# Organosilicon Chemistry. Part 21.[1] Reactions of *NN*-Bistrifluoromethylamino-oxyl and Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) with Vinylsilanes, and Pyrolysis of the Resulting Adducts [2]

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The oxyl $(CF_3)_2N{\cdot}O^{\cdot}$ and the oxadiazapentane $(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$ on reaction with the vinylsilanes $CH_2{:}CH{\cdot}SiX_3$, $CH_2{:}CCl{\cdot}SiX_3$, and $CHCl{:}CH{\cdot}SiX_3$ give the corresponding adducts in high yield; with the silane *cis*-$MeCH{:}CH{\cdot}SiCl_3$ reaction with the diazapentane affords the 1 : 1 adduct (50%) and the allylic substitution product $(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}CH{:}CH{\cdot}SiCl_3$ (50%). The adducts on thermolysis generally rearrange, *e.g.* $RCH_2{\cdot}CH(SiX_3){\cdot}O{\cdot}N(CF_3)_2 \longrightarrow RCH_2{\cdot}CH(O{\cdot}SiX_3){\cdot}N(CF_3)_2$ [R = $(CF_3)_2N{\cdot}O$ or $(CF_3)_2N$], but those containing two or three fluorine substituents on silicon, and/or chlorine in the alkyl group, undergo elimination reactions. Three different modes of elimination can occur involving: (*i*) nucleophilic attack by fluorine in the α-$(CF_3)_2N{\cdot}O$ group on silicon to eliminate a fluorosilane and perfluoro-2-azapropene and form a carbonyl compound, *e.g.* $(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}CH(SiF_3){\cdot}O{\cdot}N(CF_3)_2 \longrightarrow SiF_4 + CF_3{\cdot}N{:}CF_2 + (CF_3)_2N{\cdot}CH_2{\cdot}CHO$; (*ii*) nucleophilic attack by an α-chlorine atom on silicon to eliminate a chlorosilane and form an amide, *e.g.* $(CF_3)_2N{\cdot}CH_2{\cdot}CCl(SiCl_3){\cdot}O{\cdot}N(CF_3)_2 \longrightarrow SiCl_4 + (CF_3)_2N{\cdot}CH_2{\cdot}CO{\cdot}N(CF_3)_2$; and (*iii*) intramolecular elimination of bis(trifluoromethyl)amine followed by intermolecular elimination of hexafluorodisilane and chloroketen to give an ester, *i.e.* $(CF_3)_2N{\cdot}O{\cdot}CHCl{\cdot}CH(SiF_3){\cdot}O{\cdot}N(CF_3)_2 \longrightarrow (CF_3)_2NH + (CF_3)_2N{\cdot}O{\cdot}CHCl{\cdot}CO{\cdot}SiF_3$ followed by $2(CF_3)_2N{\cdot}O{\cdot}CHCl{\cdot}CO{\cdot}SiF_3 \longrightarrow Si_2F_6 + CHCl{:}C{:}O + (CF_3)_2N{\cdot}O{\cdot}CHCl{\cdot}CO_2{\cdot}N(CF_3)_2$.

*NN*-BISTRIFLUOROMETHYLAMINO-OXYL (1) reacts with the vinylsilanes $CH_2{:}CH{\cdot}SiX_3$ (X = Cl or Me) to give the corresponding 2 : 1 adducts (2a) and (2b) in high yield (>90%).[3] With $CH_2{:}CH{\cdot}SiMe_2H$ hydrogen abstraction occurs in preference to addition to the double bond and the resulting compound $CH_2{:}CH{\cdot}SiMe_2{\cdot}O{\cdot}N(CF_3)_2$ reacts with further oxyl (1) to give the 2 : 1 adduct (2c). The adducts (2b) and (2c) rearrange thermally (50—100 °C) to give the alkoxysilanes $(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}CH(O{\cdot}SiX_3){\cdot}N(CF_3)_2$ {$X_3 = Me_3$ (3b) or $X_3 = Me_2[O{\cdot}N(CF_3)_2]$ (3c)} but the adduct (2a) is stable up to 200 °C.[3,4]

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[1] Part 20, A. M. Devine, R. N. Haszeldine, and A. E. Tipping, *J.C.S. Dalton*, 1975, 1837.

[2] Reported in part as a preliminary communication, T. R. Fernandes, R. N. Haszeldine, and A. E. Tipping, *J. Fluorine Chem.*, 1975, **6**, 195.

[3] R. N. Haszeldine, D. J. Rogers, and A. E. Tipping, *J.C.S. Dalton*, 1976, 1056.

[4] R. N. Haszeldine, D. J. Rogers, and A. E. Tipping, *J. Organometallic Chem.*, 1973, **54**, C5.

In the present work the reactions of oxyl (1) and perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (4) with a

$$\underset{(1)}{(CF_3)_2N\cdot O^{\bullet}} \quad \underset{(2)}{(CF_3)_2N\cdot O\cdot CH_2\cdot CH(SiX_3)\cdot O\cdot N(CF_3)_2} \quad \underset{(4)}{(CF_3)_2N\cdot O\cdot N(CF_3)_2}$$

$$X_3 = Cl_3 (a), Me_3 (b), Me_2[O\cdot N(CF_3)_2] (c), MeCl_2 (d), Me_2Cl (e), MeF_2 (f), Me_2F (g), \text{or } (OMe)_3 (h)$$

$$\underset{(5)}{(CF_3)_2N\cdot O\cdot CH_2\cdot CCl(SiX_3)\cdot O\cdot N(CF_3)_2} \quad \underset{(6)}{(CF_3)_2N\cdot O\cdot CHCl\cdot CH(SiX_3)\cdot O\cdot N(CF_3)_2}$$

$$X = F (a), Cl (b), \text{or } Me (c)$$

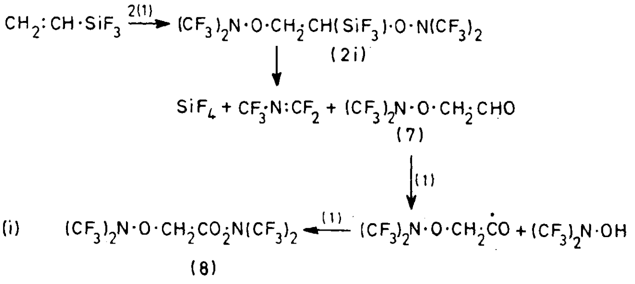
variety of vinyl-, 1-chlorovinyl-, and 2-chlorovinylsilanes have been investigated in order to determine the influence of (*i*) silicon substituents and (*ii*) vinylic chlorine atoms on the formation of adducts and on the subsequent thermal stabilities of such adducts.

## RESULTS AND DISCUSSION

*Reactions of Oxyl* (1).—The conditions used and the products obtained from the reactions of the oxyl (1) with the vinyl- and chlorovinyl-silanes are summarized in Table 1.

rapidly at low temperature to give the hydroxylamine and the esters $RCO_2\cdot N(CF_3)_2$ in near quantitative yield.[5]

A similar decomposition of the 2 : 1 adduct (5a) also



occurred under the reaction conditions but only to a minor extent (10%) [equation (ii)]. With 1-chlorovinyl-

$$(5a) \longrightarrow \underset{(9)}{(CF_3)_2N\cdot O\cdot CH_2\cdot COCl} + SiF_4 + CF_3\cdot N{:}CF_2 \qquad \text{(ii)}$$

trimethylsilane the initially formed 2 : 1 adduct (5c) decomposed in a different manner to afford the amide (10) [equation (iii)]. The thermal rearrangements and/or decompositions of the 2 : 1 adducts are discussed later.

TABLE 1

Reactions of vinylsilanes with *NN*-bistrifluoromethylamino-oxyl

| | Amount of silane | Amount of oxyl | | | Unchanged silane | Product (%) [a] | | Analysis (%) Found | | | | Analysis (%) Calc. | | | | B.p. | λ/μm of |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | mmol | mmol | $\theta_c$/°C | $t$/h | (%) | | | C | H | N | F | C | H | N | F | ($\theta_c$/°C) | C:O str. |
| $CH_2{:}CH\cdot SiCl_3$ | 10.0 | 15.0 | 20 | 18 | 35 | (2a) | 99 | | | | | | | | | | |
| $CH_2{:}CH\cdot SiMeCl_2$ | 10.0 | 20.0 | 20 | 4 | 3 | (2d) | 96 | 17.8 | 1.3 | 6.0 | 47.4 | 17.6 | 1.2 | 5.8 | 47.8 | | |
| $CH_2{:}CH\cdot SiMe_2Cl$ | 10.0 | 20.0 | 20 | 2 | | (2e) | 98 | 21.3 | 2.1 | 6.4 | 49.6 | 21.0 | 2.0 | 6.1 | 49.9 | | |
| $CH_2{:}CH\cdot SiF_3$ | 10.0 | 20.0 | 20 | 36 | 20 | $SiF_4$ | 100 | | | | | | | | | | |
| | | | | | | $CF_3\cdot N{:}CF_2$ | 100 | | | | | | | | | | |
| | | | | | | $(CF_3)_2N\cdot OH$ | 40 | | | | | | | | | | |
| | | | | | | (7) | 60 | 22.4 | 1.7 | | | 22.7 | 1.4 | | | 86—87 | 5.70s |
| | | | | | | (8) | 40 | 19.2 | 0.8 | | 60.0 | 19.0 | 0.5 | | 60.0 | 126—127 | 5.42s |
| $CH_2{:}CH\cdot SiMeF_2$ | 11.0 | 20.0 | 20 | 10 | 9 | (2f) | 99 | 18.9 | 1.7 | | 59.4 | 18.9 | 1.4 | | 59.9 | | |
| $CH_2{:}CH\cdot SiMe_2F$ | 11.0 | 20.0 | 20 | 3 | 9 | (2g) | 100 | 21.9 | 2.2 | | 55.7 | 21.8 | 2.0 | | 56.1 | | |
| $CH_2{:}CH\cdot Si(OMe)_3$ | 11.0 | 20.0 | 20 | 3 | 9 | (3b) | 100 | 22.0 | 2.3 | | 47.2 | 22.3 | 2.4 | | 47.1 | | |
| $CH_2{:}CCl\cdot SiF_3$ | 10.0 | 20.0 | 20 | 96 | | $SiF_4$ | 10 | | | | | | | | | | |
| | | | | | | $CF_3\cdot N{:}CF_2$ | 10 | | | | | | | | | | |
| | | | | | | (9) | 10 | | | | | | | | | | |
| | | | | | | (10a) | 90 | 15.6 | 0.4 | | | 15.0 | 0.4 | | | | |
| $CH_2{:}CCl\cdot SiMe_3$ | 5.0 | 10.0 [c] | −23 | 5 | | $ClSiMe_3$ | 90 | | | | | | | | | | |
| | | | | | | (10) | 90 | 20.2 | 1.0 | | 62.6 | 20.0 | 0.6 | | 63.0 | 104—105 | 5.57m,<br>5.64s |
| $CH_2{:}CCl\cdot SiCl_3$ | 18.8 | 26.0 | 20 | 3 | 30 | (10b) | 99 | 13.8 | 0.8 | | 42.5 | 13.6 | 0.4 | | 42.8 | | |
| *trans*-$CHCl{:}CH\cdot SiF_3$ | 12.0 | 20.0 | 20 | 288 | 16 | (6a) | 100 [d] | 15.2 | 0.5 | | 58.8 | 14.9 | 0.4 | | 59.0 | | |
| *trans*-$CHCl{:}CH\cdot SiCl_3$ | 15.0 | 20.0 | 20 | 240 | 33 | (6b) | 95 [e] | 13.8 | 0.8 | | 42.5 | 13.6 | 0.4 | | 42.8 | | |
| *trans*-$CHCl{:}CH\cdot SiMe_3$ | 5.0 | 10.0 | 20 | 12 | | $(CF_3)_2N\cdot OH$ | (7.5) | | | | | | | | | | |
| | | | | | | (6c) | 92 [d] | 23.0 | 2.6 | | 48.3 | 23.0 | 2.4 | | 48.4 | | |

[a] Yields based on silane used, *i.e.* not recovered; where total yield is >100%, decomposition of the 2 : 1 adduct has taken place. [b] A correct elemental analysis could not be obtained because of slow decomposition. [c] The oxyl was released in small quantities into a tube containing the silane at −23 °C; attempted reactions carried out with mixtures of the reactants in sealed tubes at 0 and −23 °C gave only a charred residue. [d] Two diastereoisomers in the ratio 67 : 33. [e] As in [d] but ratio of 56 : 44.

All the reactions gave high yields of the corresponding 2 : 1 adducts (2), (5), or (6) with the exceptions of those with trifluoro(vinyl)silane and 1-chlorovinyltrimethylsilane which yielded products consistent with the initial formation of 2 : 1 adducts and then decomposition of these under the conditions employed. With the trifluorosilane (2i) decomposition of the 2 : 1 adduct occurred to an appreciable extent before all the oxyl (1) had been used up, and the compounds $(CF_3)_2N\cdot OH$ and (8) are formed *via* hydrogen abstraction by oxyl (1) of the aldehydic hydrogen atom in the decomposition product (7) [equation (i)].

Reactions of the oxyl (1) with simple aldehydes RCHO (R = Ph, Me, Et, or $Me_3C$) have been reported to proceed

$$\begin{aligned} CH_2{:}CCl\cdot SiMe_3 &\xrightarrow{2(1)} (CF_3)_2N\cdot O\cdot CH_2\cdot CCl(SiMe_3)\cdot O\cdot N(CF_3)_2 \\ &\qquad\qquad \downarrow\ (5c) \\ &Me_3SiCl + \underset{(10)}{(CF_3)_2N\cdot O\cdot CH_2\cdot CO\cdot N(CF_3)_2} \qquad \text{(iii)} \end{aligned}$$

All three *trans*-2-chlorovinylsilanes gave 2 : 1 adducts (6) as mixtures of two diastereoisomers; the major products are considered to be the sterically favoured products of *anti* addition [equation (iv)].

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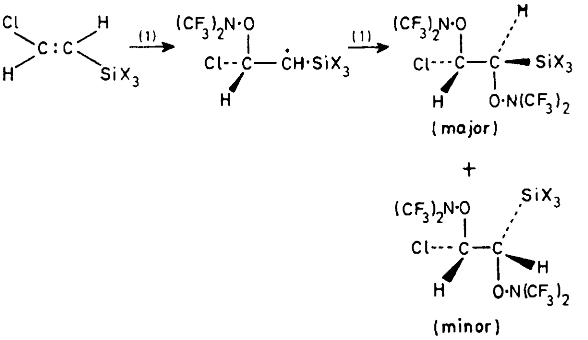
[5] R. E. Banks, D. R. Choudhury, and R. N. Haszeldine, *J.C.S. Perkin I*, 1973, 80.

The rates of reaction of the oxyl with the vinylsilanes increased as electron-withdrawing chlorine or fluorine



(iv)

atoms on silicon were replaced by electron-releasing methyl groups; the fluorosilyl compounds were less reactive than their chlorosilyl counterparts. The reactions of the chlorovinylsilanes $CH_2{:}CCl{\cdot}SiF_3$, $CHCl{:}CH{\cdot}SiF_3$, and $CHCl{:}CH{\cdot}SiCl_3$ with oxyl (1) were much slower than those of the corresponding vinylsilanes, but surprisingly $CH_2{:}CCl{\cdot}SiCl_3$ was more reactive than $CH_2{:}CH{\cdot}SiCl_3$. The 2-chlorovinylsilanes are less reactive than the corresponding 1-chlorovinylsilanes probably because of increased steric hindrance to oxyl (1) attack at a CHCl group relative to attack at a $CH_2$ group.

$(CF_3)_2N{\cdot}CH_2{\cdot}CH(SiX_3){\cdot}O{\cdot}N(CF_3)_2$

(11) $X_3$ = $Cl_3$(a), $Me_3$(b), $MeCl_2$(c), $Me_2Cl$(d), or $F_3$(e)

$(CF_3)_2N{\cdot}CH_2{\cdot}CH(O{\cdot}SiX_3){\cdot}N(CF_3)_2$

(12) $X_3$ = $Cl_3$(a), $Me_3$(b), $MeCl_2$(c), or $Me_2Cl$(d)

$(CF_3)_2N{\cdot}CH_2{\cdot}CCl(SiX_3){\cdot}O{\cdot}N(CF_3)_2$

(13) X = Cl (a) or F(b)

$(CF_3)_2N{\cdot}CHCl{\cdot}CH(SiX_3){\cdot}O{\cdot}N(CF_3)_2$

(14) X = Cl (a) or F(b)

TABLE 2

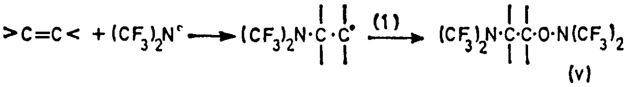
Reactions of vinylsilanes with perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane)

| | Amount of silane | Amount of diazapentane | | | | Analysis (%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Found | | | | Calc. | | | | B.p. | λ/μm of |
| | mmol | mmol | t/h | Product (%)[a] | | C | H | N | F | C | H | N | F | (θc/°C) | C:O str. |
| $CH_2{:}CH{\cdot}SiCl_3$ | 6.0 | 6.0 | 48 | (11a) | 100 | 15.3 | 0.7 | | 46.7 | 15.0 | 0.6 | | 47.2 | | |
| $CH_2{:}CH{\cdot}SiMeCl_2$ | 7.5 | 7.5 | 48 | (11c) | 100 | 18.5 | 1.5 | | 48.9 | 18.2 | 1.3 | | 49.3 | | |
| $CH_2{:}CH{\cdot}SiMe_2Cl$ | 7.5 | 7.5 | 48 | (11d) | 100 | 14.3 | 0.5 | | 43.6 | 14.0 | 0.4 | | 44.1 | | |
| $CH_2{:}CH{\cdot}SiMe_3$ | 5.0 | 5.0 | 48 | (12b) | 100 | 25.7 | 3.0 | | 54.2 | 25.7 | 2.85 | | 54.2 | 137—138 | |
| $CH_2{:}CH{\cdot}SiF_3$ | 5.0 | 5.0 | 96 | (11e) | 100 | 17.4 | 0.9[b] | | | 16.7 | 0.7 | | | | |
| $CH_2{:}CCl{\cdot}SiCl_3$ | 5.0 | 5.0 | 48 | (12a) | 100 | 14.3 | 0.5 | | 43.6 | 14.0 | 0.4 | | 44.1 | | |
| $CH_2{:}CCl{\cdot}SiF_3$ | 4.0 | 4.0 | 48 | $SiF_4$[c] | 75 | | | | | | | | | | |
| | | | | $CF_3{\cdot}N{:}CF_2$ | 75 | | | | | | | | | | |
| | | | | $SiF_3Cl$[c] | 25 | | | | | | | | | | |
| | | | | (16) | 75 | 21.1 | 1.2 | | | 21.3 | 0.9 | | | 95—96 | 5.56s |
| | | | | (17) | 25 | 20.4 | 0.6 | 7.5 | | 20.8 | 0.6 | 8.0 | | 107—108 | 5.46m,<br>5.56s |
| *trans*-$CHCl{:}CH{\cdot}SiCl_3$ | 5.0 | 5.0 | 240 | (14a) | 100[d] | 14.1 | 0.6 | | 43.8 | 14.0 | 0.4 | | 44.1 | | |
| *trans*-$CHCl{:}CH{\cdot}SiF_3$ | 5.0 | 5.0 | 24 | (25b) | 100[e] | 15.1 | 0.6 | 6.2 | 61.0 | 15.4 | 0.4 | 6.0 | 61.0 | | |
| *cis*-$MeCH{:}CH{\cdot}SiCl_3$ | 8.0 | 6.0 | 48 | $(CF_3)_2NH$ | 50 | | | | | | | | | | |
| | | | | (18) | 50 | 17.5 | 1.6 | | | 17.5 | 1.2 | | | 149—150 | |
| | | | | (15) | 50[f] | 16.8 | 1.1 | | | 16.9 | 1.0 | | | | |

[a] Yields based on diazapentane except where indicated; with silane $CH_2{:}CCl{\cdot}SiF_3$ yields are >100% because of decomposition of the initially formed adduct, while with $MeCH{:}CH{\cdot}SiCl_3$ yields are >100% because of hydrogen abstraction by 50% of attacking $(CF_3)_2N^{\cdot}$. [b] Correct analysis could not be obtained because of slow decomposition. [c] Yield based on silane used. [d] Mixtures of two diastereoisomers in the ratio 67 : 33. [e] As in *d* but ratio of 60 : 40. [f] As in *d* but ratio of 50 : 50.

*Reactions of the Oxadiazapentane* (4).—The reactions were carried out at *ca.* 20 °C and the reaction times, reactant ratios, and products obtained with the vinyl- and chlorovinyl-silanes are summarized in Table 2.

In all the reactions, except that with the propenylsilane, high yields of 1 : 1 adducts were formed initially by cleavage of (4) into $(CF_3)_2N^{\cdot}$ and $(CF_3)_2N{\cdot}O^{\cdot}$ followed by attack on the olefin by the $(CF_3)_2N^{\cdot}$ radical [equation (v)]. The adducts (11b) and (13b) were not stable under



$$>C{=}C< + (CF_3)_2N^{\cdot} \longrightarrow (CF_3)_2N{\cdot}\overset{|}{\underset{|}{C}}{\cdot}\overset{|}{\underset{|}{C}}{}^{\cdot} \xrightarrow{(1)} (CF_3)_2N{\cdot}\overset{|}{\underset{|}{C}}{\cdot}\overset{|}{\underset{|}{C}}{\cdot}O{\cdot}N(CF_3)_2 \qquad (v)$$

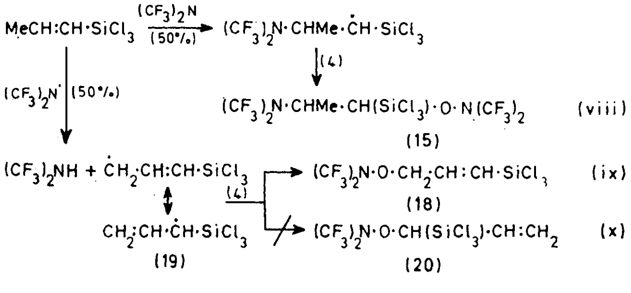
the reaction conditions; the former adduct rearranged to (12b) while the latter deomposed by two distinct paths [equations (vi) and (vii)]. The rearrangements and decompositions are discussed later.

The olefin *cis*-$MeCH{:}CH{\cdot}SiCl_3$ reacted by addition (50%) to give adduct (15) [equation (viii)] and by allylic

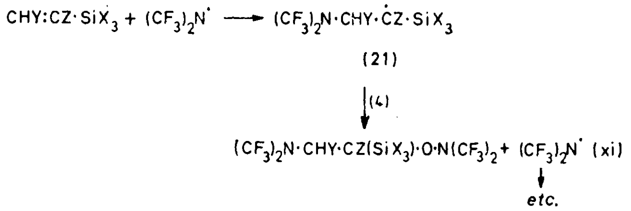
$$\begin{tikzcd}
(13b) \arrow[r, "(75\%)"] \arrow[d, "(25\%)"] & SiF_4 + CF_3{\cdot}N{:}CF_2 + \underset{(16)}{(CF_3)_2N{\cdot}CH_2{\cdot}COCl} \quad (vi) \\
SiF_3Cl + (CF_3)_2N{\cdot}CH_2{\cdot}CO{\cdot}N(CF_3)_2 \quad (vii) &
\end{tikzcd}$$

abstraction (50%) to afford the allyl radical (19) and hence the substitution product (18) [equation (ix)]. One feature of the abstraction reaction was that the radical (19) reacted exclusively at the terminal position and the product (20) resulting from reaction at the $CH{\cdot}SiCl_3$ group [equation (x)] was not detected; compound (18) was identified by its n.m.r. spectra: $^1H$, τ 3.5 (2 H, CH:CH) and 5.5 (2 H, d of m, $O{\cdot}CH_2{\cdot}CH$); $^{19}F$, δ −8.7 p.p.m. [$(CF_3)_2N{\cdot}O$].

The structures of the adducts were established by (*i*) their thermal rearrangements or decompositions (see later) and (*ii*) their n.m.r. spectra which were similar to those of the corresponding oxyl 2 : 1 adducts except for the expected changes, *e.g.* upfield shift of *ca.* 0.8 p.p.m. for $CH_2{\cdot}N$ relative to $CH_2{\cdot}O$ and replacement of a $^{19}F$ absorption at *ca.* −10 p.p.m. $[(CF_3)_2N{\cdot}O]$ by one at *ca.* −18 p.p.m. $[(CF_3)_2N]$. The $CH_2$ n.m.r. absorptions of adducts (11) and (13) appeared as doublets (coupling to adjacent CH) and singlets, respectively, whereas the same absorptions in the corresponding oxyl adducts (2) and (5) showed the non-equivalence of the two $CH_2$ protons, *i.e.* they appeared as AB doublet and AB patterns, respectively.



The formation of mixtures of disastereoisomeric adducts with the silanes *trans*-$CHCl{:}CH{\cdot}SiX_3$ (X = F or Cl) and *cis*-$CHMe{:}CH{\cdot}SiCl_3$, and allylic abstraction from the methyl group of the latter vinylsilane, are consistent with radical reactions rather than four-centre *syn* additions, and the adduct structures show that initial $(CF_3)_2N^{\cdot}$ radical attack occurs at the vinylic carbon atoms not bonded to silicon to afford the more stable intermediate radicals (21) which undergo chain transfer with (4) at oxygen exclusively [equation (xi)].

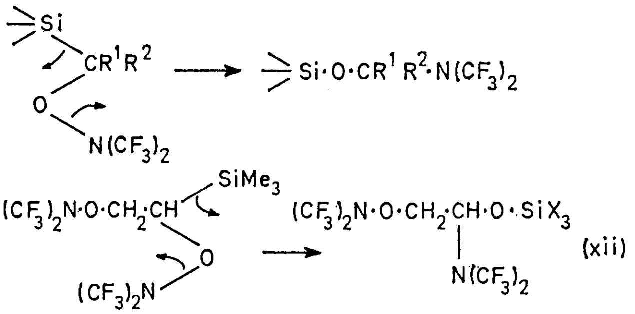


Although the relative rates of reaction of the diazapentane (4) with the vinylsilanes were not studied in the same detail as were the corresponding rates of reaction of the oxyl (1), it was observed that the addition to the silane $CH_2{:}CH{\cdot}SiX_3$ (X = F) was much slower than addition to the silanes ($X_3$ = $Cl_3$, $MeCl_2$, $Me_2Cl$, or $Me_3$). However, the addition of (4) to the chlorovinylsilane $CHCl{:}CH{\cdot}SiCl_3$ was much slower than to the corresponding trifluorosilane $CHCl{:}CH{\cdot}SiF_3$ which was totally unexpected and is difficult to explain.

In contrast to the oxyl adducts (2b) and (4a) with the silanes $CH_2{:}CH{\cdot}SiMe_3$ and $CH_2{:}CCl{\cdot}SiF_3$, respectively, which are thermally stable at room temperature, the corresponding diazapentane adducts (11b) and (13b) rearranged and decomposed, respectively, *in situ* at *ca.* 20 °C, while a reversal of stability was observed with the adducts formed with the vinylsilane $CH_2{:}CH{\cdot}SiF_3$, *i.e.* the oxyl adduct (2; X = F) was unstable at *ca.* 20 °C but the diazapentane adduct (11e) was stable.

*Thermolysis of the Adducts.*—The conditions used, the products obtained, and analytical data on the new compounds are shown in Table 3. From the Table it is apparent that the adducts can be divided into two classes, *i.e.* those that rearrange and those that undergo elimination reactions.

(*a*) *Rearrangement.* It has been postulated[3,4] that the thermal rearrangement of the oxyl adducts (2b) and (2c) is a concerted reaction occurring *via* a four-centre transition state [equation (xii)], and an elementary kinetic study of the rearrangement of adduct (2b) showed that the reaction was first order with an activation energy of *ca.* 100 kJ $mol^{-1}$.[3] This mechanism is consistent with the present observation that the adducts (6b), (6c), and (14a), each present as a mixture of two diastereoisomers, on rearrangement gave compounds (16b), (16c), and (17), respectively, as mixtures of diastereoisomers in the same proportions as the reactant silanes. Thus the rearrangement occurs either with retention or with inversion of configuration at the α-carbon atom; the proposed mechanism requires retention of configuration.



Elementary kinetic studies of the rearrangements of silanes (2e) (at 90 and 105 °C) and (2d) (at 140 and 155 °C) were carried out; first-order kinetics were observed with rate constants [for (2e)] of $(4.75 \pm 0.20) \times 10^{-5}\ s^{-1}$ at 90 °C and $(1.86 \pm 0.30) \times 10^{-4}\ s^{-1}$ at 105 °C and [for (2d)] of $(1.09 \pm 0.20) \times 10^{-4}\ s^{-1}$ at 140 °C and $(5.02 \pm 0.20) \times 10^{-4}\ s^{-1}$ at 155 °C, from which activation energies of *ca.* 105 and 150 kJ $mol^{-1}$, respectively, were obtained. Silanes (2d) and (2e), as indicated in Table 3, rearrange less readily than (2b).

For the oxyl adducts (2) the ease of rearrangement is in the order for $X_3$ in $SiX_3$: $Me_3 > Me_2F > MeF_2 > Me_2Cl > (OMe)_3 > MeCl_2 > Cl_3$, and for the chlorovinylsilane adducts (6), $Me_3 > Cl_3$; the adduct (6b; X = Cl) rearranges more readily than (2a; X = Cl). A similar order of ease of rearrangement is found for the diazapentane adducts (11), $X_3 = Me_3 > Me_2Cl > MeCl_2 > Cl_3$, and the chlorovinylsilane adduct (14a; X = Cl) rearranges more readily than the vinylsilane adduct (11a; X = Cl). It was also observed that the diazapentane adducts (11) rearranged more readily than the corresponding oxyl adducts (2), *e.g.* (2b) was stable at 20 °C but (11b) rearranged.

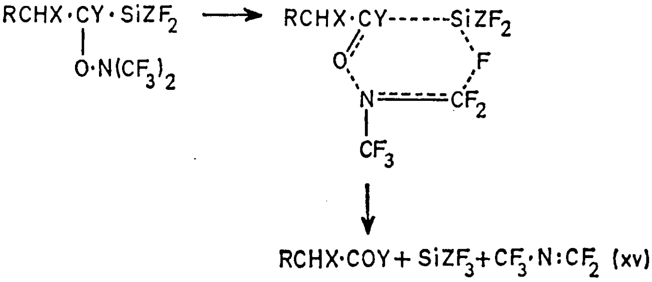
Thermal isomerizations involving insertion of oxygen into an Si–C bond are not common and are so far restricted to the rearrangements of β-silylketones[6] [equation (xiii)]. It has also been reported[7] that tris(organosilyl)-hydroxylamines undergo thermal rearrangement to silylaminosiloxanes [equation (xiv)].

$$R^1_3Si{\cdot}CH_2{\cdot}COR^2 \xrightarrow{100\text{–}180\ ^\circ C} R^1_3Si{\cdot}O{\cdot}CR^2{:}CH_2 \quad (xiii)$$

$$(R^1_3Si)_2N{\cdot}O{\cdot}SiR^2_3 \xrightarrow{200\ ^\circ C} R^1_3Si{\cdot}NR^1{\cdot}SiR^1_2{\cdot}O{\cdot}SiR^2_3 \quad (xiv)$$

(*b*) *Elimination.* The adducts which decomposed rather than rearranged all contained two or three fluorine substituents on silicon and/or a chlorine atom on the α carbon, and three distinct modes of decomposition (A)—(C) were observed.

(*i*) *Type* (*A*). This took place exclusively with the silanes (2i) (at 20 °C), (11e) (at 150 °C), and (2f) (at 90 and 110 °C), and to a major extent with the chloroalkyltrifluorosilanes (5a) (at 35 °C), (13b) (at 20 °C), and (6a) (at 100 °C). Such decompositions are considered to be initiated by nucleophilic attack by fluorine in the α-(CF$_3$)$_2$N·O group on the electron-deficient silicon, and to involve a concerted reaction *via* a six-centre transition state [equation (xv)].



(xv)

Surprisingly, although the 1-chloroalkylsilanes (5a)

TABLE 3

Thermolysis of the vinylsilane adducts

$(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}CH(O{\cdot}SiX_3){\cdot}N(CF_3)_2$
(22) $X_3$ = $Cl_3$(a), $MeCl_2$(b), $Me_2Cl$(e), $MeF_2$(f), $Me_2F$(g), or $(OMe)_3$(h)

$CHCl{:}C{:}O$
(23)

$(CF_3)_2N{\cdot}O{\cdot}CHCl{\cdot}CHO$
(25)

$(CF_3)_2N{\cdot}O{\cdot}CHCl{\cdot}CO_2{\cdot}N(CF_3)_2$
(24)

$(CF_3)_2N{\cdot}CHCl{\cdot}CH(O{\cdot}SiCl_3){\cdot}N(CF_3)_2$
(28)

$(CF_3)_2N{\cdot}O{\cdot}CHCl{\cdot}CH(O{\cdot}SiX_3){\cdot}N(CF_3)_2$
(26) X = Cl (a) or Me (b)

$(CF_3)_2N{\cdot}CH_2{\cdot}CHO$
(27)

| $RCHY{\cdot}CZ(SiX_3){\cdot}O{\cdot}N(CF_3)_2$ | | | | | | | | Analysis (%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Found | | | | Calc. | | | | | |
| R | $X_3$ | Y | Z | Amount/mmol | $\theta_c$/°C | *t*/h | Products (%) | C | H | N | F | C | H | N | F | B.p. ($\theta_c$/°C) | λ/μm of C:O str. |
| $(CF_3)_2N{\cdot}O$ | $Cl_3$ | H | H | 3.0 | 220 | 1.5 | (22a) 100 | 14.6 | 0.9 | | 45.6 | 14.5 | 0.6 | | 45.8 | 160—161 | |
| $(CF_3)_2N{\cdot}O$ | $MeCl_2$ | H | H | 3.0 | 150 | 15 | (22d) 100 | 17.6 | 1.7 | | 47.4 | 17.6 | 1.4 | | 47.8 | 153—154 | |
| $(CF_3)_2N{\cdot}O$ | $Me_2Cl$ | H | H | 2.0 | 100 | 12 | (22e) 100 | 21.4 | 2.1 | 6.1 | 49.7 | 21.1 | 2.0 | 6.1 | 50.0 | 148—149 | |
| $(CF_3)_2N{\cdot}O$ | $F_3$ | H | H [a] | 8.0 | 20 | 36 | $SiF_4$ 100, $CF_3{\cdot}N{:}CF_2$ 100, (7) 100 | | | | | | | | | | |
| $(CF_3)_2N{\cdot}O$ | $MeF_2$ | H | H | 3.2 | 70 | 288 | (22f) 100 | 19.1 | 1.6 | | 59.9 | 18.9 | 1.35 | | 59.9 | 125—126 | |
| $(CF_3)_2N{\cdot}O$ | $MeF_2$ | H | H | 3.0 | 110<br>or 90 | 4<br>8 | $MeSiF_3$ 100, $CF_3{\cdot}N{:}CF_2$ 100, (7) 100 | | | | | | | | | | |
| $(CF_3)_2N{\cdot}O$ | $Me_2F$ | H | H | 2.5 | 75 | 100 | (22g) 100 | 22.0 | 2.2 | | 55.9 | 21.8 | 2.0 | | 56.1 | 131—132 | |
| $(CF_3)_2N{\cdot}O$ | $(OMe)_3$ | H | H | 4.0 | 130 | 15 | (22h) 100 | 22.5 | 2.2 | | 47.0 | 22.3 | 2.4 | | 47.1 | 171—172 | |
| $(CF_3)_2N{\cdot}O$ | $F_3$ | H | Cl | 3.1 | 35 | 8 | $SiF_4$ 85, $CF_3{\cdot}N{:}CF_2$ 85, $SiF_3Cl$ 15, (9) 85, (10) 15 | | | | | | | | | | |
| $(CF_3)_2N{\cdot}O$ | $Me_3$ | H | Cl [a] | 5.0 | − 23 | 5 | $Me_3SiCl$ 90, (10) 90 | | | | | | | | | | |
| $(CF_3)_2N{\cdot}O$ | $Cl_3$ | H | Cl | 1.8 | 100 [b] | 8 | $SiCl_4$ 98, (10) 100 | | | | | | | | | | |
| $(CF_3)_2N{\cdot}O$ | $F_3$ | Cl | H | 4.0 | 100 | 15 | $SiF_4$ 75, $CF_3{\cdot}N{:}CF_2$ 75, $(CF_3)_2NH$ 25, $Si_2F_6$ 25, (23) 25 | | | | | | | | | | |
| | | | | | | | (24) 25 | 20.0 | 0.6 | | 45.9 | 19.6 | 0.8 | | 46.4 | 90—91 | 5.67 |
| | | | | | | | (25) 75 | 17.5 | 0.4 | | 55.4 | 17.5 | 0.3 | | 55.4 | 111—112 | 5.40 |
| $(CF_3)_2N{\cdot}O$ | $Cl_3$ | Cl | H [c] | 1.5 | 150 | 40 | (26a) 100 [c] | 14.0 | 0.7 | | 42.4 | 13.6 | 0.4 | | 42.8 | 173—174 | |
| $(CF_3)_2N{\cdot}O$ | $Me_3$ | Cl | H [d] | 2.0 | 70 | 72 | (26b) 100 [d] | 23.4 | 2.4 | | 48.2 | 23.0 | 2.4 | | 48.4 | 153—154 | |
| $(CF_3)_2N$ | $Cl_3$ | H | H | 2.5 | 200 | 16 | (12a) 100 | 15.3 | 1.0 | | 47.1 | 15.0 | 0.65 | | 47.3 | 157—158 | |
| $(CF_3)_2N$ | $MeCl_2$ | H | H | 2.0 | 150 | 8 | (12c) 100 | 18.5 | 1.4 | | 49.0 | 18.2 | 1.3 | | 49.4 | 151—152 | |
| $(CF_3)_2N$ | $Me_2Cl$ | H | H | 1.2 | 100 | 15 | (12d) 100 | 22.0 | 2.2 | | 51.4 | 21.8 | 2.0 | | 51.8 | 148—149 | |
| $(CF_3)_2N$ | $Me_3$ | H | H [a] | 5.0 | 20 | 48 | (12b) 100 | | | | | | | | | | |
| $(CF_3)_2N$ | $F_3$ | H | H | 1.5 | 150 | 8 | $SiF_4$ 100, $CF_3{\cdot}N{:}CF_2$ 100, (27) 100 | 24.6 | 1.7 | | | 24.6 | 1.5 | | | 88—89 | 5.67 |
| $(CF_3)_2N$ | $Cl_3$ | H | Cl | 1.5 | 100 | 8 | $SiCl_4$ 100, (17) 100 | | | | | | | | | | |
| $(CF_3)_2N$ | $F_3$ | H | Cl [a] | 4.0 | 20 | 48 | $SiF_4$ 75, $CF_3{\cdot}N{:}CF_2$ 75, $SiF_3Cl$ 25, (16) 75 | | | | | | | | | | |
| $(CF_3)_2N$ | $Cl_3$ | Cl | H [d] | 2.0 | 150 | 85 | (28) 100 [d] | 14.2 | 0.6 | | 44.2 | 14.0 | 0.4 | | 44.2 | 166—167 | |
| $(CF_3)_2N$ | $F_3$ | Cl | H | 1.0 | 150 | 16 | $SiF_4$, 80, $CF_3{\cdot}N{:}CF_2$, $(CF_3)_2NH$, $Si_2F_6$ [e] | | | | | | | | | | |

[a] Adducts not isolated since they decomposed *in situ*. [b] A reaction carried out under the same conditions in the presence of ethylene gave identical products. [c] Mixtures of diastereoisomers in the ratio 56 : 44. [d] As in *c* but in the ratio 67 : 33. [e] Two unidentified higher-boiling compounds formed in the ratio 80 : 20.

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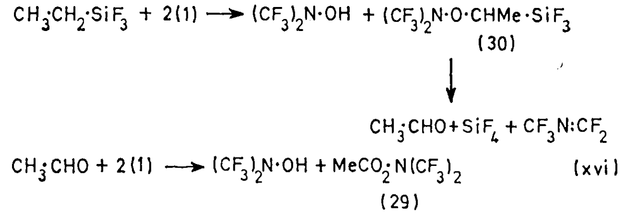
[6] A. G. Brook, D. M. MacRae, and W. W. Limburg, *J. Amer. Chem. Soc.*, 1967, **89**, 5493.

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

and (13b) decomposed at comparable temperatures [indicating that replacement of a β-$(CF_3)_2N{\cdot}O$ group by a $(CF_3)_2N$ group had little effect on the ease of decomposition], the silanes (2i) and (11e) decomposed at greatly different temperatures (20 and 150 °C, respectively); the reason for this difference in reactivity is not apparent. An interesting observation was that silane (2f), which decomposed quantitatively by route (A) at 90 or 110 °C, when heated for an extended period at a lower temperature (70 °C) underwent rearrangement exclusively. This indicates that with this silane the factors which control rearrangement and decomposition are delicately balanced.

The reaction of oxyl (1) with ethyltrifluorosilane[3] gives a mixture of silicon tetrafluoride, perfluoro-2-azapropene, the hydroxylamine $(CF_3)_2N{\cdot}OH$, and the ester (29), which were postulated to be formed *via* decomposition of the α-substitution compound (30) by path (A) [equation (xvi)].



$$CH_3{\cdot}CH_2{\cdot}SiF_3 + 2(1) \longrightarrow (CF_3)_2N{\cdot}OH + \underset{(30)}{(CF_3)_2N{\cdot}O{\cdot}CHMe{\cdot}SiF_3}$$

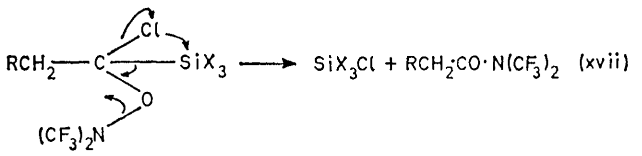
$$\downarrow$$

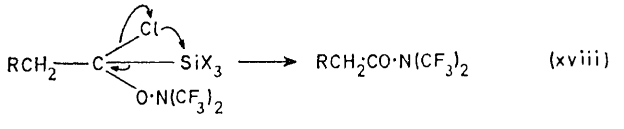
$$CH_3{\cdot}CHO + SiF_4 + CF_3N{:}CF_2$$

$$CH_3{\cdot}CHO + 2(1) \longrightarrow (CF_3)_2N{\cdot}OH + \underset{(29)}{MeCO_2{\cdot}N(CF_3)_2} \qquad \text{(xvi)}$$

The aldehyde $(CF_3)_2N{\cdot}CH_2{\cdot}CHO$ (27) on reduction with $Li[AlH_4]$ gave the corresponding alcohol $(CF_3)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ (66%).

(*ii*) *Type* (*B*). The 1-chloroalkylsilanes (5b) (at 100 °C), (5c) (at −23 °C), and (13a) (at 100 °C) decomposed exclusively by this route, while the silanes (5a) and (13b) decomposed similarly to a minor extent, 15 (at 35) and 25% (at 20 °C), respectively. The decompositions presumably involve initial nucleophilic attack by the α-chlorine atom on silicon and could occur by a concerted mechanism *via* a four-centre transition state [equation (xvii)] or *via* a carbene intermediate [equation (xviii)]. It has been reported previously that 1-fluoroalkyl- and 1-chloroalkyl-trihalogenosilanes on thermolysis undergo α elimination to give carbenes [*e.g.* equations (xix)[8] and (xx)[9]].





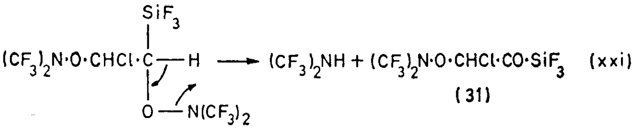
$$CCl_3{\cdot}SiF_3 \xrightarrow{100\text{–}120\,^{\circ}C} SiF_3Cl + \ddot{C}Cl_2 \qquad \text{(xix)}$$

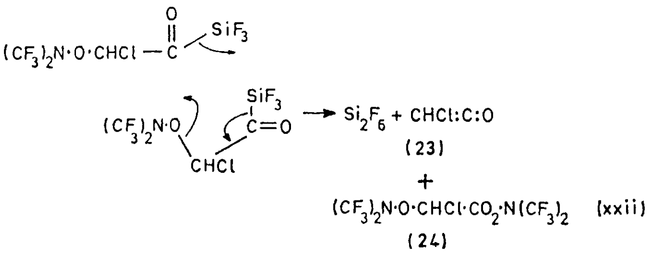
$$CH_3{\cdot}CCl_2{\cdot}SiF_2Cl \longrightarrow SiF_2Cl_2 + CH_3{\cdot}\ddot{C}Cl \qquad \text{(xx)}$$

In order to determine whether a concerted mechanism or elimination *via* a carbene intermediate was taking place in the present decompositions, the silane (5b) was pyrolysed at 100 °C in the presence of ethylene to act as a carbene trap. Quantitative decomposition occurred to give the same products as obtained in the absence of ethylene and the cyclopropane $(CF_3)_2N{\cdot}O{\cdot}CH_2{\cdot}\overline{C[O{\cdot}N(CF_3)_2]{\cdot}CH_2{\cdot}CH_2}$ was not detected. This result indicates that the rearrangement occurs *via* a concerted mechanism, although it is possible, but less likely, that a carbene is formed which undergoes intramolecular rearrangement at a faster rate than it undergoes intermolecular addition to the olefin.

The ease of decomposition of the silanes by route (B) follows the order $SiMe_3 > SiF_3 > SiCl_3$ which is not the order expected ($SiF_3 > SiCl_3 > SiMe_3$) on the basis of the greater the electron deficiency at silicon the easier will be nucleophilic attack by the α-chlorine atom, *cf.* decompositions of $R_FSiF_3$ (*ca.* 150 °C)[9,10] and $R_FSiCl_3$ (*ca.* 220 °C).[11] It is possible, however, that the electron-releasing methyl groups weaken the α-C–Si bond, thus making decomposition more favourable with silane (5c).

(*iii*) *Type* (*C*). This mode of decomposition was only observed with the 2-chloroalkylsilane (6a) (at 100 °C) and competed to a minor extent (25%) with decomposition *via* route (A). The products $(CF_3)_2NH$, $Si_2F_6$, chloroketen (23), and the ester (24) are best explained by decomposition involving two steps, *i.e.* an initial elimination of the amine, probably *via* a four-centre transition state to afford the carbonyl compound (31) [equation (xxi)], followed by an intermolecular elimination between two molecules of intermediate (31) *via* a six-centre transition state [equation (xxii)]. Carbonyl compounds of type $CH_2{:}C(O{\cdot}SiR_3){\cdot}NMe{\cdot}COMe$, when heated at *ca.* 180 °C, eliminate keten and form silylated acetamides $R_3Si{\cdot}NMe{\cdot}COMe$.[12]





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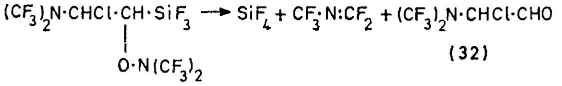
A preliminary investigation of the thermal decomposition of the corresponding diazapentane adduct (14b) at 100 °C was also carried out. The adduct decomposed to give a low-boiling mixture of $SiF_4$, $(CF_3)_2NH$, $CF_3\cdot N{:}CF_2$, $Si_2F_6$, and an unidentified component, and a higher-boiling mixture of a carbonyl compound (*ca.* 80%) [i.r. band at 5.65 μm ($C{:}O$ str.) and $^{19}F$ n.m.r. band at −18.0 p.p.m.; *cf.* $(CF_3)_2N\cdot CH_2\cdot CHO$, i.r. 5.67 μm, $^{19}F$ band at −18.5 p.p.m.], probably 2-chloro-2-bis(trifluoromethyl)aminoacetaldehyde (32) formed by decomposition *via* path (A) [equation (xxiii)], and an unidentified compound (*ca.* 20%). The unidentified compound contained a band in its i.r. spectrum at 5.95 μm and showed bands in its $^{19}F$ n.m.r. spectrum at −17.8(s) and −17.5(s) p.p.m. (ratio 1 : 1) both assigned to $(CF_3)_2N$ absorptions. However, the compound was not the amide $(CF_3)_2N\cdot CHCl\cdot CO\cdot N(CF_3)_2$ expected if minor decomposition had taken place by path (C), as shown by comparison of the above spectral data with those for the amide $(CF_3)_2N\cdot CH_2\cdot CO\cdot N(CF_3)_2$ [i.r. 5.46 and 5.56 μm, $^{19}F$ n.m.r. −18.3(s) and −21.9(s) p.p.m.]. The minor decomposition path is therefore unknown, although the compounds $(CF_3)_2NH$ and $Si_2F_6$, expected if decomposition had occurred by path (C), were present in the products.



$$(CF_3)_2N\cdot CHCl\cdot \underset{\displaystyle O\cdot N(CF_3)_2}{\underset{|}{CH}}\cdot SiF_3 \longrightarrow SiF_4 + CF_3\cdot N{:}CF_2 + \underset{(32)}{(CF_3)_2N\cdot CHCl\cdot CHO} \qquad (xxiii)$$

With silanes where elimination occurred *via* the two competing routes (A) and (B) or (C) the major mode of reaction was by path (A). Elimination *via* route (A) required a higher temperature if a hydrogen atom in the alkyl group was replaced by a chlorine atom, particularly in the 2 position. This is surprising since the β-carbon atom is not involved in the elimination.

Although the 1-chloroalkylsilanes decomposed exclusively or partly by route (B) *via* elimination of a chlorosilane, no such elimination involving a β-chlorine atom was observed even though such eliminations take place in the thermolyses of 2-chloroalkylsilanes, *e.g.* $CH_2Cl\cdot CH_2\cdot SiMe_3$ and $CH_2Cl\cdot CH_2\cdot SiCl_nEt_{3-n}$ ($n = 0$—3).[13] However, such decompositions afford alkenes and to date no alkenes containing vinylic $(CF_3)_2N\cdot O$ groups have been reported although many attempts have been made to prepare them.

## EXPERIMENTAL

Reactants and products were handled, where possible, in a conventional vacuum system to avoid contact with air or moisture. Products were separated by fractional condensation *in vacuo* or by preparative-scale g.l.c. [Pye 104 machine using columns (2—10 m) packed with silicone elastomer (SE 30), dinonyl phthalate (DNP) or silicone oil (MS 550) (10—30% w/w) on Celite] and were examined by some or all of the following techniques; i.r. spectroscopy (Perkin-Elmer 257 spectrophotometer using 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 instrument operating at 100.0 MHz for $^1H$ and 94.1 MHz for $^{19}F$ with internal tetramethylsilane and external trifluoroacetic acid as the respective references), mass spectrometery (A.E.I. MS902 spectrometer), and g.l.c. [Pye 104 machine using columns (2 m) packed with the same stationary phases as the preparative-scale columns]. Boiling points were determined by Siwoloboff's method.

*NN*-Bistrifluoromethylamino-oxyl was prepared from the corresponding hydroxylamine by oxidation with silver(II) oxide [14] and perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) was made by reaction of the oxyl with trifluoronitrosomethane.[14] All the vinylsilanes were prepared from trichloro(vinyl)silane by standard literature methods except for trichloro(prop-1-enyl)silane which was synthesized (80%) by the hexachloroplatinic(IV) acid-catalysed addition of trichlorosilane to propyne.

*Reactions of* NN-*Bistrifluoromethylamino-oxyl with Vinylsilanes.*—The reactions were carried out in sealed Pyrex ampoules (*ca.* 300 cm$^3$) *in vacuo*, except for those with the silanes $CH_2{:}CH\cdot SiCl_3$ (*ca.* 100 cm$^3$ tube), $CH_2{:}CCl\cdot SiMe_3$ (*ca.* 150 cm$^3$ tube), and $CHCl{:}CH\cdot SiMe_3$ (*ca.* 150 cm$^3$ tube). With the silane $CH_2{:}CCl\cdot SiMe_3$ extensive charring occurred at both 0 and −23 °C and so small quantities of the oxyl were condensed into the tube containing the silane at −23 °C with reaction being completed before further addition was carried out. The conditions used, the yields of isolated products, and elemental-analysis data for the new products obtained are shown in Table 1. Compounds (7) and (8) were separated by g.l.c. (4 m SE 30 at 45 °C).

*Reactions of Perfluoro*(2,4-*dimethyl*-3-*oxa*-2,4-*diazapentane*) *with Vinylsilanes.*—The reactions were carried out in sealed Pyrex ampoules (*ca.* 60 cm$^3$) *in vacuo* at room temperature in the dark. The conditions used, the yields of isolated products, and elemental-analysis data for the new products obtained are shown in Table 2. Mixtures of compounds (16) and (17), and of compounds (15) and (18), were separated by g.l.c. (4 m SE 30 at 50 °C).

*Pyrolysis of the Vinylsilane Adducts.*—The thermolyses of the adducts were carried out in sealed Pyrex ampoules (*ca.* 30 cm$^3$) *in vacuo* except for certain adducts which decomposed *in situ* during their preparation. The conditions used, the yields of isolated products, and elemental-analysis and boiling-point data for the new compounds obtained are shown in Table 3. Compounds (9) and (10) were separated by g.l.c. (10 m SE 30 at 35 °C) as were (24) and (25) (4 m DNP at 70 °C).

The pyrolysis of [1-(*NN*-bistrifluoromethylamino-oxy)-2-bis(trifluoromethyl)amino-2-chloroethyl]trifluorosilane (14b) (0.45 g, 1.0 mmol) at 150 °C gave (*i*) silicon tetrafluoride (0.8 mmol, 80%), (*ii*) a mixture (*ca.* 1.0 mmol) of perfluoro-2-azapropene and an unidentified second component, (*iii*) a mixture (*ca.* 0.3 mmol) of bis(trifluoromethyl)amine and hexafluorodisilane, and (*iv*) a higher-boiling liquid which was shown by $^{19}F$ n.m.r. spectroscopy to contain two components (ratio 4 : 1); signal for major component at $\delta$ −18.0 p.p.m. [$(CF_3)_2N$] and signals for minor component at −17.8 [s, $(CF_3)_2N$] and −17.5 p.p.m. [s, $(CF_3)_2N$] in the ratio 1 : 1.

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The liquid showed bands in its i.r. spectrum at $\lambda_{max.}$ 5.65 (C:O str.) and 5.95 μm (C:O or C:C str.).

*Thermolysis of* [1,2-*bis*(NN-*bistrifluoromethylamino-oxy*)-*ethyl*]*dichloro*(*methyl*)*silane* (2d) *and* [1,2-*bis*(*NN-bistrifluoromethylamino-oxy*)*ethyl*]*chlorodimethylsilane* (2e).—Samples of the two silanes were sealed in n.m.r. tubes and heated for various lengths of time [(2d) at 140 and 155 °C, (2e) at 90 and 105 °C] and the $^{19}F$ n.m.r. spectra were integrated (*ca.* 10 times) after each period of heating. The values obtained for $(a - x)$ [where $a$ = initial concentration of reactant silane and $(a - x)$ = concentration of silane after time $t$] and for $\log_{10}[a/(a - x)]$ are shown in Table 4. In all cases plots of $\log_{10}[a/(a - x)]$ against time ($t$) gave straight lines, as expected for first-order reactions, from the gradients of which the rate constants were calculated.

TABLE 4

Thermal isomerization of the silanes (2d) and (2e)

| (2d) | | | | | | (2e) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| At 140 °C | | | At 155 °C | | | At 90 °C | | | At 105 °C | | |
| $(a - x)$ | $\log_{10}[a/(a - x)]$ | $t$/min | $(a - x)$ | $\log_{10}[a/(a - x)]$ | $t$/min | $(a - x)$ | $\log_{10}[a/(a - x)]$ | $t$/min | $(a - x)$ | $\log_{10}[a/(a - x)]$ | $t$/min |
| 52 | 0.000 | 0 | 52 | 0.000 | 0 | 52 | 0.000 | 0 | 52 | 0.000 | 0 |
| 47.5 | 0.039 | 15 | 38 | 0.136 | 10 | 50 | 0.017 | 15 | 42 | 0.093 | 15 |
| 42.5 | 0.088 | 30 | 28 | 0.268 | 20 | 48 | 0.035 | 30 | 38 | 0.136 | 30 |
| 38.5 | 0.131 | 45 | 20.5 | 0.404 | 30 | 46 | 0.053 | 45 | 32 | 0.211 | 45 |
| 34.5 | 0.178 | 60 | 15.5 | 0.525 | 40 | 44 | 0.072 | 60 | 26 | 0.301 | 60 |
| 28.5 | 0.261 | 90 | 9.5 | 0.738 | 55 | 40 | 0.114 | 90 | 20 | 0.415 | 90 |
| 24 | 0.336 | 120 | 6.2 | 0.924 | 70 | 37 | 0.148 | 120 | 14 | 0.570 | 120 |
| 19.5 | 0.426 | 150 | 4.0 | 1.113 | 85 | 34 | 0.185 | 150 | 10 | 0.716 | 150 |
| 16.2 | 0.507 | 180 | 2.5 | 1.318 | 100 | 31 | 0.224 | 180 | 7 | 0.871 | 180 |

*Reduction of* 2-[*Bis*(*trifluoromethyl*)*amino*]*acetaldehyde*.—A solution of the aldehyde (0.29 g, 1.5 mmol) in dry diethyl ether (5 cm$^3$) was slowly added to a stirred slurry of lithium tetrahydridoaluminate (0.30 g, 8.0 mmol) in dry diethyl ether (5 cm$^3$). The resulting mixture was heated under reflux (30 min), cooled, and then treated with cold aqueous sulphuric acid (*ca.* 8% v/v, 10 cm$^3$). The ether layer was separated and the aqueous layer was extracted with diethyl ether (3 × 3 cm$^3$). The extracts were combined and separated by fractional condensation *in vacuo* to afford 2-[*bis*(*trifluoromethyl*)*amino*]*ethanol* (0.19 g, 1.0 mmol, 66%) (Found: C, 24.5; H, 2.7%; *M* 197. $C_4H_5F_6NO$ requires C, 24.3; H, 2.5%; *M* 197), b.p. 96—97 °C, $\lambda_{max.}$ 2.96br (O–H str.), 3.36, 3.39, and 3.45w (C–H str.), 10.36 [C–N str. in $(CF_3)_2N$], and 14.50m μm [($CF_3$ def.); $m/e$ 197 (1, $M^+$)], 166 {62, $[(CF_3)_2N{\cdot}CH_2]^+$}, and 77 (100%, $[C_2HF_2N]^+$). N.m.r. spectra: $^1H$, τ 4.50 (1 H, s, OH), 6.50 (2 H, t, $CH_2{\cdot}O$, $J$ 3 Hz), and 6.85 (2 H, t, $CH_2{\cdot}N$); $^{19}F$, δ −18.8 p.p.m. [s, $(CF_3)_2N$].

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