Nitroxide Chemistry. Part IX.[1] Reaction of *NN*-Bistrifluoromethylamino-oxyl with Tetramethylsilane, Chloromethylsilanes, and Methoxymethylsilanes

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Reaction of the oxyl $(CF_3)_2N{\cdot}O{\cdot}$ with the silanes Me_nSiCl_{4-n} (n = 1—4) involves formation of silyl esters $R_3Si{\cdot}CO_2{\cdot}N(CF_3)_2$ *via* the disubstitution compounds $R_3Si{\cdot}CH[O{\cdot}N(CF_3)_2]_2$. Under the conditions employed the silyl esters are unstable and decompose either by a radical mechanism to give carbon dioxide and bistrifluoromethylamino and silyl ($R_3Si{\cdot}$; R_3 = Me_3 or Me_2Cl) radicals or by an intramolecular elimination of carbon monoxide to afford the hydroxylamine $R_3Si{\cdot}O{\cdot}N(CF_3)_2$ (R_3 = $MeCl_2$ or Cl_3) which competes with the radical mechanism. The silanes $(MeO)_nSiMe_{4-n}$ (n = 3 and 4) react to give the substitution products $(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}SiMe(OMe)_2$ and $(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}Si(OMe)_3$, respectively. Further oxyl attack on the latter product gives exclusively the silane $[(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}O]_2Si(OMe)_2$.

REACTIONS of *NN*-bistrifluoromethylamino-oxyl, (I), with a wide variety of organic compounds, *e.g.* alkanes, alkenes, alkynes, allenes, and alkylbenzenes, have been reported.[1,2] However, the only report of reactions of (I) with silicon compounds[3] concerns hydrogen-abstraction reactions with hydrosilanes to give the substituted silanes (II) [equation (1)]. Silanes of type (II) have also been prepared by reaction of the appropriate chlorosilane with the reagents $(CF_3)_2N{\cdot}O^-Na^+$ (ref. 4) or $(CF_3)_2N{\cdot}OH$.[5]

$$R_3SiH + \underset{(I)}{(CF_3)_2N{\cdot}O{\cdot}} \longrightarrow (CF_3)_2N{\cdot}OH + R_3Si{\cdot}$$
$$\xrightarrow{(I)} \underset{(II)}{R_3Si{\cdot}O{\cdot}N(CF_3)_2} \qquad (1)$$

As part of a more general investigation into attack of (I) on alkyl- and vinyl-silanes, its reactions with Me_nSiCl_{4-n} (n = 1—4) and $(MeO)_nSiMe_{4-n}$ (n = 3 and 4) are now reported.

RESULTS AND DISCUSSION

(a) *The Silanes* Me_nSiCl_{4-n}.—Reaction of an equimolar mixture of oxyl (I) and tetramethylsilane at room temperature gave unchanged silane (61% recovered), carbon dioxide (36% based on one methyl group in silane reacted), perfluoro-2-azapropene, (III) (6% on oxyl), *NN*-bistrifluoromethylamine, (IV) (8% on oxyl), *NN*-bistrifluoromethylhydroxylamine, (V) (49% on oxyl), fluorotrimethylsilane, (VI) (15% on silane, 6%

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[1] Part VIII, R. E. Banks, J. M. Birchall, A. K. Brown, R. N. Haszeldine, and F. Moss, *J.C.S. Perkin I*, 1975, 2033.

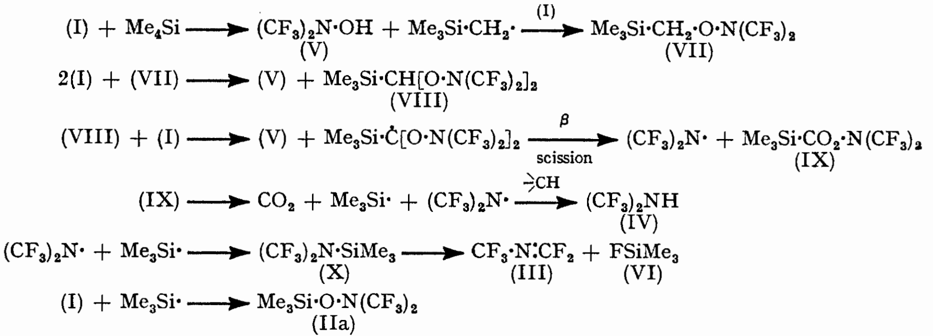
[2] R. E. Banks, D. R. Choudhury, and R. N. Haszeldine, *J.C.S. Perkin I*, 1973, 80, 1092 and refs. therein.

[3] H. G. Ang, *Chem. Comm.*, 1968, 1320.

[4] R. E. Banks, R. N. Haszeldine, and D. L. Hyde, *Chem. Comm.*, 1967, 413.

[5] A. C. Delany, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1968, 2537.

on oxyl), *NN*-bistrifluoromethyl-*O*-trimethylsilylhydroxylamine, (IIa) (22% on silane, 8% on oxyl), (*NN*-bistrifluoromethylamino-oxylmethyl)trimethylsilane, (VII) (28% on silane, 11% on oxyl), and a number of unidentified compounds. The initial reaction of (I) with Me_4Si is hydrogen abstraction leading to the substitution product (VII); the other products result from further oxyl attack on silane (VII) (Scheme 1).



$$\begin{array}{l}
\text{(I)} + Me_4Si \longrightarrow \underset{\text{(V)}}{(CF_3)_2N{\cdot}OH} + Me_3Si{\cdot}CH_2{\cdot} \xrightarrow{\text{(I)}} \underset{\text{(VII)}}{Me_3Si{\cdot}CH_2{\cdot}O{\cdot}N(CF_3)_2} \\
2\text{(I)} + \text{(VII)} \longrightarrow \text{(V)} + \underset{\text{(VIII)}}{Me_3Si{\cdot}CH[O{\cdot}N(CF_3)_2]_2} \\
\text{(VIII)} + \text{(I)} \longrightarrow \text{(V)} + Me_3Si{\cdot}\dot{C}[O{\cdot}N(CF_3)_2]_2 \xrightarrow[\text{scission}]{\beta} (CF_3)_2N{\cdot} + \underset{\text{(IX)}}{Me_3Si{\cdot}CO_2{\cdot}N(CF_3)_2} \\
\text{(IX)} \longrightarrow CO_2 + Me_3Si{\cdot} + (CF_3)_2N{\cdot} \xrightarrow{\geqslant CH} \underset{\text{(IV)}}{(CF_3)_2NH} \\
(CF_3)_2N{\cdot} + Me_3Si{\cdot} \longrightarrow \underset{\text{(X)}}{(CF_3)_2N{\cdot}SiMe_3} \longrightarrow \underset{\text{(III)}}{CF_3{\cdot}N{:}CF_2} + \underset{\text{(VI)}}{FSiMe_3} \\
\text{(I)} + Me_3Si{\cdot} \longrightarrow \underset{\text{(IIa)}}{Me_3Si{\cdot}O{\cdot}N(CF_3)_2}
\end{array}$$

SCHEME 1

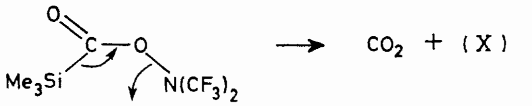
Formation of the substitution product (XI) and the ester (XII) in the reaction of (I) with the hydrocarbon analogue neopentane [equation (2)] has been explained similarly,[6] but unlike the silyl ester (IX) the hydrocarbon ester (XII) was stable under the reaction conditions.

$$Me_4C + \text{(I)} \longrightarrow \underset{\text{(XI)}}{Me_3C{\cdot}CH_2{\cdot}O{\cdot}N(CF_3)_2} + \underset{\text{(XII)}}{Me_3C{\cdot}CO_2{\cdot}N(CF_3)_2} \quad (2)$$

Silyl esters of type $R_3Si{\cdot}CO_2Me$ (R = alkyl or aryl) are reported to be thermally unstable[7] and also highly susceptible to nucleophilic attack at silicon[8] with resulting cleavage of the Si–C bond. It is therefore possible that hydroxylamine (IIa), CO_2, and amine (IV) are formed to some extent by nucleophilic attack of hydroxylamine (V) on the ester (IX) [equation (3)].

$$\begin{array}{l}
\text{(V)} + \text{(IX)} \longrightarrow Me_3Si{\cdot}\overset{+}{O}H{\cdot}N(CF_3)_2 + CO_2 + (CF_3)_2N^- \\
\qquad\qquad\qquad \Big\downarrow {\scriptstyle (CF_3)_2N^-} \qquad\qquad\qquad\qquad (3) \\
\qquad\qquad\quad \text{(IIa)} + \text{(IV)}
\end{array}$$

Decomposition of the silyl ester (IX) could also occur to some extent to give the silyl amine (X) directly *via* a four-centre transition state. The amine (X) is known to be unstable at room temperature and to decompose to give a mixture of compounds (III) and (VI)[9] probably *via* a four-centre transition state. Thus isolation of compounds (III) and (VI) in equimolar amounts in the present reaction is strong evidence for intermediacy of the amine (X).



For spectroscopic identification compound (IIa) was prepared in high yield by reaction of chlorotrimethylsilane with $[(CF_3)_2N{\cdot}O]_2Hg$, (XV) (94%), and with hydroxylamine (V) (100%, 15% conversion).

The surprising features of the reaction are the non-detection in the products of perfluoro(2,4-dimethyl-2,4-diaza-3-oxapentane), (XIII) (a product in the corresponding neopentane reaction), and the bistrifluoromethylamino-compound (XIV) formed by combination reactions of the bistrifluoromethylamino-radical [equations (4) and (5)]. However, it is possible

$$(CF_3)_2N{\cdot} + \text{(I)} \longrightarrow \underset{\text{(XIII)}}{(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2} \quad (4)$$

$$(CF_3)_2N{\cdot} + Me_3Si{\cdot}CH_2{\cdot} \longrightarrow \underset{\text{(XIV)}}{Me_3Si{\cdot}CH_2{\cdot}N(CF_3)_2} \quad (5)$$

that these compounds are two of the unidentified products formed in the reaction.

In order to obtain more information on the further reaction of silane (VII) with (I) attempts were made to synthesise the silane by reaction of (XV) first with (chloromethyl)trimethylsilane and then with the more reactive (iodomethyl)trimethylsilane [equation (6)]. Although some reaction occurred in the latter case (*ca.* 5%), the identified products (V) and (VI) indicated that the desired nucleophilic attack on carbon had not taken place.

$$2Me_3Si{\cdot}CH_2X + [(CF_3)_2N{\cdot}O]_2Hg\ \text{(XV)} \longrightarrow HgX_2 + \underset{\text{(VII)}}{2Me_3Si{\cdot}CH_2{\cdot}O{\cdot}N(CF_3)_2} \quad (6)$$

The reaction of (I) with chlorotrimethylsilane (1 : 1 molar ratio) at room temperature was much slower than that with $SiMe_4$ and gave unchanged Me_3SiCl (58% recovered), CO_2 (58% on silane), hydrogen chloride (30% on silane), (III) (trace), IV) (26%), (V) (28%), (IIa) (36% on silane, 13% on oxyl), (*NN*-bistrifluoromethylamino-oxy)chlorodimethylsilane, (IIb) (53% on silane, 19% on oxyl), bis(*NN*-bistrifluoromethylamino-oxy)dimethylsilane, (XVI) (7% on silane, 5% on oxyl),

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[6] R. E. Banks, R. N. Haszeldine, and B. Justin, *J. Chem. Soc.* (*C*), 1971, 2777.

[7] R. G. Severson, *J. Amer. Chem. Soc.*, 1951, **73**, 1424; A. G. Brook and R. J. Mauris, *ibid.*, 1957, **79**, 971.

[8] A. G. Brook and N. V. Schwartz, *J. Org. Chem.*, 1962, **27**, 2311.

[9] H. G. Ang, *J. Chem. Soc.* (*A*), 1968, 2734.

and a number of unidentified minor compounds. Silanes (IIb) (22%) and (XVI) (78%) were unambiguously synthesised by reaction of (XV) with dichlorodimethylsilane at room temperature [equation (7)]. The observed products are considered to be formed as shown on Scheme 2.

$$\mathrm{Me_2SiCl_2 + (XV) \longrightarrow \underset{(IIb)}{Me_2SiCl{\cdot}O{\cdot}N(CF_3)_2} + \underset{(XVI)}{Me_2Si[O{\cdot}N(CF_3)_2]_2}} \qquad (7)$$

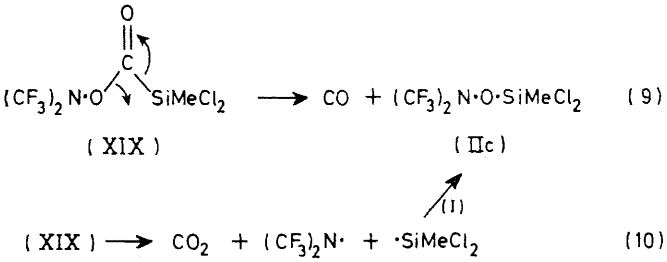
$$\begin{aligned}
&\mathrm{Me_3SiCl + 2(I) \longrightarrow (V) + \underset{(XVII)}{Me_2SiCl{\cdot}CH_2{\cdot}O{\cdot}N(CF_3)_2}}\\
&\mathrm{(XVII) + 3(I) \longrightarrow 2(V) + Me_2SiCl{\cdot}\dot{C}[O{\cdot}N(CF_3)_2]_2}\\
&\qquad\qquad\qquad \Big\downarrow \beta\ \text{scission}\\
&\mathrm{\underset{(XVIII)}{Me_2SiCl{\cdot}CO_2{\cdot}N(CF_3)_2} + (CF_3)_2N{\cdot} \xrightarrow{\geq CH} (IV)}\\
&\mathrm{(XVIII) \longrightarrow CO_2 + (CF_3)_2N{\cdot} + Me_2SiCl{\cdot} \xrightarrow{(I)} (IIb)}\\
&\mathrm{(V) + Me_3SiCl \longrightarrow HCl + (IIa)}\\
&\mathrm{(V) + (IIb) \longrightarrow HCl + (XV)}
\end{aligned}$$

SCHEME 2

The major features of the reaction are (*i*) the failure to detect the expected major product (XVII), (*ii*) the absence of significant amounts of the azapropene (III) and chlorofluorodimethylsilane in the products, and (*iii*) the formation of silanes (IIb) and (XVI) as major products. The first observation indicates that in the slow $\mathrm{Me_3SiCl}$ reaction the formation of the substituted silane (XVII) is slow relative to further oxyl attack on silane (XVII), *i.e.* hydrogen abstraction from $\mathrm{Me_3SiCl}$ by oxyl (I) is the rate-determining step. In the much faster $\mathrm{Me_4Si}$ reaction, the reaction of the substituted silane (VII) with oxyl takes place at a slower rate than does oxyl attack on the reactant silane. Thus in the $\mathrm{Me_3SiCl}$ reaction the initial substitution product (XVII) reacts further as fast as it is formed while in the $\mathrm{Me_4Si}$ reaction the concentration of the substitution product (VII) builds up and it can be isolated. The absence of azapropene (III) and $\mathrm{FSiMe_2Cl}$ indicates that decomposition of the intermediate silyl ester (XVIII) takes place exclusively by a radical mechanism as shown (Scheme 2) and there is no contribution from a non-radical mechanism [equation (8)]. Since attack of (I) on $\mathrm{Me_3SiCl}$ is slow, reaction of the product hydroxylamine (V) with $\mathrm{Me_3SiCl}$ and the chlorosilane (IIb) can successfully compete.

$$\mathrm{(XVIII) \not\longrightarrow CO_2 + (CF_3)_2N{\cdot}SiMe_2Cl \longrightarrow (III) + FSiMe_2Cl} \qquad (8)$$

There was no reaction between (I) and $\mathrm{Me_2SiCl_2}$ (2 : 1 molar ratio) at room temperature (28 d), but at 70 °C reaction slowly took place and gave unchanged $\mathrm{Me_2SiCl_2}$ (48% recovered), carbon monoxide (68%), $\mathrm{CO_2}$ (11%), (III) (2%), (IV) (25%), (V) (51%), (*NN*-bistrifluoromethylamino-oxyl)dichloromethylsilane, (IIc) (84% based on silane, 22% on oxyl), and several minor unidentified compounds. It is considered that the intermediate silyl ester (XIX) is formed, but, unlike the silyl esters (IX) and (XVIII), it mainly decomposes by an intramolecular mechanism to give silane (IIc) and CO [equation (9)] and it only decomposes to a minor extent by a radical mechanism to give $\mathrm{CO_2}$ [equation (10)].



$$\mathrm{(CF_3)_2N{\cdot}O{\cdot}CO{\cdot}SiMeCl_2 \longrightarrow CO + \underset{(IIc)}{(CF_3)_2N{\cdot}O{\cdot}SiMeCl_2}} \qquad (9)$$

$$\mathrm{(XIX) \longrightarrow CO_2 + (CF_3)_2N{\cdot} + {\cdot}SiMeCl_2 \xrightarrow{(I)} (IIc)} \qquad (10)$$

Since this reaction was carried out at 70 °C while the other reactions were at room temperature, it is possible that silyl esters $\mathrm{R_3Si{\cdot}CO_2{\cdot}N(CF_3)_2}$ decompose preferentially by elimination of CO at 70 °C and by a radical mechanism to give $\mathrm{CO_2}$ at room temperature. Alternatively, it is possible that the silyl esters are mainly decomposed at room temperature *via* oxyl attack at silicon [equation (11)], while at 70 °C thermal decomposition of the silyl esters can occur readily. Surprisingly there was no evidence for reaction of hydroxylamine (V) with the reactant chlorosilane or the chlorosilane (IIc) as observed in the $\mathrm{Me_3SiCl}$ reaction.

$$\mathrm{(I) + \underset{(XVIII)}{Me_2SiCl{\cdot}CO_2{\cdot}N(CF_3)_2} \longrightarrow \underset{(IIb)}{(CF_3)_2N{\cdot}O{\cdot}SiMe_2Cl} + CO_2 + (CF_3)_2N{\cdot}} \qquad (11)$$

The reaction of (I) with methyltrichlorosilane (1 : 1 molar ratio) was very slow (12 weeks) at 70 °C and gave $\mathrm{MeSiCl_3}$ (74% recovered), CO (55%), $\mathrm{CO_2}$ (43%), (IV) (30%), (V) (49%), (*NN*-bistrifluoromethylamino-oxy)-trichlorosilane, (IId) (84% based on silane, 17% on oxyl), and minor unidentified products. A sample of silane (IId) for comparison purposes was prepared by reaction of (I) with trichlorosilane, but trifluorosilane did not react with the oxyl under comparable conditions (room temperature).

The reaction of $\mathrm{MeSiCl_3}$ with oxyl (I) is thus similar to that with $\mathrm{Me_2SiCl_2}$ except that the comparable amounts of CO and $\mathrm{CO_2}$ isolated indicate either (*i*) that the silyl ester (XX) decomposes to a comparable extent by intramolecular elimination [equation (12)] and a radical reaction [equation (13)] at 70 °C or (*ii*) that attack of (I) on ester (XX) [*cf.* equation (11)] competes successfully with the thermal elimination of CO.

$$\mathrm{\underset{(XX)}{(CF_3)_2N{\cdot}O{\cdot}CO{\cdot}SiCl_3} \longrightarrow CO + \underset{(IId)}{(CF_3)_2N{\cdot}O{\cdot}SiCl_3}} \qquad (12)$$

$$\mathrm{(XX) \longrightarrow CO_2 + (CF_3)_2N{\cdot} + Cl_3Si{\cdot} \xrightarrow{(I)} (IId)} \qquad (13)$$

(b) *Methoxysilanes*.—Reaction of oxyl (I) with tetramethoxysilane (1 : 1 molar ratio) at room temperature gave unchanged silane (60% recovered), (V) (50%), and the substitution products (XXI) (73%) and (XXII) (27%); using a 2 : 1 molar ratio of oxyl to silane, compounds (XXI) and (XXII) were obtained in a similar ratio. Further reaction of the initially formed compound

(XXI) with oxyl thus occurs at a second methoxy-group rather than the $(CF_3)_2N{\cdot}O{\cdot}CH_2$ group as found

$(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}Si(OMe)_3$ (XXI) $[(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}O]_2Si(OMe)_2$ (XXII)

with Me_4Si and the chloromethylsilanes. The C–H bonds in the $(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}O$ group must therefore be deactivated towards oxyl attack probably as a result of the two oxygen atoms. A similar deactivation has been observed in the reaction of dimethyl ether with (I) where the initial product $(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}OMe$ reacts with further oxyl exclusively at the free methyl group.[10]

The reaction of (I) with trimethoxymethylsilane (1 : 1 molar ratio) at room temperature gave unchanged silane (47% recovered), (V) (50%), the substitution compound (XXIII) (95% on silane, 48% on oxyl), and a minor component of longer g.l.c. retention time, probably the disubstitution compound (XXIV) (*ca.* 4% on silane, *ca.* 20% on oxyl) or, less likely, the disubstitution compound

$(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}SiMe(OMe)_2$
(XXIII)

$[(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}O]_2SiMe(OMe)$
(XXIV)

$(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}Si(OMe)_2{\cdot}CH_2{\cdot}O{\cdot}N(CF_3)_2$
(XXV)

(XXV). Since compound (XXIII) was the only monosubstitution product detected it is apparent that attack of (I) on a methoxy-group is preferred to attack on a methyl group and so it is probable that further oxyl attack on compound (XXIII) occurs at a second methoxy-group to give (XXIV) rather than at the methyl group to give (XXV).

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system to avoid contact with air or moisture. The oxyl (I) was prepared by oxidation of *NN*-bistrifluoromethylhydroxylamine with silver(I) oxide[11] and was stored at room temperature in a blackened Pyrex bulb fitted with a Springham's greaseless stopcock (Viton diaphragm). Reactions were carried out *in vacuo* in Pyrex ampoules (*ca.* 300 cm^3 unless stated to the contrary). Products were separated by fractional condensation *in vacuo* or by g.l.c. [Perkin-Elmer F21 instrument using columns (2—8 m) of Silicone SE30 oil or dinonyl phthalate (DNP) (10—30%) on Celite as indicated in the text] and were examined by molecular-weight determination (Renault's method), i.r. spectroscopy (Perkin-Elmer model 257 spectrophotometer with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 or Hitachi R20A spectrometers operating at 60.0 MHz for ^1H and 56.46 MHz for ^{19}F, or a Varian Associates HA100 spectrometer operating at 100.0 MHz for ^1H and 94.1 MHz for ^{19}F, using internal tetramethylsilane and external trifluoroacetic acid as the respective references), and mass spectrometry (A.E.I. MS902 instrument). Spectroscopic data for the compounds are in Supplementary Publication No. SUP 21467 (9 pp.).* B.p.s were determined by Siwoloboff's method.

The silanes employed were either commercial samples which were carefully purified before use or they were prepared by standard methods.

Reactions of Bistrifluoromethylamino-oxyl, (I).—(a) *With tetramethylsilane.* A mixture of (I) (5.04 g, 30.0 mmol) and Me_4Si (2.64 g, 30.0 mmol), kept *in vacuo* at room temperature (48 h), gave (*i*) carbon dioxide (0.18 g, 4.2 mmol, 36%; *M* 44), (*ii*) a mixture (1.34 g, 12.6 mmol) shown by i.r. spectroscopy and g.l.c. (4 m SE30 at 20 °C) to consist of *NN*-bistrifluoromethylamine, (IV) (0.37 g, 2.5 mmol, 8%), perfluoro-2-azapropene, (III) (0.23 g, 1.7 mmol, 6%), and unchanged Me_4Si (0.74 g, 8.4 mmol, 28% recovered), (*iii*) unchanged Me_4Si (0.89 g, 10.0 mmol, 33% recovered), (*iv*) a colourless liquid (2.90 g, 17.4 mmol) shown by i.r. spectroscopy and g.l.c. (2 m SE30 and 2 m DNP at 50 °C) to consist of *NN*-bistrifluoromethylhydroxylamine, (V) (2.49 g, 14.7 mmol, 49%), fluorotrimethylsilane, (VI) (0.17 g, 1.7 mmol, 15%), and *NN*-bistrifluoromethyl-*O*-trimethylsilylhydroxylamine, (IIa) (0.24 g, 1.0 mmol, 9%), and (*v*) a colourless liquid (1.59 g) which was separated by g.l.c. (7 m SE30 at 60 °C) into its components (IIa) (0.38 g, 1.5 mmol, 13%), (*NN-bistrifluoromethylamino-oxymethyl*)*trimethylsilane*, (VII) (0.81 g, 3.2 mmol, 28%) (Found: C, 28.5; H, 4.4. $C_6H_{11}F_6NOSi$ requires C, 28.2; H, 4.3%), b.p. 90—91 °C, and a mixture (0.40 g) of four unknown compounds.

(b) *With chlorotrimethylsilane.* A mixture of (I) (3.90 g, 23.2 mmol) and Me_3SiCl (2.16 g, 20.0 mmol), kept at room temperature (12 d), gave (*i*) a mixture (0.31 g, 7.5 mmol; *M* 41) of carbon dioxide (0.23 g, 4.9 mmol, 58%) and hydrogen chloride (0.08 g, 2.5 mmol, 30%) as determined by mass spectrometry and i.r. spectroscopy, (*ii*) (IV) (0.90 g, 5.9 mmol, 26%) contaminated with a trace of (III) (i.r.), (*iii*) a colourless liquid (2.88 g, 21.2 mmol) which was identified by i.r. spectroscopy and g.l.c. (2 m DNP at 50 °C) as a mixture of (V) (1.12 g, 6.6 mmol, 28%), unchanged Me_3SiCl (1.25 g, 11.5 mmol, 58% recovered), and (IIa) (0.51 g, 3.1 mmol, 36%), and (*iv*) a colourless liquid (1.43 g) from which the two major components were separated by g.l.c. (4 m DNP at 65 °C) and identified as (*NN*-bistrifluoromethylamino-oxy)chlorodimethylsilane, (IIb) (1.17 g, 4.5 mmol, 53%) (Found: C, 18.6; H, 2.2. Calc. for $C_4H_6ClF_6NOSi$: C, 18.3; H, 2.3%) and *bis*(*NN-bistrifluoromethylamino-oxy*)*dimethylsilane*, (XVI) (0.24 g, 0.6 mmol, 7%) (Found: C, 18.2; H, 1.7. $C_6H_6F_{12}N_2O_2Si$ requires C, 18.3; H, 1.5%), b.p. 113—114 °C, n_D^{20} 1.3000.

(c) *With dimethyldichlorosilane.* A mixture of (I) (4.05 g, 24.0 mmol) and Me_2SiCl_2 (1.55 g, 12.0 mmol) heated at 70 °C (21 d) gave (*i*) carbon monoxide (0.12 g, 4.2 mmol, 68%; *M* 28), (*ii*) CO_2 (0.03 g, 0.7 mmol, 11%; *M* 44), (*iii*) a mixture (0.97 g, 6.4 mmol; *M* 151) of (IV) (0.92 g, 6.0 mmol, 25%) and (III) (0.05 g, 0.4 mmol, 2%), (*iv*) a mixture (3.93 g), which was separated by g.l.c. (2 m dnp at 50 °C) into its three components, (V) (2.07 g, 12.2 mmol, 51%), unchanged Me_2SiCl_2 (0.75 g, 5.8 mmol, 48% recovered), and (*NN*-bistrifluoromethylamino-oxy)dichloromethylsilane, (IIc) (1.10 g, 3.9 mmol, 63%), and (*v*) a mixture (0.56 g) which was shown by g.l.c. (2 m dnp at 50 °C (to consist of (IIc) (0.36 g, 1.3 mmol, 21%) and three unidentified components (0.20 g).

(d) *With trichloromethylsilane.* A mixture of (I) (3.36 g, 20.0 mmol) and $MeSiCl_3$ (3.17 g, 20.7 mmol), heated at

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

[10] R. E. Banks, A. K. Brown, and R. N. Haszeldine, unpublished work.

[11] R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *J. Chem. Soc.* (*C*), 1966, 901.

70 °C (12 weeks), gave (*i*) CO (0.08 g, 2.9 mmol, 55%), (*ii*) CO_2 (0.10 g, 2.3 mmol, 43%), (*iii*) (IV) (0.92 g, 6.1 mmol, 30%), (*iv*) a colourless liquid (4.76 g) which was separated by g.l.c. (2 m DNP at 50 °C) into its components (V) (1.68 g, 9.9 mmol, 49%), unchanged $MeSiCl_3$ (2.20 g, 15.4 mmol, 74% recovered), and *NN*-bistrifluoromethyl-*O*-trichlorosilylhydroxylamine, (IId) (0.88 g, 2.9 mmol, 55%), and (*v*) a liquid (0.74 g) which was shown by g.l.c. (2 m dnp at 50 °C) to consist of (IId) (0.47 g, 1.5 mmol, 29%) and several unidentified components (0.27 g).

(e) *With tetramethoxysilane.* A mixture of (I) (1.11 g, 6.6 mmol) and $(MeO)_4Si$ (1.00 g, 6.6 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 70 cm^3) and kept at room temperature (4 h), gave (*i*) (V) (0.55 g, 3.3 mmol, 50%) and (*ii*) a higher-boiling fraction (1.56 g) which was separated by g.l.c. (6 m SE30 at 120 °C) into its three components identified as unchanged $(MeO)_4Si$ (0.61 g, 4.0 mmol, 60% recovered), (NN-*bistrifluoromethylamino-oxymethoxy*)*trimethoxysilyl ether*, (XXI) (0.61 g, 1.9 mmol, 73%) (Found: C, 22.5; H, 3.7; F, 35.7. $C_6H_{11}F_6NO_5Si$ requires C, 22.6; H, 3.6; F, 35.7%), b.p. 148—149 °C, n_D^{20} 1.3313, and *bis*-[(NN-*bistrifluoromethylamino-oxy*)*methoxy*]*dimethoxysilane*, (XXII) (0.34 g, 0.7 mmol, 27%) (Found: C, 20.1; H, 2.2; F, 46.9. $C_8H_{10}F_{12}N_2O_6Si$ requires C, 19.8; H, 2.1; F, 46.9%), b.p. 176—177 °C, n_D^{20} 1.3191.

(f) *With trimethoxymethylsilane.* A mixture of (I) (2.91 g, 17.3 mmol) and $(MeO)_3SiMe$ (2.46 g, 18.1 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 70 cm^3) and kept at room temperature (1 h), gave (*i*) (V) (1.21 g, 7.3 mmol, 42%), (*ii*) a mixture (0.96 g) which was shown by g.l.c. (2 m DNP at 75 °C) to consist of (V) (0.24 g, 1.4 mmol, 8%) and unchanged $(MeO)_3SiMe$ (0.72 g, 5.3 mmol, 29% recovered), and (*iii*) a mixture (3.18 g) which was separated by g.l.c. (7 m SE30 at 100 °C) into its components, unchanged $(MeO)_3SiMe$ (0.56 g, 4.1 mmol, 28% recovered), [(NN-*bistrifluoromethylamino-oxy*)*methoxy*]*dimethoxymethylsilane*, (XXIII) (2.45 g, 8.3 mmol, 95%) (Found: C, 24.1; H, 3.9. $C_6H_{11}F_6NO_4Si$ requires C, 23.8; H, 3.6%), b.p. 132—133 °C; n_D^{20} 1.3330, and a component (*ca.* 0.15 g) with a longer g.l.c. retention time.

(g) *With trichlorosilane.* A mixture of (I) (3.36 g, 20.0 mmol) and $HSiCl_3$ (1.35 g, 10.0 mmol), sealed *in vacuo* in a Pyrex ampoule and kept at room temperature (3 h), gave unchanged $HSiCl_3$ (0.01 g, 0.03 mmol, 0.3% recovered) and a mixture (4.69 g) which was separated by g.l.c. (4 m DNP at 50 °C) into its components (V) (1.67 g, 9.9 mmol, 49%) and (IId) (2.98 g, 9.9 mmol, 99%) (Found: C, 8.2; N, 4.9; F, 37.5. Calc. for $C_2Cl_3F_6NOSi$: C, 7.9; N, 4.6; F, 37.7%), b.p. 83—84 °C, n_D^{20} 1.3296.

(h) *With trifluorosilane.* A mixture of (I) (1.68 g, 10.0 mmol) and $HSiF_3$ (0.43 g, 5.0 mmol), kept at room temperature (7 d) gave only unchanged reactants (100%, recovered).

Reactions of Bis(*bistrifluoromethylamino-oxy*)*mercury*(II), (XV), *with Silanes.*—(a) *With* Me_3SiCl. A mixture of (XV) (1.84 g, 3.4 mmol) and Me_3SiCl (0.74 g, 6.8 mmol), contained in a Pyrex ampoule (*ca.* 70 cm^3) which was shaken at room temperature (18 h), gave (IIa) (1.54 g, 6.4 mmol, 94%) (Found: C, 25.0; H, 3.7. Calc. for $C_5H_9F_6NOSi$: C, 24.9; H, 3.7%), b.p. 78—79 °C (lit.,[5] 69 °C), n_D^{20} 1.3139, and a white residue (0.88 g) of mercury(II) chloride.

(b) *With* Me_2SiCl_2. A mixture of (XV) (2.68 g, 5.0 mmol) and Me_2SiCl_2 (0.64 g, 5.0 mmol), reacted as in the previous experiment (12 h), gave a mixture (1.23 g) which was separated by g.l.c. (4 m DNP at 70 °C) into its two components, (XVI) (0.94 g, 3.9 mmol, 78%) (Found: C, 18.2; H, 1.7. Calc. for $C_6H_6F_{12}N_2O_2Si$: C, 18.3; H, 1.5%) and (IIb) (0.29 g, 1.1 mmol, 22%) (Found: C, 18.6; H, 2.2. Calc. for $C_4H_6ClF_6NOSi$: C, 18.3; H, 2.3%). A residue (1.36 g) consisting mainly of $HgCl_2$ remained in the reaction tube.

(c) *With iodomethyltrimethylsilane.* A mixture of (XV) (1.68 g, 3.1 mmol) and $Me_3Si(CH_2I)$ (1.03 g, 4.8 mmol), reacted as in experiment (a) (8 d), gave a volatile fraction (1.30 g) which was shown by g.l.c. (2 m SE30 at 100 °C) to contain unchanged $Me_3Si(CH_2I)$ (0.98 g, 4.6 mmol, 95% recovered), (V) (0.13 g, 0.8 mmol), (VI) (*ca.* 0.05 g, *ca.* 0.5 mmol), and two unidentified components (*ca.* 0.15 g). An attempted reaction between equimolar quantities of (chloromethyl)trimethylsilane and (XV) carried out under the same conditions gave only unchanged reactants.

Reaction of (V) *with* Me_3SiCl.—A mixture of (V) (1.69 g, 10.0 mmol) and Me_3SiCl (1.08 g, 10.0 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 20 cm^3) and kept at room temperature (28 d), gave HCl (0.05 g, 1.4 mmol, 93%) and a higher-boiling liquid (2.72 g) which was shown by g.l.c. (2 m dnp at 50 °C) to consist of (IIa) (0.36 g, 1.5 mmol, 100%), unchanged Me_3SiCl (0.91 g, 8.4 mmol, 84% recovered), and unchanged (V) (1.44 g, 8.5 mmol, 85% recovered).

We thank I.C.I. Limited (Nobel Division) and Midland Silicones Limited for gifts of chloromethylsilanes.

[5/595 *Received, 2nd April,* 1975]