.48 g, 3.8 mmol, 19%) (iii) hydroxylamine **5** (1.21 g, 7.2 mmol, 36%) which condensed at −78 °C; (iv) a −23 °C fraction (4.93 g) which was shown by GLC methods (2 m SE30 at 60 °C) to consist mainly of unchanged disilacyclobutane **4** (4.80 g, 33.0 mmol, 82% recovered); and (v) a 0 °C fraction (0.62 g) which was combined with the non-volatile residue (0.72 g) and separated by preparative-scale GLC (10 m SE30 at 120 °C) to give 2,4-difluoro-2,4-dimethyl-2,4-disilapentane (**12**) (0.07 g, 0.4 mmol, 6%) (Analysis: Found: C, 35.3; H, 8.5; F, 22.5%. Calc. for $C_5H_{14}F_2Si_2$: C, 35.7; H, 8.4; F, 22.6%) and 2-[bis(trifluoromethyl)amino-oxy]-4-fluoro-2,4-dimethyl-2,4-disilapentane (**13**) (nc) (1.10 g, 3.6 mmol, 51%)

(Analysis: Found: C, 26.8; H, 4.7; F, 41.8; N, 4.3%. $C_7H_{14}F_7NOSi_2$ requires: C, 26.5; H, 4.4; F, 42.1; N, 4.4%), b.p. 166 °C. ^{1}H NMR (neat) δ: 0.48 (complex, $2Me_2Si$ and CH_2Si) ppm. ^{19}F NMR δ: +8.5 [s, 6F, $(CF_3)_2NO$]; −75.2 (sept., 1F, SiF, J=8.0 Hz) ppm. MS *m/z*: 302 [8.2%, $(M-CH_3)^+$]; 153 (37.6, $C_4H_{11}F_2Si_2^+$); 149 (100.0, $C_5H_{14}FSi_2^+$); 141 (57.9, $C_3H_{11}F_2Si_2^+$); 139 (22.0, $C_3H_9F_2Si_2^+$); 77 (43.9, $C_2H_6FSi^+$); 73 (31.5, $C_3H_9Si^+$); 69 (29.7, CF_3^+); 63 (17.2, CH_4FSi^+); 47 (15.7, FSi^+).

Reactions of 3-[bis(trifluoromethyl)amino-oxy]-1-chloro-1-methyl-1-silacyclobutane (9)

(a) With hydrogen chloride

A mixture of hydrogen chloride (1.08 g, 30.0 mmol) and silacyclobutane **9** (2.88 g, 10.0 mmol), treated *in vacuo* in a Rotaflo tube (*c.* 100 cm^3) at 100 °C (7 d), gave unchanged hydrogen chloride (0.91 g, 24.9 mmol, 83% recovered) and a mixture of a non-volatile liquid and carbonaceous material which was separated by preparative-scale GLC (6 m OVI at 80 °C) to afford unchanged silacyclobutane **9** (0.37 g, 1.3 mmol, 13% recovered) and {2-[bis(trifluoromethyl)amino-oxy]-propyl}dichloromethylsilane (**14**) (1.40 g, 4.3 mmol, 49%).

(b) With hydrochloric acid

The silacyclobutane **9** (1.20 g, 4.2 mmol) was added dropwise to stirred concentrated hydrochloric acid (5 cm^3) at 0 °C, and the resulting solution heated at 60 °C (12 h) and then cooled. Extraction with diethyl ether (3×2 cm^3) followed by washing with water (3×2 cm^3), drying ($MgSO_4$) and removal of the solvent *in vacuo* gave a colourless oil identified as poly-{2-[bis-(trifluoromethyl)amino-oxy]propyl]methylsiloxane (**15**) (0.98 g, 85%) [Analysis: Found: C, 26.4; H, 3.3%; M, 890. Calc. for $(C_6H_9F_6NO_2Si)_3H_2O$: C, 26.2; H, 3.3%; M, 825] by a comparison of its IR, ^{1}H, ^{19}F NMR and mass spectra with those reported previously [3].

Reactions of mercury(II) bis(trifluoromethyl)amino-oxyl (26)

(a) With 1,1-dichloro-1-silacyclobutane (2) (1:1 molar ratio)

A mixture of silacyclobutane **2** (0.71 g, 5.0 mmol) and mercurial **26** (2.68 g, 5.0 mmol), shaken at room temperature (12 h), gave volatile material which was separated by GLC methods (3.5 m SE30 at 80 °C) to afford unchanged silacyclobutane **2** (0.13 g, 0.9 mmol, 18% recovered) and 1,1-bis[bis(trifluoromethyl)amino-oxy]-1-silacyclobutane (**29**) (nc) (1.50 g, 3.7 mmol, 90%) (Analysis: Found: C, 20.8, H, 1.6; F, 56.1%. $C_7H_6F_{12}N_2O_2Si$ requires: C, 20.6, H, 1.5; F, 55.7%), b.p. 145 °C. ^{1}H NMR (neat) δ: 1.86 (complex, $3CH_2$) ppm. ^{19}F NMR δ: +8.0 [s, $2(CF_3)_2NO$] ppm. MS *m/z*: 238 {3.4%, $[M-(CF_3)_2NO]^+$}; 174 (3.6, $C_3H_4F_4NOSi^+$); 150 (11.3, $C_2HF_5NO^+$); 114 (25.2, $C_2F_4N^+$); 83 (16.4 CF_3N^+); 69 (100.0, CF_3^+); 47 (12.1, FSi^+); 41 (49.7, $C_3H_5^+$).

(b) With 1,1-dichloro-1-silacyclobutane (2) (1:2 molar ratio)

A mixture of silacyclobutane **2** (1.42 g, 10.0 mmol) and mercurial **26** (2.68 g, 5.0 mmol), shaken at room temperature (12 h), gave volatile material which was separated by GLC methods (3 m SE30 at 80 °C) to afford unchanged silacyclobutane **2** (0.65 g, 4.6 mmol, 46% recovered), the disubstituted silacyclobutane **29** (1.66 g, 4.1 mmol, 76%) and 1-[bis(trifluoromethyl)amino-oxy]-1-chloro-1-silacyclobutane (**28**) (nc) (0.33 g, 1.2 mmol, 22%) (Analysis: Found: C, 22.2; H, 2.3; F, 42.1%. $C_5H_6ClF_6NOSi$ requires: C, 21.9; H, 2.2; F, 41.7%), b.p. 126 °C. ^{1}H NMR ($CDCl_3$) δ: 1.88 (complex, $3CH_2$) ppm. ^{19}F NMR δ: +8.1 [s, $2(CF_3)_2NO$] ppm. MS *m/z*: 169 (3.0%, $C_2HF_6NO^+$); 150 (7.1, $C_2HF_5NO^+$); 81 (22.3, $C_2F_3^+$); 69 (100.0, CF_3^+); 63/65 (30.9, $ClSi^+$); 41 (55.3, $C_3H_5^+$).

(c) With 1-chloro-1-methyl-1-silacyclobutane (3) (1:2 molar ratio)

A mixture of silacyclobutane **3** (1.90 g, 15.6 mmol) and mercurial **26** (4.20 g, 7.8 mmol), shaken at room temperature (12 h), gave volatile material (3.7 g) which was separated by preparative-scale GLC (6 m OVI at 75 °C) to afford unchanged silacyclobutane **3** (0.20 g, 1.7 mmol, 11% recovered) and 1-[bis(trifluoromethyl)amino-oxy]-1-methyl-1-silacyclobutane (**27**) (nc) (3.47 g, 13.7 mmol, 98%) (Analysis: Found: C, 28.7; H, 3.8; F, 45.1%. $C_6H_9F_6NOSi$ requires: C, 28.5; H, 3.6; F, 45.1%), b.p. 115 °C. ^{1}H NMR (neat) δ: 1.70 (complex, 6H, $3CH_2$); 0.42 (s, 3H, CH_3) ppm. ^{19}F NMR δ: +8.0 [s, $(CF_3)_2NO$] ppm. MS *m/z*: 161 (4.9%, $C_2H_3F_4NOSi^+$); 146 (15.1, CF_4NOSi^+); 114 (33.1, $C_2F_4N^+$); 109 (18.4, $C_3H_7F_2Si^+$); 90 (18.4, $C_3H_7FSi^+$); 85 (16.8, $C_4H_9Si^+$); 81 (100.0, $CH_3F_2Si^+$); 79 (67.8, CHF_2Si^+); 77 (67.8, $C_2H_6FSi^+$); 69 (69.9, CF_3^+); 53 (44.5, C_2HSi^+); 47 (57.0, FSi^+); 43 (35.5, CH_3Si^+); 41 (49.7, $C_3H_5^+$).

Results and discussion

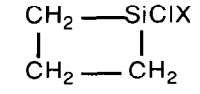
The reactions of oxyl **1** with the silacyclobutanes **2** and **3** and the 1,3-disilacyclobutane **4** were first investigated to determine where attack by the oxyl took place and whether silacyclobutanes containing $(CF_3)_2NO$ groups were formed in good yield and could be isolated readily. The results obtained are shown in Table 1.

TABLE 1. Reaction of the oxyl $(CF_3)_2NO\cdot$ (1) with silacyclobutanes at room temperature

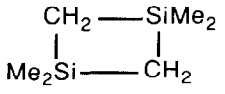
Silane	Molar ratio silane: 1	Recovered silane (%)	Products (%)[a]			
			5	6	7	Others
2	1:1	56.5	49	trace		8, 38.5(87)[b]
3	1:1	51	51	trace	trace	9, 40(82); 10, 8(8)[c]
4	2:1	82	36	17	19	CO_2, 18; 12, (6); 13, 18(51)

[a]Yields based on reactant 1; figures in parentheses are yields based on silane used, i.e. not recovered.
[b]Small amount of the oxadiazapentane $(CF_3)_2NON(CF_3)_2$ also formed.
[c]Compound 10 underwent partial rearrangement to the 2-silatetrahydrofuran 11 on GLC separation (90 °C).

$(CF_3)_2NO\cdot$ (1)



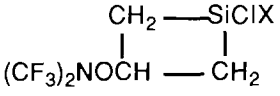
(2) X = Cl
(3) X = Me



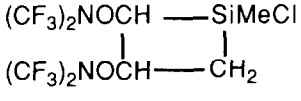
(4)

$(CF_3)_2NOH$ (5) $(CF_3)_2NH$ (6)

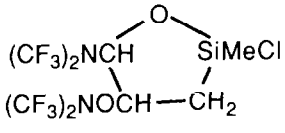
$CF_3N{=}CF_2$ (7)



(8) X = Cl
(9) X = Me



(10)



(11)

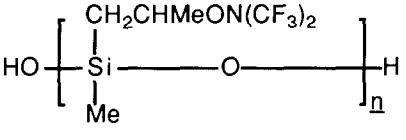
$Me_2SiFCH_2SiMe_2F$ (12)

$Me_2SiFCH_2SiMe_2ON(CF_3)_2$ (13)

The 3-[bis(trifluoromethyl)amino-oxy]-1-silacyclobutanes **8** and **9** were identified by their NMR spectra. Compound **9** was formed as a mixture of two isomers **9a** and **9b** (2:1 ratio) as shown by two separate ^1H NMR absorptions for the methyl hydrogens, but it was not possible to determine which was the major isomer. The presence in the ^1H NMR spectra of absorptions at δ_H *c.* 4.8 [pentet, 1H, $CH_2{-}CH(O{-})CH_2{-}$, $J=7$ Hz] and *c.* 2 (complex, 4H, $2CH_2Si$) ppm and an absorption in the ^{19}F NMR spectra at δ_F 9.8–9.9 [β-$(CF_3)_2NO$] ppm proved conclusively that the $(CF_3)_2NO$ group was in the 3-position in both compounds.

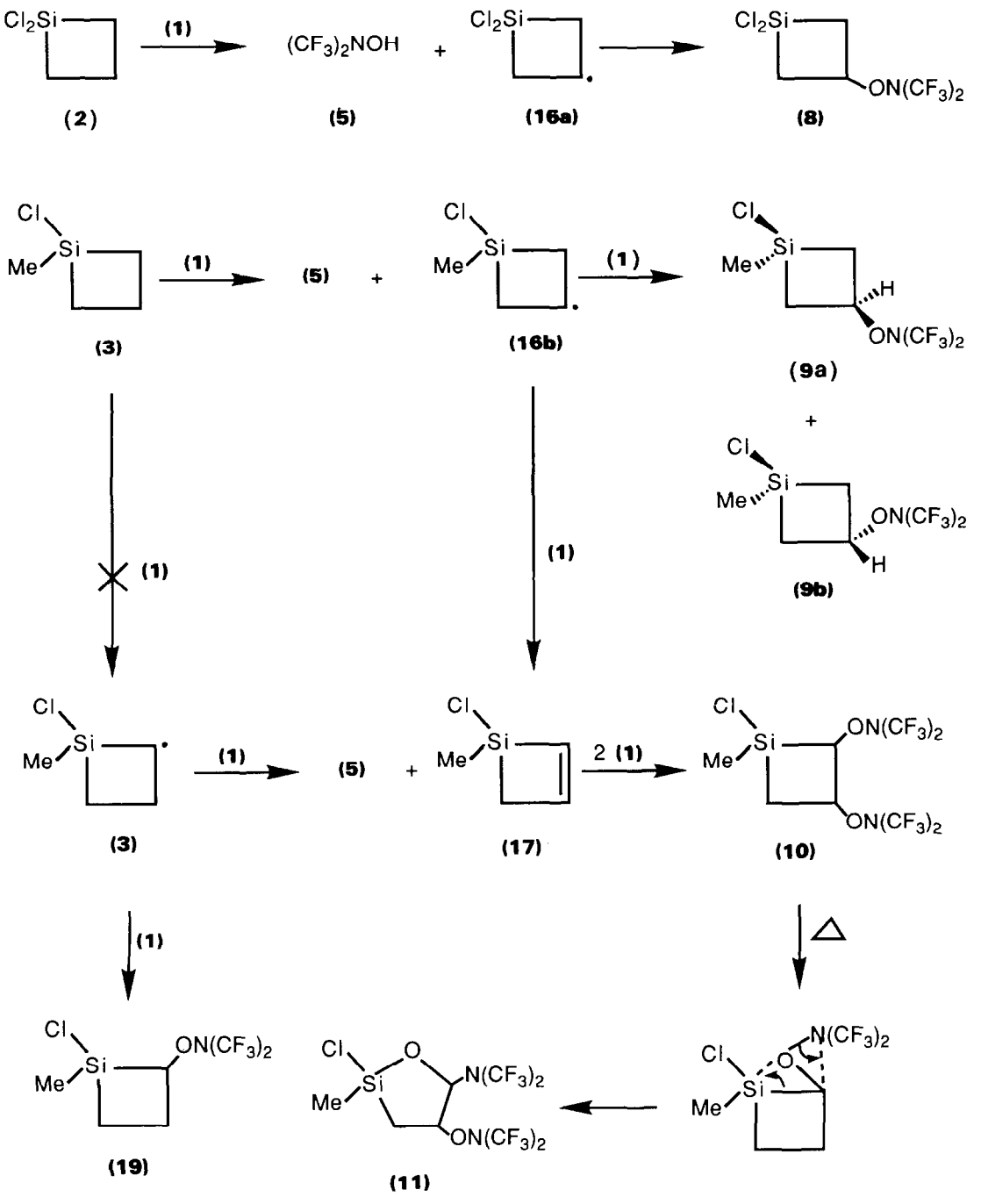
Further confirmation of the structure of compound **9** was obtained from its reactions with hydrogen chloride and concentrated hydrochloric acid. The reaction with hydrogen chloride (1:3 molar ratio) at 100 °C afforded {2-[bis(trifluoromethyl)amino-oxy]propyl}methyldichlorosilane (**14**) (49%) via Si–C bond cleavage and this compound was identified by a comparison of its IR, ^1H, ^{19}F NMR and mass spectra with those of the same compound synthesised by the reaction of oxyl **1** with the dialkyldichlorosilane $Pr^nSiMeCl_2$ [3]. On reaction with concentrated hydrochloric acid, the polysiloxane **15** ($n=3$, 85%) was formed and this gave spectral data (IR, ^1H, ^{19}F NMR and mass) which were identical to those of polysiloxane **15** ($n=4$) produced by hydrolysis of the dichlorosilane **14** with water [3].

$(CF_3)_2NOCHMeCH_2SiMeCl_2$ (14)



(15)

The higher-boiling mixture (8%) separated by GLC (90 °C) from the reaction involving silacyclobutane **3** was identified as a 2:1 mixture of the 2,3-disubstituted

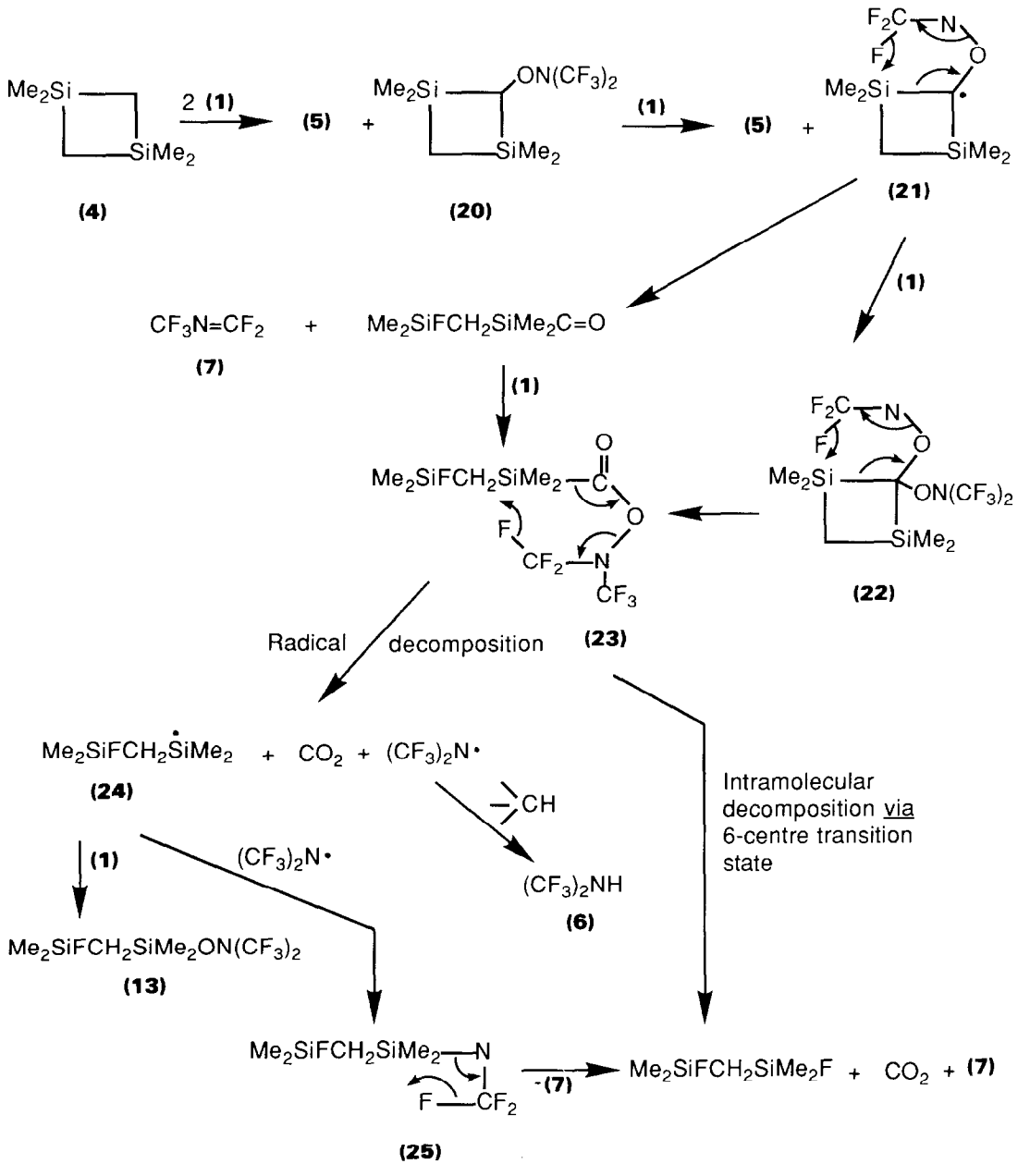


Scheme 1.

silacyclobutane **10** and the isomeric 2-silatetrahydrofuran **11** (formed by thermal rearrangement of **10**) by the NMR data obtained, i.e. δ_H 6.20 (1H, N–CH–O in **11**), 4.05 (5H, α and β >CH–O in **10** and **11**); 1.20 (6H, CH_2Si in **10** and **11**); 0.38 (9H, CH_3Si in **10** and **11**) ppm and δ_F +20.5 [6F, $(CF_3)_2N$ in **11**]; +8.5 [18F, β-$(CF_3)_2NO$ in **10** and **11**]; +7.8 [12F, α-$(CF_3)_2NO$ in **10**] ppm.

Products **8** and **11** are considered to have been formed as shown in Scheme 1.

Initial attack by oxyl **1** on the silacyclobutanes **2** and **3** gave the β-radicals **16** which were captured by oxyl **1** to afford compounds **8** and **9**. With β-radical **16b**, hydrogen abstraction by oxyl **1** leading to the silacyclobutene **17** competed to a small extent with coupling to give **9**. The α,β-disubstituted cyclobutane **10** was

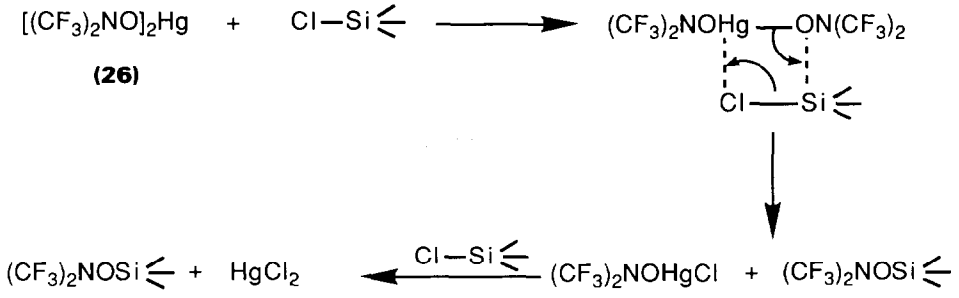


Scheme 2.

then formed by addition of oxyl **1** across the double bond of silacyclobutene **17**. It is considered far less likely that compound **10** was formed via hydrogen abstraction from the 2-position of silacyclobutane **3** to give the α-radical **18** which then underwent further abstraction leading to silacyclobutene **17**. This is because radical **18** would also have been expected to couple with oxyl **1** to afford the 2-substituted silacyclobutane **19** which was not detected in the products.

The thermal rearrangement of **10** to **11**, via a four-centre transition state, parallels the thermal rearrangement of other alkylsilanes substituted by the $(CF_3)_2NO$ group on a carbon α to silicon reported previously [2–4].

Hence, all the products **8–11** can be explained by exclusive abstraction of hydrogen by oxyl **1** from the 3-position leading to the β-radicals **16**. It is considered that the reasons for β-attack are that (i) the α-positions are deactivated due to the steric bulk of the groups on silicon and repulsion between the lone pairs on chlorine and those on the attacking oxyl **1** and (ii), perhaps more importantly, the β-radicals **16** are hyperconjugatively stabilised by four β-hydrogens while the α-radicals **18** are hyperconjugatively stabilised by



Scheme 3.

only two β-hydrogens. These factors have been advanced previously to explain the results obtained from oxyl **1** attack on the alkylsilanes $RSiF_3$ [2], $RSiCl_3$ [2] and R_2SiCl_2 [2, 3].

From the reaction of oxyl **1** with disilacyclobutane **4**, compounds containing $(CF_3)_2NO$ groups bonded to carbon were not detected and the 1,3-disilapentanes **12** and **13** were the only silicon-containing products isolated; appreciable amounts of the decomposition products CO_2, amine **6** and azapropene **7** were also formed.

The disilanes **12** and **13** were characterized by their NMR spectra, i.e. for **12**; δ_H 0.50 (d, 12H, $2SiMe_2$, $J_{F-H}=8$ Hz); 0.20 (t, 2H, $SiCH_2Si$, $J_{F-H}=8$ Hz) ppm and δ_F −75 (nonet, SiF, $J_{Me-F}\simeq J_{CH_2-F}=8$ Hz) ppm which is consistent with the formula $Me_2SiFCH_2SiMe_2F$ and for **13**; δ_H 0.48 (complex, $SiMe_2$ and $SiCH_2Si$) ppm with an absence of absorption at *c.* 4 ppm expected for $CHON(CF_3)_2$ and δ_F +8.5 [s, 6F, $ON(CF_3)_2$]; −75.2 (nonet, $Me_2SiF-CH_2$, $J_{Me-F}\simeq J_{CH_2-F}=8$ Hz) ppm which is consistent with the formula $(CF_3)_2NOSiMe_2CH_2SiMe_2F$.

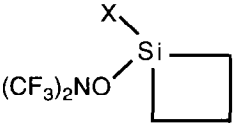
The observed products CO_2 and compounds **5–7**, **12** and **13** can be rationalized as being formed via initial attack at a CH_2 group leading to the monosubstituted compound **20**, followed by abstraction of the methine hydrogen to give the intermediate radical **21**, the precursor of the α,α-disubstituted disilacyclobutane **22**. Decomposition of radical **21** and/or the disilacyclobutane **22** then occurred via a six-centre transition state leading to the silyl ester **23** as shown in Scheme 2.

Although decomposition of ester **23** via a six-centre transition state would give the difluorodisilane **12**, the products including **12** can be explained by decomposition of **23** by a radical mechanism to afford the silyl radical **24**, the $(CF_3)_2N^{\cdot}$ radical and carbon dioxide. Trapping of the silyl radical **24** by oxyl **1** gave the disilane **13**, while coupling with the $(CF_3)_2N^{\cdot}$ radical led to compound **25** containing a $(CF_3)_2N$ group bonded to silicon. Compounds analogous to **25** have been found to be unstable and to decompose via a four-centre transition state to give azapropene **7** and a fluorosilane [10]. The remaining product amine **6** was formed by hydrogen abstraction by the radical $(CF_3)_2N^{\cdot}$.

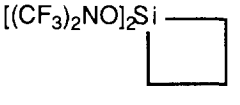
The surprising feature of the reaction was the reactivity of the monosubstituted compound **20** towards further attack by oxyl **1** even though the reaction was carried out using an excess of disilane **4**.

The mercurial $[(CF_3)_2NO]_2Hg$ (**26**) has been used widely for the replacement of halogen by the $(CF_3)_2NO$ group and reaction with the silane $ClSiMe_3$ has been reported to give the compound $(CF_3)_2NOSiMe_3$ in high yield (94%) [1].

In the present work, treatment of the monochlorosilacyclobutane **3** with mercurial **26** (2:1 molar ratio) at room temperature gave unchanged **3** (10% recovered) and the substitution product **27** (98%). An analogous reaction with the dichlorosilacyclobutane **2** gave unchanged **2** (46% recovered), the monosubstitution product **28** (22%) and the disubstitution product **29** (76%), while use of a 1:1 molar ratio of reactants afforded unchanged **2** (18% recovered) and compound **29** (90%). The products are presumably formed via a four-centre transition state with the driving force for the reaction being the formation of strong Si−O and Hg−Cl bonds (Scheme 3).



(27) X = Me
(28) X = Cl



(29)

The ease of formation of the disubstitution product **29** relative to that of the monosubstitution product **30** can be explained by the $(CF_3)_2NO$ group having a

larger electron-withdrawing $-I$ effect than chlorine, thus rendering the silicon atom more electron-deficient in the monosubstitution product **30** than in the reactant silacyclobutane **2** and hence more susceptible to nucleophilic attack.

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