Nitroxide Chemistry. Part X.[1] Reactions of *NN*-Bistrifluoromethylamino-oxyl with Alkyltrihalogenosilanes and Vinylsilanes; Rearrangement of (1-*NN*-Bistrifluoromethylamino-oxyalkyl)silanes [2]

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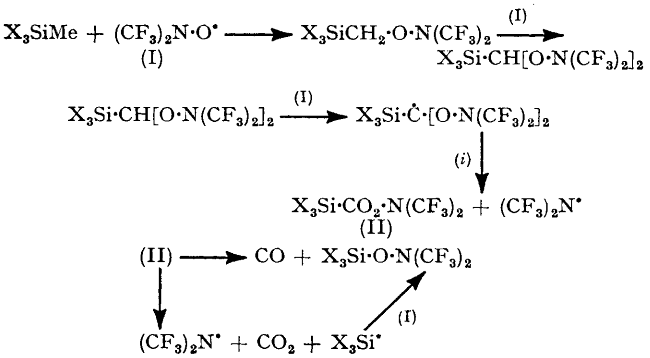
The reactions of the oxyl $(CF_3)_2N{\cdot}O^{\cdot}$ with various alkyltrichlorosilanes and alkyltrifluorosilanes show that the α position of the alkyl group is deactivated towards radical attack and the effect is more pronounced with alkyltrichlorosilanes. A novel rearrangement of type $N{\cdot}O{\cdot}C{\cdot}Si \longrightarrow N{\cdot}C{\cdot}O{\cdot}Si$ occurs on heating (1-*NN*-bistrifluoromethylamino-oxyalkyl)silanes, and the ease of rearrangement is in the order $(CF_3)_2N{\cdot}O{\cdot}CR_2{\cdot}SiMe_3 > (CF_3)_2N{\cdot}O{\cdot}CHR{\cdot}SiMe_3 > (CF_3)_2N{\cdot}O{\cdot}CR_2{\cdot}SiCl_3 > (CF_3)_2N{\cdot}O{\cdot}CHR{\cdot}SiCl_3$. On further heating the rearranged silane $(CF_3)_2N{\cdot}CMe_2{\cdot}O{\cdot}SiCl_3$ eliminates *NN*-bistrifluoromethylamine to give quantitatively the vinyl compound $CH_2{:}CMe{\cdot}O{\cdot}SiCl_3$.

THE major products from the reactions of the oxyl (I) with the silanes Me_nSiCl_{4-n} (n = 1—4) arose *via* attack on a methyl group to give unstable silyl esters (II) which decomposed by an intramolecular mechanism with elimination of carbon monoxide or by a radical mechanism to give carbon dioxide (Scheme 1).[1] With tetramethoxysilane the initial product $(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}Si(OMe)_3$ underwent further oxyl attack at a second methoxy-group to give $[(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}O]_2Si(OMe)_2$, while with trimethoxymethylsilane no evidence was obtained for oxyl attack on the methyl group.[1]



SCHEME 1 (*i*), β scission

In the present work the reactions of oxyl (I) with a series of alkyltrihalogenosilanes (Table 1) and some vinylsilanes have been investigated.

RESULTS AND DISCUSSION

The major products (VIIa) and (VIIIa) from the trichloroethylsilane reaction are formed *via* oxyl (I) attack on the β and α positions of the ethyl group, respectively.

$CF_3{\cdot}N{:}CF_2$ (III) $(CF_3)_2NH$ (IV)

$(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$ (V) $(CF_3)_2N{\cdot}OH$ (VI)

$(CF_3)_2N{\cdot}O{\cdot}CHR{\cdot}CH_2{\cdot}SiCl_3$ (VIIa) R = H; (VIIb) R = Me; (VIIc) R = Et

$(CF_3)_2N{\cdot}O{\cdot}CHR{\cdot}CH_2{\cdot}SiF_3$ (VIId) R = Me

$(CF_3)_2N{\cdot}O{\cdot}CMeR{\cdot}SiCl_3$ (VIIIa) R = H; (VIIIb) R = Me

$(CF_3)_2N{\cdot}O{\cdot}SiX_3$ (IXa) X = Cl; (IXb) X = F

$(CF_3)_2N{\cdot}O{\cdot}COMe$ (X) $(CF_3)_2N{\cdot}O{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}SiCl_3$ (XI)

However, the formation of the minor products (IXa) and (X) showed that Si–C cleavage has occurred to some extent, and in order to determine how these products were formed the compounds (VIIa) and (VIIIa) were separately treated with further oxyl (I) at room temperature. The reaction of compound (VIIIa) with the oxyl (1 : 2 molar ratio) gave unchanged (VIIIa) (33% recovered), (III) (trace), (IV) (trace), (V) (20%), (VI) (40%), (IXa) (71% based on silane), (X) (88% on silane),

TABLE 1

Reaction of oxyl (I) with alkyltrihalogenosilanes

Silane	Reactant ratio oxyl : silane	Time	Recovered silane (%)	Products (%) * (III)	(IV)	(V)	(VI)	(VII)	Others
$EtSiCl_3$	1 : 1	2 d	54	1	1	2	49	(VIIa) 21 (46)	(VIIIa) 20 (44), (IXc) 2.5 (5), (X) 4 (8),
$EtSiF_3$	1 : 1	28 d	80	15		8	44		SiF_4 15 (77), (IXb) 4 (17), (X) 20 (97)
Pr^nSiCl_3	1 : 1	4 h	50				49	(VIIb) 50 (100)	
Pr^nSiCl_3	2 : 1	4 h					50	(VIIb) 49 (98)	
Pr^nSiF_3	2 : 1	5 h	12	5			51	(VIId) 37 (84)	SiF_4 5 (12)
Pr^iSiCl_3	1 : 1	18 h	49	Trace	Trace		52		(VIIIb) 49 (96)
Pr^iSiCl_3	2 : 1	18 h					50		(VIIIb) 50 (100)
Bu^nSiCl_3	1 : 1	3 h	50	Trace		Trace	49	(VIIc) 17.5 (35)	(XI) 32.5 (65)
Bu^nSiCl_3	2 : 1	3 h					50	(VIIc) 17.5 (35)	(XI) 32.5 (65)

* Yields based on oxyl; figures in parentheses are yields based on silane used.

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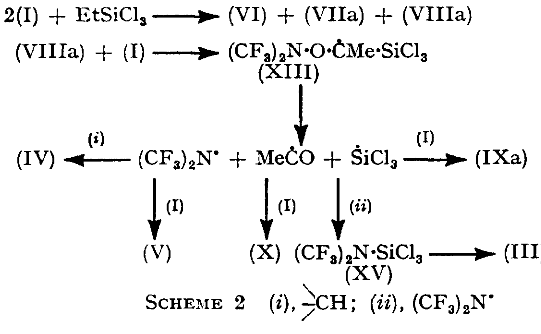
[1] Part IX, R. N. Haszeldine, D. J. Rogers, and A. E. Tipping, *J.C.S. Dalton*, 1975, 2225.

[2] Reported in part as a preliminary communication, R. N. Haszeldine, D. J. Rogers, and A. E. Tipping, *J. Organometallic Chem.*, 1973, **54**, C5.

and minor unidentified products. Compound (VIIa) reacted more slowly with the oxyl (1 : 3 molar ratio) and gave (V) (35%), (VI) (49%), the ester $(CF_3)_2N\cdot O_2C\cdot CH_2\cdot SiCl_3$, (XII) (78% based on silane), and four unidentified minor compounds.

The minor products (IXa) and (X) observed in the products from the reaction with $EtSiCl_3$ are thus formed *via* further oxyl (I) attack on the α-substitution product (VIIIa) (Scheme 2), and initial oxyl attack on the α and β positions of the ethyl group occurred in the ratio 27 : 23. It is possible that decomposition of the radical (XIII) occurs partly by an intramolecular elimination [equation (1)] and mainly by β scission [equation (2)] followed by attack of the oxyl on the intermediate silyl ketone (XIV) at carbonyl carbon.

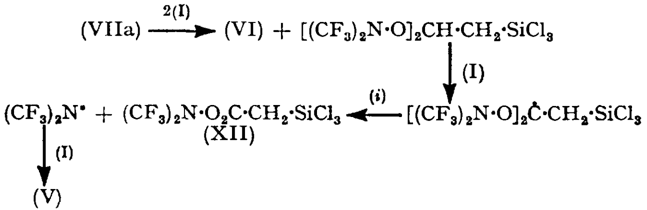


SCHEME 2 (*i*), $\rangle CH$; (*ii*), $(CF_3)_2N^{\bullet}$

$$(XIII) \longrightarrow (CF_3)_2N\cdot SiCl_3 + Me\dot{C}O \qquad (1)$$

$$\begin{tikzcd} (XIII) \arrow[r] & (CF_3)_2N^{\bullet} + \underset{(XIV)}{MeCO\cdot SiCl_3} \arrow[d, "(I)"] \\ & (X) + \dot{S}iCl_3 \end{tikzcd} \qquad (2)$$

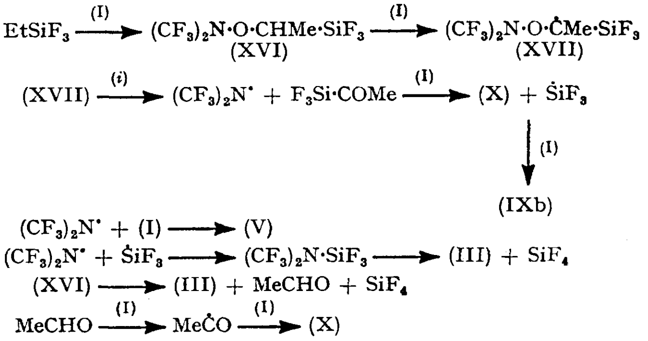
The products formed by reaction of the oxyl (I) with the silane (VIIa) are considered to arise as shown in Scheme 3.



SCHEME 3 (*i*), β scission

The faster rate of reaction of oxyl (I) with silane (VIIIa) than with silane (VIIa) can be accounted for by the former silane giving rise to a tertiary radical.

The reaction of the oxyl (I) with trifluoroethylsilane surprisingly gave no substitution products similar to (VIIa) and (VIIIa), and all the identified products can be explained by exclusive attack on the α position of the ethyl group (Scheme 4). The proposed decomposition of the 1-substituted ethylsilane (XVI) to give the azapropene (III), acetaldehyde, and silicon tetrafluoride is in agreement with observations[3] on the decomposition of the silanes $(CF_3)_2N\cdot O\cdot CH_2\cdot CH(SiF_3)\cdot O\cdot N(CF_3)_2$ and $(CF_3)_2N\cdot CH_2\cdot CH(SiF_3)\cdot O\cdot N(CF_3)_2$.



SCHEME 4 (*i*), β scission

Although attack of the oxyl (I) on trichloro-n-propylsilane occurs exclusively at the β position, attack on the corresponding trifluorosilane takes place to a minor extent at the α position as shown by the presence of SiF_4 and the azapropene (III) in the products [equation (3)]. The other expected product, the ester (XVIII), was not isolated, but the i.r. spectrum of one of the product fractions showed an absorption at 5.45 μm [C⁚O str. in $RCO_2\cdot N(CF_3)_2$; *cf.* $MeCO_2\cdot N(CF_3)_2$, 5.50 μm].

$$EtSiF_3 + (I) \longrightarrow (CF_3)_2N\cdot O\cdot CHEt\cdot SiF_3 \longrightarrow EtCHO + SiF_4 + (III) \qquad (3)$$

$$EtCHO + (I) \longrightarrow Et\dot{C}O \xrightarrow{(I)} \underset{(XVIII)}{EtCO_2\cdot N(CF_3)_2} \qquad (4)$$

The high-boiling product from the reaction of trichloroisopropylsilane was shown by g.l.c. (at 90 °C) to consist of the silane (VIIIb) and the substituted alkoxytrichlorosilane (XIX) in the ratio 57 : 39. It was subsequently shown by n.m.r. spectroscopy that the initial product from the reaction is the silane (VIIIb) exclusively, but this silane isomerises to silane (XIX) when heated (*e.g.* when passed through a g.l.c. column at elevated temperature). The mechanism of the isomerisation is discussed later. Thus, in contrast to $EtSiCl_3$,

$$(VIIIb) \xrightarrow{\text{heat}} \underset{(XIX)}{(CF_3)_2N\cdot CMe_2\cdot O\cdot SiCl_3} \qquad (5)$$

oxyl (I) attack on Pr^iSiCl_3 takes place exclusively by hydrogen abstraction from the α position. With trichloro-n-butylsilane attack in the γ position is favoured over attack in the β position by a factor of *ca.* 2.

The approximate relative reactivities of the C–H bonds in the various alkyltrihalogenosilanes studied towards oxyl (I) attack are shown in Table 2 (allowance has been made for the different number of hydrogen atoms present in the various positions). The results shown in the Table can be summarised as follows: (*i*) C–H bond reactivity follows the order tertiary > secondary > primary; (*ii*) C–H bonds α to silicon are deactivated to attack relative to the same types of bond further removed from silicon (this effect is more pronounced with $SiCl_3$ compounds than with SiF_3

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[3] T. R. Fernandes, R. N. Haszeldine, and A. E. Tipping, unpublished work.

compounds); (*iii*) C–H bonds in CH_2 groups adjacent to methyl are more reactive than those in CH_2 groups flanked by other CH_2 groups.

TABLE 2

Relative reactivities of C–H bonds in alkyltrihalogenosilanes towards abstraction by oxyl (I)

$Cl_3Si–CH_2–CH_3$	1.0 0.57	$F_3Si–CH_2–CH_2–CH_3$	0.14 1.0 0
$F_3Si–CH_2–CH_3$	1.0 0	$Cl_3Si–CH–(CH_3)_2$	1.0 0
$Cl_3Si–CH_2–CH_2–CH_3$	0 1.0 0	$Cl_3Si–CH_2–CH_2–CH_2–CH_3$	0 0.54 1.0 0

The photochemical chlorination of $EtSiCl_3$ affords[4] the 1-chloroethyl and 2-chloroethyl isomers in the ratio 1.0 : 1.6—1.8 and as the chlorine atoms on silicon are replaced by ethyl groups attack becomes more favoured at the 1-position until with Et_4Si attack occurs exclusively at the 1-position. The corresponding ratio for photochemical chlorination of $EtSiF_3$ is 1 : 4.4.[5] These results can be explained by the $-I$ inductive effects of the halogenosilyl groups ($SiF_3 > SiCl_3 > RSiCl_2 > R_2SiCl$) which render electrophilic chlorine-atom attack at the electron-deficient hydrogen atoms in the 1-position relatively unfavourable. In the present work the results obtained for oxyl (I) attack on the silanes in the series $EtSiCl_3$, Pr^nSiCl_3, Bu^nSiCl_3 show clearly that the α position is deactivated and these results could be interpreted (as for chlorine-atom attack) on the basis that the oxyl (I) is an electrophilic radical. However, if this is the correct interpretation, attack of oxyl (I) on $EtSiF_3$ should result in more attack at the 2-position than observed with $EtSiCl_3$ ($-I$ effect of $SiF_3 > SiCl_3$). Since oxyl (I) attack on $EtSiF_3$ takes place exclusively at the 1-position, it is suggested that the major deactivating effect of the $SiCl_3$ group is steric in origin. The deactivation of the α position found with the SiF_3 group (only *ca.* 12% attack on the 1-position in the silane Pr^nSiF_3) can be attributed to the inductive or steric effect of the SiF_3 group.

It is thus possible that oxyl (I) is an electrophilic radical but only weakly so (exclusive attack on α position in $EtSiF_3$ and Pr^iSiCl_3), and this is in agreement with the observations that the rate of reaction of oxyl (I) with $EtSiF_3$ is much slower than with $EtSiCl_3$ and the rate of reaction with the silanes Me_nSiCl_{4-n} (n = 1—4) decreases in the order $Me_4Si > Me_3SiCl > Me_2SiCl_2 > MeSiCl_3$.[1] The faster rate of reaction of the oxyl with tetrafluoroethylene than with ethylene has been interpreted on the basis that the oxyl is not a strongly electrophilic radical.[6] The greater preference for oxyl attack on methylene groups adjacent to methyl groups than those flanked by methylene groups is in accord with the greater stabilisation of the intermediate secondary radical.

Vinylsilanes.—The oxyl (I) has been reported to react almost quantitatively with alkenes[7] and perfluoroalkenes[8] to give the corresponding 2 : 1 adducts. Similarly the reactions with trichlorovinylsilane, trimethylvinylsilane, and allyltrichlorosilane gave the 2 : 1 adducts (XXa) (98%), (XXb) (96%), and (XXI) (93%),

$$(CF_3)_2N·O·CH_2·CH(SiX_3)·O·N(CF_3)_2$$

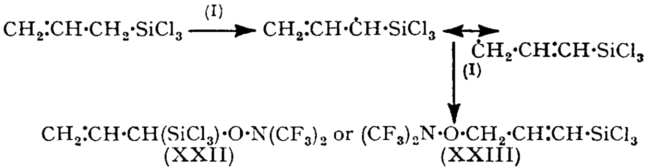
(XXa) X = Cl

(XXb) X = Me

$$(CF_3)_2N·O·CH_2·CH(CH_2·SiCl_3)·O·N(CF_3)_2$$

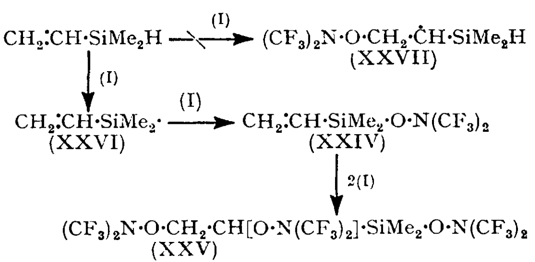
(XXI)

respectively. In the trimethylvinylsilane reaction a small amount of the hydroxylamine (VI) was also formed suggesting that oxyl attack on the methyl groups in the reactant silane, $CH_2{:}CH·SiMe_3$ or on C–H bonds in the adduct (XXb) had occurred to some extent. A small amount (4%) of hydroxylamine (VI) and an unidentified compound (*ca.* 2%) with a shorter g.l.c. retention time than the 2 : 1 adduct (XXI) were also observed in the products from the allyltrichlorosilane reaction. It is probable that some oxyl attack on allylic hydrogen took place to afford eventually compounds (XXII) or (XXIII) (Scheme 5).



SCHEME 5

The reaction of the oxyl (I) with dimethylvinylsilane was highly exothermic at room temperature and caused the reaction vessel to explode. A reaction (1 : 1 molar ratio) carried out at −78 °C gave unchanged silane (48% recovered), hydroxylamine (VI) (47%), the vinylsilane (XXIV) (87% based on silane, 45% based on oxyl), and three minor components one of which was identified as compound (XXV) (*ca.* 2%). Further reaction of the oxyl with the vinylsilane (XXIV) (2 : 1 molar ratio) at room temperature gave the trisubstituted compound (XXV) (100%). Thus the oxyl reacts with dimethylvinylsilane by abstraction of the hydrogen atom bonded to silicon to give (XXVI) rather than by addition to the vinyl group to give (XXVII) (Scheme 6).



SCHEME 6

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[4] V. F. Mironov and V. A. Ponomarenko, *Izvest. Akad. Nauk S.S.S.R.*, 1957, 199.

[5] V. A. Ponomarenko and D. A. Snegovia, *Zhur. obshchei Khim.*, 1957, **27**, 2067.

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

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

[8] R. E. Banks, R. N. Haszeldine, and T. Myerscough, *J. Chem. Soc.* (*C*), 1971, 1951.

Rearrangement Reactions.—Thermal isomerisations involving insertion of oxygen into a Si–C bond are uncommon, examples being restricted to the rearrangement of alkyl silylmethyl ketones[9] [equation (6)]. A recent

$$R_3Si{\cdot}CH_2{\cdot}COR' \xrightarrow{80\text{—}175\ ^\circ\text{C}} R_3Si{\cdot}O{\cdot}CR'{:}CH_2 \quad (6)$$

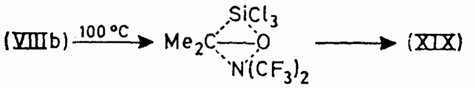
study has shown that tris(organosilyl)hydroxylamines isomerise thermally to silylaminodisiloxanes[10] [equation (7)].

$$(R_3Si)_2N{\cdot}O{\cdot}SiR_3 \xrightarrow{200\ ^\circ\text{C}} R_3Si{\cdot}NR{\cdot}SiR_2{\cdot}O{\cdot}SiR_3 \quad (7)$$

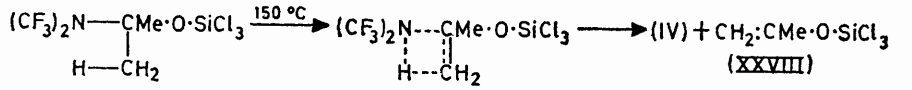
During the course of the present work several [1-(*NN*-bistrifluoromethylamino-oxy)alkyl]silanes were observed to rearrange on g.l.c. columns at elevated temperature or in the mass spectrometer [*e.g.* equation (5)]. The trichlorosilane (VIIIb) when heated at 100 °C (2 h) gave the rearranged silane (XIX) (98%), the amine (IV) (2%), and a compound which was later identified as the trichlorosilyl vinyl ether $CH_2{:}CMe{\cdot}O{\cdot}SiCl_3$, (XXVIII). When the rearranged silane (XIX) was heated at 150 °C, quantitative elimination of amine (IV) took place to afford the ether (XXVIII). That the rearrangement did not involve an interchange of groups on silicon and α carbon of the type found with silanes $RCF_2{\cdot}SiCl_3$[11] [equation (8)] to give silane (XXIX) [equation (9)] was shown by a consideration of the ^{19}F n.m.r. spectrum of compound (XIX). The spectrum showed a band at −27 p.p.m. (reference TFA) in the region expected for the group $(CF_3)_2N{\cdot}C$ in (XIX), but not for the group $(CF_3)_2N{\cdot}O{\cdot}Si$ (*ca.* −10 p.p.m.) in the compound (XXIX).

$$RCF_2{\cdot}SiCl_3 \xrightarrow{\text{heat}} RCFCl{\cdot}SiFCl_2 \longrightarrow RCCl_2{\cdot}SiF_2Cl \quad (8)$$

$$\underset{\text{(VIIIb)}}{(CF_3)N{\cdot}O{\cdot}CMe_2{\cdot}SiCl_3} \overset{\text{heat}}{\not\longrightarrow} \underset{\text{(XXIX)}}{(CF_3)_2N{\cdot}O{\cdot}SiCl_2{\cdot}CMe_2Cl} \quad (9)$$



$$(\text{VIIIb}) \xrightarrow{100\ ^\circ\text{C}} Me_2C(SiCl_3)(O)N(CF_3)_2 \longrightarrow (\text{XIX}) \quad (10)$$



$$(CF_3)_2N{-}\underset{H{-}CH_2}{CMe{\cdot}O{\cdot}SiCl_3} \xrightarrow{150\ ^\circ\text{C}} (CF_3)_2N{\cdots}\underset{H{\cdots}CH_2}{CMe{\cdot}O{\cdot}SiCl_3} \longrightarrow (\text{IV}) + \underset{(\text{XXVIII})}{CH_2{:}CMe{\cdot}O{\cdot}SiCl_3} \quad (11)$$

The isomerisation of silane (VIIIb) to silane (XIX) is of the $N{\cdot}O{\cdot}C{\cdot}Si \longrightarrow N{\cdot}C{\cdot}O{\cdot}Si$ type, and an intramolecular concerted mechanism *via* a four-centred transition state [equation (10)] is suggested. The driving force for the rearrangement is presumably conversion of the relatively weak N–O and Si–C bonds into the relatively strong N–C and Si–O bonds. The decomposition of the rearranged silane (XIX) may also involve a four-centre transition state [equation (11)].

Rearrangement of the 2 : 1 adduct (XXb) occurred at a lower temperature (50 °C, 12 h) than that of the trichlorosilane (VIIIb) to give the rearranged silane (XXX) (100%) which was stable to 250 °C. Since the rearranged silane (XXX) was stable to 250 °C and the 2 : 1 adduct was readily available, an elementary kinetic study of the rearrangement was made by recording the ^{19}F n.m.r. spectrum after varying intervals of time at both 60 and 80 °C; the absorptions were integrated *ca.* 10 times and the mean taken, values obtained for the concentration $(a - x)$ of silane (XXb) after varying times t being shown in Table 3. The plots of $\log_{10}[a/(a - x)]$ [a = initial concentration of silane (XXb)] at 60 and 80 °C gave straight lines, as expected for first-order reactions, from the gradients of which the rate constants were calculated to be $(9.03 \pm 0.90) \times 10^{-5}$ s^{-1} at 60 °C and $(6.53 \pm 0.60) \times 10^{-4}$ s^{-1} at 80 °C; the activation energy for the rearrangement is therefore 97.0 ± 8.0 kJ mol^{-1} and the value of the pre-exponential factor A is $(1.2 \pm 0.2) \times 10^{11}$ s^{-1}. Bearing in mind the experimental errors inherent in the procedure used, the observed first-order kinetics are consistent with the rearrangement being unimolecular and taking place *via* a four-centre transition state.

TABLE 3

Thermal isomerisation of [1,2-bis(*NN*-bistrifluoromethylamino-oxy)ethyl]trimethylsilane, (XXb)

At 60 °C			At 80 °C		
$(a - x)$	$\log_{10}$-$[a/(a - x)]$	t/min	$(a - x)$	$\log_{10}$-$[a/(a - x)]$	t/min
20.0	0.000	0	12.2	0.000	0
18.5	0.034	15	8.1	0.179	10
17.0	0.071	30	5.3	0.362	20
15.5	0.111	45	3.8	0.507	30
14.5	0.140	60	2.7	0.655	40
13.0	0.187	75	1.8	0.831	50
11.5	0.240	105			
9.5	0.323	135			
8.0	0.398	165			
7.0	0.466	195			
6.0	0.523	225			

Rearrangement of the silane (XXV) took place at 150 °C (1 h) to give a quantitative yield of the silane (XXXI), but the silane (XXa) was stable to 200 °C. A later investigation[3] has shown that the latter rearranges to the silyl ether (XXXII) at 230 °C. The

$$\underset{\text{(XXb)}}{(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}CH(SiMe_3){\cdot}O{\cdot}N(CF_3)_2} \xrightarrow{50\ ^\circ\text{C}} \underset{\text{(XXX)}}{(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}CH(O{\cdot}SiMe_3){\cdot}N(CF_3)_2} \quad (12)$$

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[9] A. G. Brook, D. M. Macrae, and W. W. Limburg, *J. Amer. Chem. Soc.*, 1967, **89**, 5493.

[10] P. Boudjouk and R. West, *J. Amer. Chem. Soc.*, 1971, **93**, 5901.

[11] W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, *J. Organometallic Chem.*, 1970, **23**, C17.

silane $\mathrm{(CF_3)_2N{\cdot}O{\cdot}CHMe{\cdot}SiCl_3}$, (VIIIa), was stable at 100 °C during g.l.c. purification and the silane $\mathrm{(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}SiMe_3}$ was stable at 60 °C.[1]

$$\underset{\mathrm{(XXXI)}}{\mathrm{(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}CH[N(CF_3)_2]{\cdot}O{\cdot}SiMe_2{\cdot}O{\cdot}N(CF_3)_2}}$$

$$\underset{\mathrm{(XXXII)}}{\mathrm{(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}CH(O{\cdot}SiCl_3){\cdot}N(CF_3)_2}}$$

The observed ease of rearrangement is $\mathrm{(CF_3)_2N{\cdot}O{\cdot}CRR'{\cdot}SiX_3 > (CF_3)_2N{\cdot}O{\cdot}CHR{\cdot}SiX_3 > (CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}SiX_3}$. Steric factors may play an important role in the rearrangement, because silanes which contained the groups $\mathrm{SiMe_3}$ or $\mathrm{SiMe_2{\cdot}O{\cdot}N(CF_3)_2}$ rearranged readily when the α-methylene group was monosubstituted, but silanes containing the less bulky $\mathrm{SiCl_3}$ group rearranged readily only when the α-methylene group was disubstituted.

NN-Bistrifluoromethylamino-oxy-substituted alkenes have been postulated as reaction intermediates,[8] but not isolated, and since trifluoro(polyfluoroalkyl)silanes, $\mathrm{RCF_2{\cdot}SiF_3}$, decompose at *ca.* 150 °C to give carbenes,[12]

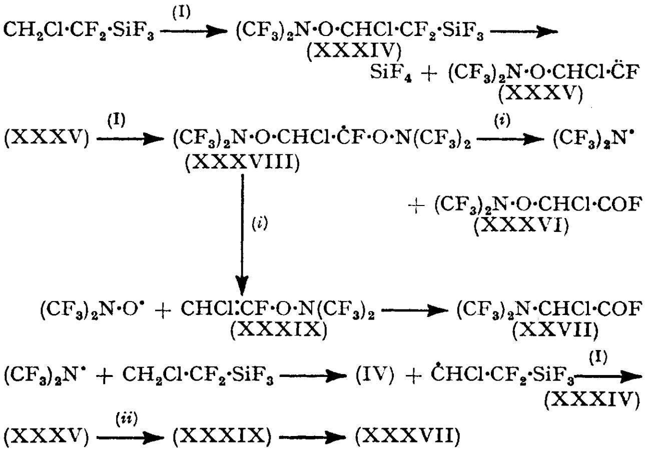
$$\underset{\mathrm{(XXXIII)}}{\mathrm{CH_2Cl{\cdot}CF_2{\cdot}SiF_3}} \xrightarrow{150\ ^\circ\mathrm{C}} \mathrm{SiF_4} + \mathrm{CH_2Cl{\cdot}\ddot{C}F} \longrightarrow \mathrm{CH_2{:}CFCl} \quad (13)$$

which, if not trapped, rearrange to olefins, *e.g.* equation (13), the decomposition of a similar trifluorosilane containing an *NN*-bistrifluoromethylamino-oxy-group in the β position might lead to an *NN*-bistrifluoromethylamino-oxy-substituted alkene. The preparation of silane (XXXIV) by the route shown in equation (14) was thus investigated as a possible precursor of carbene (XXXV).

$$\mathrm{(XXXIII)} \xrightarrow{2\,\mathrm{(I)}} \underset{\mathrm{(XXXIV)}}{\mathrm{(CF_3)_2N{\cdot}O{\cdot}CHCl{\cdot}CF_2{\cdot}SiF_3}} \quad (14)$$

$$\mathrm{(XXXIV)} \xrightarrow{150\ ^\circ\mathrm{C}} \mathrm{SiF_4} + \underset{\mathrm{(XXXV)}}{\mathrm{(CF_3)_2N{\cdot}O{\cdot}CHCl{\cdot}\ddot{C}F}} \longrightarrow \mathrm{(CF_3)_2N{\cdot}O{\cdot}CH{:}CFCl} \quad (15)$$

Attempted reaction of the oxyl (I) with silane (XXXIII) at room temperature resulted in an almost quantitative recovery of reactants after 2 weeks. When the reaction was repeated at 60 °C (48 h), some oxyl was recovered unchanged (40%) together with a complex mixture of products including $\mathrm{SiF_4}$ (66%). The normal temperature for α elimination in (XXXIII) is 120—150 °C and so the formation of $\mathrm{SiF_4}$ at 60 °C was unexpected. A mixture (2 : 1) of oxyl (I) and silane (XXXIII) heated at 150 °C (1 h) gave unchanged oxyl (34% recovered), $\mathrm{SiF_4}$ (98%), amine (IV) (45%), hydroxylamine (VI) (*ca.* 10%), and a complex mixture of some ten components. The i.r. spectrum of the mixture showed strong bands at 5.3—5.7 μm (C⁚O str. and possibly C⁚C str.), and the ^{19}F n.m.r. spectrum contained bands at −101.6 and −112.4 (COF), *ca.* −20 $\mathrm{[(CF_3)_2N{\cdot}C]}$, and *ca.* −9 p.p.m. $\mathrm{[(CF_3)_2N{\cdot}O]}$. A g.l.c.–m.s. examination of the two major components of the mixture showed conclusively that they were the acyl fluorides (XXXVI) and (XXXVII). It is considered that the initial reaction is attack on the reactant silane by oxyl (I) to give the silane (XXXIV) which decomposes to $\mathrm{SiF_4}$ and carbene (XXXV). Reaction of the carbene with the oxyl affords the radical (XXXVIII) which decomposes by β scission to give the acyl fluoride (XXXVI) and the olefin (XXXIX); rearrangement of the olefin yields the acyl fluoride (XXXVII). It is also possible that compound (XXXVII) arises by rearrangement of carbene (XXXV). The proposed reaction scheme is shown in Scheme 7.



$$\mathrm{CH_2Cl{\cdot}CF_2{\cdot}SiF_3} \xrightarrow{\mathrm{(I)}} \underset{\mathrm{(XXXIV)}}{\mathrm{(CF_3)_2N{\cdot}O{\cdot}CHCl{\cdot}CF_2{\cdot}SiF_3}} \longrightarrow \mathrm{SiF_4} + \underset{\mathrm{(XXXV)}}{\mathrm{(CF_3)_2N{\cdot}O{\cdot}CHCl{\cdot}\ddot{C}F}}$$

$$\mathrm{(XXXV)} \xrightarrow{\mathrm{(I)}} \underset{\mathrm{(XXXVIII)}}{\mathrm{(CF_3)_2N{\cdot}O{\cdot}CHCl{\cdot}\dot{C}F{\cdot}O{\cdot}N(CF_3)_2}} \xrightarrow{(i)} \mathrm{(CF_3)_2N^{\bullet}} + \underset{\mathrm{(XXXVI)}}{\mathrm{(CF_3)_2N{\cdot}O{\cdot}CHCl{\cdot}COF}}$$

$$\mathrm{(XXXVIII)} \Big\downarrow (i)$$

$$\mathrm{(CF_3)_2N{\cdot}O^{\bullet}} + \underset{\mathrm{(XXXIX)}}{\mathrm{CHCl{:}CF{\cdot}O{\cdot}N(CF_3)_2}} \longrightarrow \underset{\mathrm{(XXVII)}}{\mathrm{(CF_3)_2N{\cdot}CHCl{\cdot}COF}}$$

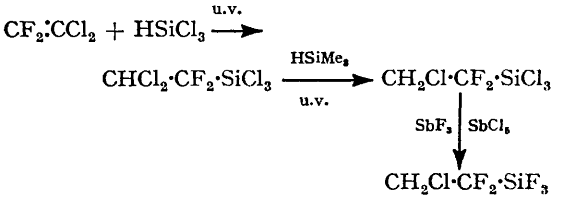
$$\mathrm{(CF_3)_2N^{\bullet}} + \mathrm{CH_2Cl{\cdot}CF_2{\cdot}SiF_3} \longrightarrow \mathrm{(IV)} + \mathrm{\dot{C}HCl{\cdot}CF_2{\cdot}SiF_3} \xrightarrow{\mathrm{(I)}} \mathrm{(XXXIV)}$$

$$\mathrm{(XXXV)} \xrightarrow{(ii)} \mathrm{(XXXIX)} \longrightarrow \mathrm{(XXXVII)}$$

SCHEME 7 (*i*), β scission; (*ii*), $\mathrm{(CF_3)_2NO}$ shift

EXPERIMENTAL

For details of the techniques used and the spectroscopic instrumentation see Part IX.[1] The reactions were carried out *in vacuo* in Pyrex ampoules (*ca.* 300 cm^3 unless stated otherwise) and g.l.c. separations used columns (2—8m) of Silicone SE 30 oil, polyethylene glycol adipate (PEGA), dinonyl phthalate (DNP), or Apiezon L grease (APL) (10—30%) on Celite. Boiling points were determined by Siwoloboff's method. The silanes used were prepared by standard methods or were commercial samples which were carefully purified, except for (2-chloro-1,1-difluoroethyl)trifluorosilane which was made by route (16).[13] Spectroscopic data for the compounds are in Supplementary Publication No. SUP 21720 (14 pp., 1 microfiche).*



$$\begin{tikzcd}
\mathrm{CF_2{:}CCl_2} + \mathrm{HSiCl_3} \arrow[r, "\mathrm{u.v.}"] & {} & \\
& \mathrm{CHCl_2{\cdot}CF_2{\cdot}SiCl_3} \arrow[r, "\mathrm{HSiMe_3}", "\mathrm{u.v.}"'] & \mathrm{CH_2Cl{\cdot}CF_2{\cdot}SiCl_3} \arrow[d, "\mathrm{SbF_3}"', "\mathrm{SbCl_5}"] \\
& & \mathrm{CH_2Cl{\cdot}CF_2{\cdot}SiF_3}
\end{tikzcd} \quad (16)$$

Reactions of NN-*Bistrifluoromethylamino-oxyl*, (I).—(a) *With trichloroethylsilane.* A mixture of the oxyl (6.72 g,

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[12] W. I. Bevan and R. N. Haszeldine, *J.C.S. Dalton*, 1974, 2509 and refs. therein.

[13] W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, *J.C.S. Dalton*, 1974, 2305; 1975, 252.

40.0 mmol) and the silane (6.48 g, 40.0 mmol), kept at room temperature (48 h), gave (*i*) a mixture (0.11 g, 0.8 mmol; *M* 142) of *NN*-bistrifluoromethylamine, (IV) (0.06 g, 0.4 mmol, 1%), and perfluoro-2-azapropene, (III) (0.05 g, 0.4 mmol, 1%), (*ii*) a mixture (4.20 g) which was shown by i.r. spectroscopy and g.l.c. (2 m DNP and APL at 50 °C) to consist of *NN*-bistrifluoromethylhydroxylamine, (VI) (3.31 g, 19.5 mmol, 49%), perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane), (V) (0.23 g, 0.8 mmol, 2%), *O*-trichlorosilyl-*NN*-bistrifluoromethylhydroxylamine, (IXa) (0.29 g, 1.0 mmol, 5%), *O*-acetyl-*NN*-bistrifluoromethylhydroxylamine, (X) [7] (0.32 g, 1.5 mmol, 8%), and a minor unidentified component (*ca.* 0.05 g), (*iii*) unchanged EtSiCl$_3$ (3.52 g, 21.7 mmol, 54%), and (*iv*) a higher-boiling liquid (5.46 g) which was separated by g.l.c. (7.5 m SE 30 at 100 °C) into its two components [1-(NN-*bistrifluoromethylamino-oxy*)-*ethyl*]*trichlorosilane*, (VIIIa) (2.65 g, 8.0 mmol, 44%) (Found: C, 14.6; H, 1.3. C$_4$H$_4$Cl$_3$F$_6$NOSi requires C, 14.6; H, 1.2%), b.p. 140—141 °C, and [2-(NN-*bistrifluoromethylamino-oxy*)*ethyl*]*trichlorosilane*, (VIIa) (2.81 g, 8.5 mmol, 46%) (Found: C, 14.9; H, 0.9%), b.p. 147 °C, n_D^{20} 1.3607.

(b) *With* [1-(NN-*bistrifluoromethylamino-oxy*)*ethyl*]*trichlorosilane*, (VIIIa). A mixture of the oxyl (I) (0.168 g, 1.0 mmol) and the silane (0.16 g, 0.5 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 5 cm^3) and kept at room temperature (48 h), gave (*i*) a mixture (trace) of (IV) and (III) (i.r.), (*ii*) a colourless liquid (0.28 g) which was shown by i.r. spectroscopy and g.l.c. (2 m DNP at 50 °C) to consist of (VI) (0.07 g, 0.4 mmol, 40%), (V) (0.06 g, 0.2 mmol, 20%), (X) (0.07 g, 0.3 mmol, 88%), (IXa) (0.08 g, 0.25 mmol, 71%), and trace amounts of several unidentified components, and (*iii*) a mixture (0.05 g) which was shown by i.r. spectroscopy and g.l.c. (2 m DNP at 90 °C) to contain unchanged silane (0.05 g, 0.16 mmol, 32% recovered) and trace amounts of unidentified components.

(c) *With* [2-(NN-*bistrifluoromethylamino-oxy*)*ethyl*]*trichlorosilane*, (VIIa).—A mixture of the oxyl (I) (0.59 g, 3.5 mmol) and the silane (0.29 g, 0.9 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 10 cm^3) and kept at room temperature (20 d), gave (*i*) (V) (0.04 g, 0.12 mmol, 7%), (*ii*) a liquid (0.47 g) which was shown by i.r. spectroscopy and g.l.c. (2 m DNP at 50 °C) to consist of (V) (0.18 g, 0.5 mmol, 28%) and (VI) (0.29 g, 1.7 mmol, 49%), (*iii*) *O*-trichlorosilylacetyl-*NN*-bistrifluoromethylhydroxylamine, (XII) (0.23 g, 0.7 mmol, 78%), and (*iv*) a higher-boiling liquid (0.12 g) which was shown by g.l.c. (2 m DNP at 100 °C) to consist of four unidentified components.

(d) *With trifluoroethylsilane.* A mixture of the oxyl (I) (3.36 g, 20.0 mmol) and the silane (2.28 g, 20.0 mmol), kept at room temperature (28 d), gave (*i*) silicon tetrafluoride (0.32 g, 3.1 mmol, 77%) (Found: *M* 104. Calc. for SiF$_4$: *M* 104), (*ii*) a mixture (2.23 g, 19.1 mmol) which was shown by i.r. spectroscopy and g.l.c. (4 m SE 30 at 20 °C) to consist of unchanged EtSiF$_3$ (1.82 g, 16.0 mmol, 80% recovered), (III) (0.40 g, 3.0 mmol, 15%), and (IV) (trace), (*iii*) a liquid (2.60 g, 13.6 mmol) which was shown by i.r. spectroscopy, coupled g.l.c. (4 m SE 30 at 50 °C)–mass spectrometry, and n.m.r. spectroscopy to consist of (VI) (1.48 g, 8.8 mmol, 44%), (V) (0.26 g, 0.8 mmol, 8%), (X) (0.72 g, 3.4 mmol, 85%), trifluoro(*NN*-bistrifluoromethylamino-oxy)silane, (IXb) (0.14 g, 0.55 mmol, 12%), and an unidentified component (trace), (*iv*) a liquid (0.20 g, 0.9 mmol), which was shown by i.r. spectroscopy and g.l.c. (2 m DNP at 50 °C) to consist of (X) (0.11 g, 0.5 mmol, 12%), (IXb) (0.05 g, 0.2 mmol, 5%), and an unidentified component (0.04 g, 0.2 mmol), and (*v*) a higher-boiling liquid (*ca.* 0.3 g) which was shown by g.l.c. (2 m DNP at 75 °C) to contain at least five components.

(e) *With trichloro-n-propylsilane.* A mixture of the oxyl (I) (2.84 g, 16.9 mmol) and the silane (3.00 g, 16.9 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 70 cm^3) and kept at room temperature (4 h), gave (VI) (1.41 g, 8.4 mmol, 49%) and a higher-boiling liquid (4.40 g) which was separated by g.l.c. (4 m SE 30 at 120 °C) into its two components, unchanged Pr^{n}SiCl$_3$ (1.49 g, 8.45 mmol, 50% recovered) and [2-(NN-*bistrifluoromethylamino-oxy*)*propyl*]*trichlorosilane*, (VIIb) (2.91 g, 8.5 mmol, 100%) (Found: C, 17.4; H, 1.8. C$_5$H$_6$Cl$_3$F$_6$NOSi requires C, 17.4; H, 1.8%), b.p. 154—155 °C. A second reaction using a 2 : 1 molar ratio of oxyl to silane gave compound (VIIb) (98%).

(f) *With trifluoro-n-propylsilane.* A mixture of the oxyl (I) (2.63 g, 15.6 mmol) and the silane (1.00 g, 7.8 mmol), kept at room temperature (5 h), gave (*i*) SiF$_4$ (0.09 g, 0.9 mmol, 12%), (*ii*) a mixture (0.17 g, 1.4 mmol; *M* 143) of (III) (0.10 g, 0.8 mmol, 5%) and unchanged Pr^{n}SiF$_3$ (0.07 g, 0.5 mmol, 6% recovered), (*iii*) a mixture (0.23 g, 1.4 mmol; *M* 159) of unchanged Pr^{n}SiF$_3$ (0.07 g, 0.5 mmol, 6% recovered) and (VI) (0.16 g, 0.9 mmol, 6%), (*iv*) a liquid (1.79 g) which was shown by g.l.c. (2 m APL and DNP at 60 °C) to be a mixture of (VI) (1.18 g, 7.0 mmol, 45%) and another component (0.61 g), and (*v*) a liquid (1.12 g) which was shown by g.l.c. (as above) to contain the same unknown component (1.07 g) and several minor unidentified components (0.05 g). The major unknown component was separated by g.l.c. (6 m APL at 50 °C) and was identified as [2-(NN-*bistrifluoromethylamino-oxy*)*propyl*]*trifluorosilane*, (VIId) (1.68 g, 5.7 mmol, 84%) (Found: C, 20.4; H, 2.1. C$_5$H$_6$F$_9$NOSi requires C, 20.3; H, 2.0%), b.p. 65 °C. A higher-boiling fraction (0.20 g) was also obtained which was shown by g.l.c. (2 m DNP at 100 °C) to contain at least three components.

(g) *With trichloroisopropylsilane.* A mixture of the oxyl (I) (3.78 g, 22.5 mmol) and the silane (4.00 g, 22.5 mmol), kept at room temperature (18 h), gave (*i*) a mixture (0.01 g) of (IV) and (III) (i.r.), (*ii*) (VI) (1.99 g, 11.8 mmol, 52%), (*iii*) unchanged Pr^{i}SiCl$_3$ (0.83 g, 4.9 mmol, 22% recovered), and (*iv*) a colourless liquid (4.89 g) which was separated by g.l.c. (3 m SE 30 at 90 °C) into its components, unchanged Pr^{i}SiCl$_3$ (1.15 g, 6.4 mmol, 27%), [1-(NN-*bistrifluoromethylamino-oxy*)-1-*methylethyl*]*trichlorosilane*, (VIIIb) (2.29 g, 6.7 mmol, 57%) (Found: C, 17.6; H, 1.9; F, 33.3. C$_5$H$_6$Cl$_3$F$_6$NOSi requires C, 17.4; H, 1.7; F, 33.1%), n_D^{20} 1.3777, and 1-(NN-*bistrifluoromethylamino*)-1-*methylethyl trichlorosilyl ether*, (XIX) (1.46 g, 4.2 mmol, 37%) (Found: C, 17.7; H, 1.9%), b.p. 160—161 °C, n_D^{20} 1.3675. A second reaction at room temperature (2 h), using a mixture of the oxyl (0.34 g, 2.0 mmol) and the silane (0.18 g, 1.0 mmol), gave (VI) (0.17 g, 1.0 mmol, 50%) and (VIIIb) (0.34 g, 1.0 mmol, 100%) as shown by n.m.r. spectroscopy.

(h) *With trichloro-n-butylsilane.* A mixture of the oxyl (I) (3.01 g, 17.9 mmol) and the silane (3.44 g, 17.9 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 70 cm^3) and kept at room temperature (3 h), gave (*i*) a mixture (0.02 g) of (IV) and (V) (i.r.), (*ii*) a liquid (1.69 g) which was shown by g.l.c. (2 m SE 30 and DNP at 50 °C) to consist of (VI) (1.49 g, 8.8 mmol, 49%) and unchanged Bu^{n}SiCl$_3$ (0.20 g, 1.0 mmol, 6% recovered), (*iii*) unchanged Bu^{n}SiCl$_3$ (1.50 g, 7.9 mmol, 44% recovered), and (*iv*) a higher-boiling liquid (3.29 g) which was separated by g.l.c. (2 m SE 30 at 120 °C) into its two components, [3-(NN-*bistrifluoromethylamino-oxy*)*butyl*]-*trichlorosilane*, (XI) (2.14 g, 5.9 mmol, 65%) (Found: C, 20.3; H, 2.2; F, 31.8. $C_6H_8Cl_3F_6NOSi$ requires C, 20.1; H, 2.2; F, 31.8%), b.p. 186—187 °C, n_D^{20} 1.3811, and [2-(NN-*bistrifluoromethylamino-oxy*)*butyl*]*trichlorosilane*, (VIIc) (1.15 g, 3.2 mmol, 35%) (Found: C, 20.3; H, 2.3%), b.p. 172—173 °C, n_D^{20} 1.3794. A second reaction using a 2 : 1 molar ratio of oxyl to silane gave the same products in the same ratio.

(i) *With trichlorovinylsilane.* A mixture of the oxyl (I) (1.68 g, 10.0 mmol) and the silane (0.81 g, 5.0 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 70 cm^3) and kept at room temperature (18 h), gave [1,2-*bis*(NN-*bistrifluoromethylamino-oxy*)*ethyl*]*trichlorosilane*, (XXa) (2.46 g, 4.9 mmol, 98%) (Found: C, 14.7; H, 0.7; F, 45.5. $C_6H_3Cl_3F_{12}N_2O_2Si$ requires C, 14.5; H, 0.6; F, 45.8%), b.p. 167—168 °C, n_D^{20} 1.3478.

(j) *With trimethylvinylsilane.* A mixture of the oxyl (I) (3.36 g, 20.0 mmol) and the silane (1.00 g, 10.0 mmol), kept at room temperature (10 min), gave (*i*) a mixture (0.01 g) of (IV) and (III) (i.r.), (*ii*) a liquid (0.15 g) which was shown by i.r. spectroscopy and g.l.c. (2 m SE 30 and DNP at 50 °C) to be (VI) contaminated with trace amounts of unidentified components, and (*iii*) [1,2-*bis*(NN-*bistrifluoromethylamino-oxy*)*ethyl*]*trimethylsilane*, (XXb) (4.19 g, 9.6 mmol, 96%) (Found: C, 24.8; H, 3.0. $C_9H_{12}F_{12}N_2O_2Si$ requires C, 24.7; H, 2.8%), n_D^{20} 1.3330.

(k) *With dimethylvinylsilane.* A mixture of the oxyl (I) (3.36 g, 20.0 mmol) and the silane (1.72 g, 20.0 mmol), kept at −78 °C (2 h), gave (*i*) unchanged dimethylvinylsilane (0.84 g, 9.8 mmol, 48% recovered), (*ii*) a mixture (2.28 g) shown by g.l.c. (2 m PEGA and DNP at 50 °C) to consist of (VI) (1.59 g, 9.4 mmol, 47%) and (XXIV) (0.69 g, 2.73 mmol, 27%), (*iii*) (NN-*bistrifluoromethylamino-oxy*)*dimethylvinylsilane*, (XXIV) (1.55 g, 6.13 mmol, 60%) (Found: C, 28.3; H, 3.6; F, 44.5. $C_6H_9F_6NOSi$ requires C, 28.4; H, 3.6; F, 45.0%), b.p. 93—94 °C, and (*iv*) a higher-boiling liquid (0.42 g) which was shown by g.l.c. (2 m PEGA at 50 °C) to consist of three components one of which was identified (see later) as [1,2-bis(*NN*-bistrifluoromethylamino-oxy)ethyl](*NN*-bistrifluoromethylamino-oxy)-dimethylsilane, (XXV) (0.15 g, 0.2 mmol, 2%).

(l) *With* (NN-*bistrifluoromethylamino-oxy*)*dimethylvinylsilane*, (XXIV). A mixture of the oxyl (I) (0.26 g, 1.4 mmol) and the silane (0.19 g, 0.7 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 5 cm^3) and kept at room temperature (30 min), gave [1,2-*bis*(NN-*bistrifluoromethylamino-oxy*)-*ethyl*](NN-*bistrifluoromethylamino-oxy*)*dimethylsilane*, (XXV) (0.45 g, 0.7 mmol, 100%) (Found: C, 20.4; H, 1.5; F, 58.1. $C_{10}H_9F_{18}N_3O_3Si$ requires C, 20.4; H, 1.5; F, 58.6%), b.p. 169—170 °C.

(m) *With allyltrichlorosilane.* A mixture of the oxyl (I) (2.52 g, 15.0 mmol) and the silane (1.34 g, 7.65 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 70 cm^3) and kept at room temperature (10 min), gave (*i*) (VI) (0.10 g, 0.6 mmol, 4%), (*ii*) a mixture (0.15 g) which was shown by g.l.c. (2 m SE 30 and DNP at 120 °C) to consist of unchanged allyltrichlorosilane (0.07 g, 0.4 mmol, 5%) and an unknown component, possibly [1-(*NN*-bistrifluoromethylamino-oxy)-prop-2-enyl]trichlorosilane, (XXII) (0.08 g, 0.25 mmol, 2%), and (*iii*) [2,3-*bis*(NN-*bistrifluoromethylamino-oxy*)-*propyl*]*trichlorosilane*, (XXI) (3.57 g, 7.0 mmol, 93%) (Found: C, 16.7; H, 1.1. $C_7H_5Cl_3F_{12}N_2O_2Si$ requires C, 16.4; H, 1.0%), b.p. 183—184 °C, n_D^{20} 1.3623.

(n) *With* (2-*chloro*-1,1-*difluoroethyl*)*trifluorosilane.* A mixture of the oxyl (I) (0.91 g, 5.4 mmol) and the silane (0.59 g, 2.7 mmol), heated at 150 °C (1 h), gave (*i*) SiF_4 (0.27 g, 2.65 mmol, 98%), (*ii*) a mixture (0.56 g, 3.4 mmol; *M* 163) of (IV) (0.25 g, 1.6 mmol, 45%) and unchanged oxyl (0.31 g, 1.84 mmol, 34% recovered), (*iii*) a mixture (0.21 g) shown by g.l.c. (2 m DNP at 50 °C) to contain five components one of which was (VI) (*ca.* 10%), and (*iv*) a higher-boiling fraction (0.45 g). The latter two fractions were combined and examined by g.l.c. (2 m DNP at 75 °C)–mass spectrometry which enabled two of the major components to be identified as (*NN*-bistrifluoromethylamino-oxy)chloroacetyl fluoride, (XXXVI), and (*NN*-bistrifluoromethylamino)chloroacetyl fluoride, (XXXVII).

In a second reaction a 2 : 1 ratio of the oxyl and silane, heated at 60 °C (48 h) in a Pyrex ampoule (*ca.* 50 cm^3), gave SiF_4 (60%), unchanged oxyl (40% recovered), (IV) (22%), (VI) (*ca.* 30%), and a complex higher-boiling mixture containing at least 15 components (g.l.c. 2 m DNP at 75 °C). An attempted reaction of the oxyl with the silane (2 : 1 molar ratio) at room temperature (14 d) gave almost quantitative recoveries of unchanged reactants.

Thermal Reactions of (NN-*Bistrifluoromethylamino-oxy-alkyl*)*silanes*.—(a) [1-(NN-*Bistrifluoromethylamino-oxy*)-1-*methylethyl*]*trichlorosilane*, (VIIIb). The silane (0.21 g, 0.62 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 5 cm^3) and heated at 100 °C (2 h), gave (IV) (0.01 g), and a higher-boiling fraction (0.19 g) which was shown by g.l.c. (2 m SE 30 at 100 °C) to consist of (XIX) (0.18 g, 0.52 mmol, 84%) and a minor component (0.01 g), identified as 1-methylvinyl trichlorosilyl ether, (XXVIII) (see later).

(b) 1-(NN-*Bistrifluoromethylamino*)-1-*methylethyl trichlorosilyl ether*, (XIX). The silane (0.46 g, 1.3 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 5 cm^3) and heated at 150 °C (4 h), gave (IV) (0.19 g, 1.24 mmol, 96%) and 1-*methylvinyl trichlorosilyl ether*, (XXVIII) (0.26 g, 1.3 mmol, 100%) (Found: C, 19.0; H, 2.8. $C_3H_5Cl_3OSi$ requires C, 18.8; H, 2.6%), b.p. 114—115 °C, n_D^{20} 1.4179.

(c) [1,2-*Bis*(NN-*bistrifluoromethylamino-oxy*)*ethyl*]*trimethylsilane*, (XXb). The silane (0.44 g, 1.0 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 5 cm^3) and heated at 50 °C (12 h), gave 1-(NN-*bistrifluoromethylamino*)-2-(NN-*bistrifluoromethylamino-oxy*)*ethyl trimethylsilyl ether*, (XXX) (0.44 g, 1.0 mmol, 100%) (Found: C, 24.8; H, 2.7. $C_9H_{12}F_{12}N_2O_2Si$ requires C, 24.7; H, 2.8%), b.p. 145—146 °C, n_D^{20} 1.3227.

A sample of the silane (XXb) was sealed in an n.m.r. tube and heated for various lengths of time at 60 °C and the ^{19}F n.m.r. spectrum integrated (10 times) after each period of heating; the experiment was then repeated at 80 °C. The values obtained for $a - x$ [a = initial concentration of silane (XXb) and $a - x$ = concentration of silane (XXb) after time t] and for $\log_{10}[a/(a - x)]$ are shown in Table 3.

(d) 1-(NN-*Bistrifluoromethylamino*)-2-(NN-*bistrifluoromethylamino-oxy*)*ethyl trimethylsilyl ether*, (XXX). The silane (0.31 g, 0.71 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 5 cm^3) and heated at 280 °C (14 h), gave a volatile fraction (0.06 g) which was shown by i.r. spectroscopy to be a mixture of SiF_4, fluorotrimethylsilane, and unidentified components, and a black residue (0.25 g) (Found: C, 17.3; H, 2.8; F, 36.5%), m.p. >360 °C.

(e) [1,2-*Bis*(NN-*bistrifluoromethylamino-oxy*)*ethyl*](NN-*bistrifluoromethylamino-oxy*)*dimethylsilane*, (XXV). The silane (0.25 g, 0.4 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 10 cm^3) and heated at 150 °C (1 h), gave 1-(NN-*bistrifluoromethylamino*)-2-(NN-*bistrifluoromethylamino-oxy*)*ethyl* (NN-*bistrifluoromethylamino-oxy*)*dimethylsilyl ether*, (XXXI) (0.25 g, 0.4 mmol, 100%) (Found: C, 20.5; H, 1.9. $C_{10}H_9F_{18}N_3O_3Si$ requires C, 20.4; H, 1.5%), b.p. 169—170 °C.

(f) [1,2-*Bis*(NN-*bistrifluoromethylamino-oxy*)*ethyl*]*trichlorosilane*, (XXa). The silane (0.50 g, 1.0 mmol), sealed *in vacuo* in a Pyrex ampoule (*ca.* 10 cm^3) and heated at 200 °C (24 h), gave only unchanged silane (100% recovered).

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