

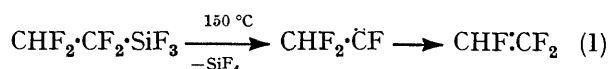
Polyfluoroalkyl Derivatives of Silicon. Part XIII.¹ Preparation and Pyrolysis of Trifluoro(halogenovinyl)silanes and (1-Fluoro-2-halogenoethyl)trihalogenosilanes

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Treatment of 1-chloro-2-fluoroethyl- or 1,2-dichloroethyl-trichlorosilane with quinoline gives trichloro(1-chlorovinyl)silane; trichloro(1,2-dibromoethyl)silane dehydrohalogenates similarly. In contrast 2-chloro-1-fluoroethyl- and 1,2-difluoroethyl-trichlorosilane give vinyl fluoride under comparable conditions. Both 1-chlorovinyl- and 1-bromovinyl-trifluorosilane, prepared from the trichlorosilyl analogues, decompose slowly at 280 °C to afford acetylene and tetrahalogenosilanes *via* the suspected intermediacy of the alkylidenecarbene $\text{CH}_2\text{:C:}$. Pyrolysis of (2-chloro-1-fluoroethyl)trifluorosilane gives vinyl chloride *via* a carbene intermediate, but the trichlorosilyl analogue yields the rearrangement compound dichloro(1,2-dichloroethyl)fluorosilane. 1,2-Difluoroethyl-trifluorosilane and -trichlorosilane both decompose *via* a non-carbene mechanism involving β elimination.

THE primary object of the present work was to determine whether alkylidenecarbenes ($\text{RR}'\text{C:C:}$) could be prepared by pyrolysis of vinylsilanes, $\text{RR}'\text{C:CX}\cdot\text{SiY}_3$ ($\text{X} = \text{Br}, \text{Cl}, \text{or F}; \text{Y} = \text{Cl or F}$). Alkylidenecarbenes have been prepared by reaction of lithium alkyls with halogenolefins²⁻⁴ and more recently by reaction of 5,5-dimethyl-3-nitroso-oxazolidin-2-one with lithium ethoxide.⁵ However, apart from the observation that the silane trichloro(1-chlorovinyl)silane decomposes at 600 °C to yield silicon tetrachloride and acetylene⁶ (possibly *via* the intermediacy of the carbene $\text{CH}_2\text{:C:}$), the use of trihalogeno-(α -halogenovinyl)silanes as precursors to alkylidene-carbenes has not been reported.

Pyrolysis of (polyhalogenoalkyl)silicon compounds is a well known method for the generation of (halogenoalkyl)carbenes,⁷⁻¹¹ *e.g.* equation (1). Trifluorosilyl com-



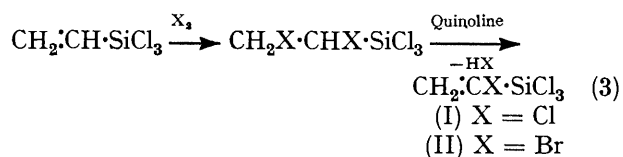
pounds are preferred to the trichlorosilyl analogues because (i) they decompose to form carbenes at a lower temperature (150 rather than *ca.* 230 °C) and (ii) they cannot rearrange by interchange between chlorine on

silicon and fluorine on the α -carbon atom of the alkyl group as occurs with trichloro(1-fluoroalkyl)silanes,¹² *e.g.* equation (2).

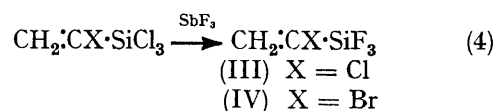


RESULTS AND DISCUSSION

Preparation of Trifluoro(α -halogenovinyl)silanes.—Trichloro(1-chlorovinyl)silane,⁶ (I), and (1-bromovinyl)trichlorosilane,¹³ (II), have both been prepared previously by the general route (3). The vinylsilanes (I) and (II)



when treated with antimony trifluoride *in vacuo* gave the corresponding trifluorosilyl compounds (III) (75%) and (IV) (78%), respectively [equation (4)].



¹ Part XII, W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, *J.C.S. Dalton*, 1974, 2305.

² B. Schlenk and W. Berman, *Annalen*, 1928, **71**, 463.

³ P. Curtin and M. Flynn, *J. Amer. Chem. Soc.*, 1959, **81**, 4714.

⁴ H. Günther and G. Bothner-By, *Chem. Ber.*, 1963, **96**, 3112.

⁵ M. S. Newman and C. D. Beard, *J. Amer. Chem. Soc.*, 1969, **91**, 5677.

⁶ L. H. Sommer, *J. Amer. Chem. Soc.*, 1954, **76**, 1618.

⁷ R. N. Haszeldine and R. J. Marklow, *J. Chem. Soc.*, 1956, 962.

⁸ D. Cooper, R. N. Haszeldine, and M. J. Newlands, *J. Chem. Soc. (A)*, 1967, 2098.

R. N. Haszeldine and J. C. Young, *Proc. Chem. Soc.*, 1959, 394.

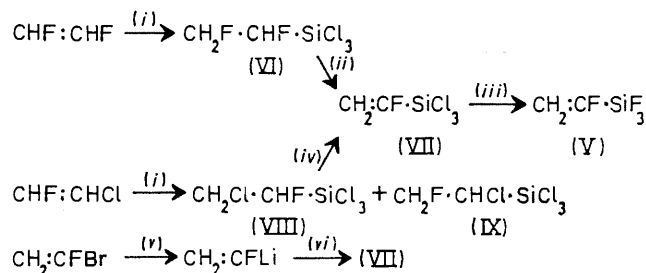
¹⁰ W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. and Ind.*, 1961, 789.

¹¹ W. I. Bevan and R. N. Haszeldine, *J.C.S. Dalton*, 1974, 2509.

¹² W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, *J. Organometallic Chem.*, 1970, **23**, C17.

¹³ C. L. Agre and W. Hilling, *J. Amer. Chem. Soc.*, 1952, **74**, 3895.

The following routes to trifluoro(1-fluorovinyl)silane, (V), were investigated (Scheme 1). Photochemical reaction of *cis*-1,2-difluoroethylene with an excess of trichlorosilane gave the expected 1:1 adduct, trichloro(1,2-difluoroethyl)silane, (VI) (85%). This adduct on treatment with quinoline at 60 °C [conditions which were



SCHEME 1 (i), HSiCl₃; (ii) -HF; (iii), SbF₃; (iv), -HCl; (v), BuⁿLi; (vi), SiCl₄.

successful for the preparation of (I) and (II)] gave unchanged silane (24%) and vinyl fluoride (43%). Attempted dehydrofluorination with sodium fluoride at 25 and 100 °C gave unchanged (VI) (85 and 40%, respectively) and low yields of mixtures of vinyl fluoride and tetrahalogenosilanes. Sodium fluoride has been used previously to dehydrofluorinate polyfluorocycloalkenes.¹⁴ The photochemical reaction of 1-chloro-2-fluoroethylene with an excess of HSiCl₃ has been reported previously⁸ and, in the present case, gave trichloro(2-chloro-1-fluoroethyl)silane, (VIII) (34%), trichloro(1-chloro-2-fluoroethyl)silane, (IX) (17%), and a mixture (7%) of the compounds 1-fluoroethyl- and 2-fluoroethyl-trichlorosilane formed by reduction of adducts (VIII) and (IX), respectively.

Reaction of adduct (IX) with quinoline gave (I) (74%), but in contrast adduct (VIII) under comparable conditions afforded unchanged (VIII) (25%) and vinyl fluoride (100%). The mode of reaction of quinoline with the various trichloro(1,2-dihalogenoethyl)silanes prepared in the present work is shown in Table 1. Thus

TABLE 1

Reaction of quinoline with trichloro(1,2-dihalogenoethyl)silanes

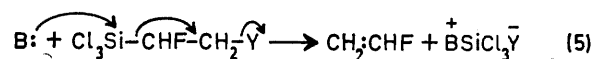
Silane	Product	Yield* (%)
CH ₂ Cl·CHCl·SiCl ₃	CH ₂ :CCl·SiCl ₃	83
CH ₂ Br·CHBr·SiCl ₃	CH ₂ :CBr·SiCl ₃	84
CH ₂ F·CHCl·SiCl ₃	CH ₂ :CCl·SiCl ₃	74
CH ₂ Cl·CHF·SiCl ₃	CH ₂ :CHF	100
CH ₂ F·CHF·SiCl ₃	CH ₂ :CHF	43

* Based on starting materials consumed, *i.e.* not recovered.

the 1,2-dihalogenoethyl compounds which contain either a CHCl or a CHBr group α to silicon dehydrohalogenate *via* attack of base at the hydrogen atom in this group to give a vinylsilane, whereas the ethylsilanes which contain

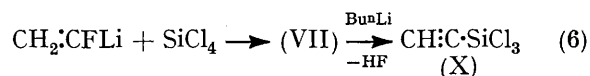
¹⁴ R. Stephens and J. C. Tatlow, unpublished work, cited in *J. Chem. Soc.*, 1965, 808.

a CHF group α to silicon react *via* nucleophilic attack at silicon to afford vinyl fluoride [equation (5)], presumably

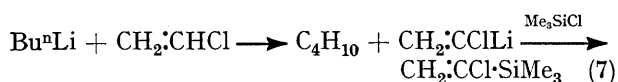


because α fluorine makes silicon more susceptible to nucleophilic attack.

The reaction of 1-bromo-1-fluoroethylene with *n*-butyl-lithium at -100 °C followed by addition of silicon tetrachloride gave *n*-butyl bromide (92%), unchanged SiCl₄ (94%), trichloroethynylsilane, (X) (5%), and a polymeric solid. The desired product (VII) was not detected, but the acetylene (X) may have arisen from it [equation (6)]. A comparable reaction using chlorotriethylsilane in place of SiCl₄ gave¹⁵ triethylethynylsilane (30%) *via* the possible intermediacy of the silane

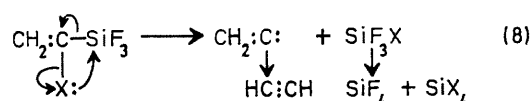


CH₂:CF·SiEt₃. The reaction between BuⁿLi, vinyl chloride, and chlorotrimethylsilane at -120 °C gives¹⁶ (1-chlorovinyl)trimethylsilane (20%) [equation (7)]. In



an attempt to prepare (1-fluorovinyl)trimethylsilane the reaction was repeated using vinyl fluoride in place of vinyl chloride; the products were unchanged olefin (92%), *n*-butyltrimethylsilane (64%), and a small amount of polymeric material.

Pyrolyses.—Compound (III) when pyrolysed *in vacuo* at 280 °C (50 h) gave unchanged (III) (65%), acetylene (97% yield), and a mixture of silicon tetrafluoride and SiCl₄. Pyrolysis of the analogue (IV) at 280 °C (40 h) gave a mixture of acetylene (*ca.* 10%) and SiF₄ and intractable tar. The formation of acetylene and tetrahalogenosilanes is readily explained by an α -elimination reaction to give the carbene CH₂:C [equation (8)], but



attempts to trap the carbene with tetramethylethylene and with trimethylsilane were unsuccessful. Although the expected cyclopropane formed between the carbene CH₂:C and the olefin may have been unstable at the high decomposition temperature required, the expected product, Me₃Si·CH:CH₂, from reaction with Me₃SiH, is stable under the reaction conditions. The failure to trap the carbene suggests that the intramolecular rearrangement to acetylene is rapid.

¹⁵ F. G. Drakesmith, O. J. Steward, and P. J. Tarrant, *J. Org. Chem.*, 1968, **33**, 472.

¹⁶ W. R. Bamford and B. C. Pant, *J. Chem. Soc. (C)*, 1967, 1470.

Pyrolyses of compounds (VI) and (VIII) and also the corresponding trifluorosilyl compounds (XI) and (XII), formed in 74 and 64% yield, respectively, by reaction of (VI) and (VIII) with antimony trifluoride, are shown in Table 2. Silane (XI) afforded only vinyl fluoride

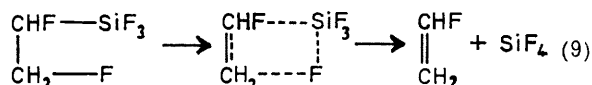
TABLE 2

Pyrolyses of silanes of the type $\text{CH}_2\text{X}\cdot\text{CHF}\cdot\text{SiY}_3$
(X and Y = Cl or F)

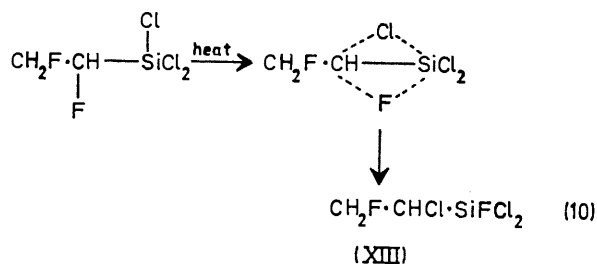
Silane	Conditions, $\theta_c/^\circ\text{C}$ (t/h)	Products	Yield (%)
$\text{CH}_2\text{F}\cdot\text{CHF}\cdot\text{SiCl}_3$ (VI)	150 (17)	$\text{CH}_2\text{:CHF}$	22
		$\text{CH}_2\text{:CHCl}$	48
		$\text{CH}_2\text{F}\cdot\text{CHCl}\cdot\text{SiFCl}_2$ (XIII)	28
$\text{CH}_2\text{F}\cdot\text{CHF}\cdot\text{SiF}_3$ (XI)	150 (15)	$\text{CH}_2\text{:CHF}$	97
$\text{CH}_2\text{Cl}\cdot\text{CHF}\cdot\text{SiCl}_3$ (VIII) *	170 (17)	$\text{CH}_2\text{:CHF}$	6
		$\text{CH}_2\text{:CHCl}$	93
		$\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{SiFCl}_2$ (XIV)	99
$\text{CH}_2\text{Cl}\cdot\text{CHF}\cdot\text{SiF}_3$ (XII)	170 (17)	$\text{CH}_2\text{:CHCl}$	99

* Present as a 9 : 1 mixture of (VIII) and $\text{CH}_2\text{F}\cdot\text{CHCl}\cdot\text{SiCl}_3$, (IX).

(97%) and SiF_4 when pyrolysed alone or in the presence of added tetramethylethylene as a carbene trap, and β elimination rather than formation of a carbene intermediate is implied [equation (9)].



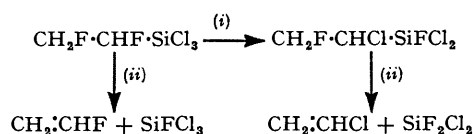
Silanes of the type $\text{CHF}_2\cdot\text{CHF}\cdot\text{SiX}_3$ (X = Cl or F) have been observed previously to decompose similarly by a β -elimination process.¹⁷ Pyrolysis of the trichlorosilyl analogue (VI) gave a mixture of tetrahalogenosilanes, vinyl fluoride, vinyl chloride, and a mixture of unchanged silane (10%) and a compound which had the same molecular weight as (VI) and contained bands in its i.r. (10.1 μm , Si-F str.) and n.m.r. (+46 p.p.m. relative to external trifluoroacetic acid) spectra as expected for a SiFCl_2 group. This compound is considered to be dichloro(1-chloro-2-fluoroethyl)fluorosilane, (XIII), formed by interchange of halogen between silicon and its α -carbon atom [equation (10)]. Such interchange has



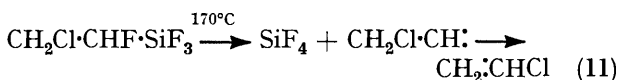
been observed¹² previously on pyrolysis of silanes of the type $\text{RCF}_2\cdot\text{SiCl}_3$ and $\text{RCFCl}\cdot\text{SiCl}_3$. The mixture of olefins

¹⁷ D. Cooper, R. N. Haszeldine, M. J. Newlands, and E. Rodger, unpublished work.

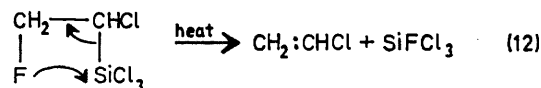
probably arises by reactions involving β elimination (Scheme 2). Trifluorosilane (XII) on pyrolysis yielded a

SCHEME 2 (i), Heat; (ii), β elimination.

mixture of SiF_4 (99%) and vinyl chloride (99%) [equation (11)], but an attempt to trap the intermediate carbene with tetramethylethylene was unsuccessful.



Pyrolysis of a mixture of the trichlorosilanes (VIII) and (IX) (9 : 1) gave the rearranged product dichloro(1,2-dichloroethyl)fluorosilane, (XIV) [93% based on (VIII); i.r. 10.32 μm (Si-F str.), ¹⁹F n.m.r. 46.0 p.p.m., cf. (XIII) bands at 10.1 μm and 46 p.p.m., respectively], vinyl chloride, SiCl_4 , and a trace amount of SiF_4 . The vinyl chloride probably arises mainly by a β elimination of fluorine from silane (IX) [equation (12)]. However, the



yield of tetrahalogenosilanes (SiF_4 and SiCl_4) was somewhat higher than calculated for decomposition of (IX) alone. This suggests that a small amount of α elimination from silane (VIII) or, more likely, β elimination from the rearranged silane (XIV), is occurring. Silane (XIV) could also decompose by α elimination, but this is most unlikely.

Thus the silanes $\text{CH}_2\text{F}\cdot\text{CHF}\cdot\text{SiX}_3$ (X = F or Cl) decompose by a β -elimination process while $\text{CH}_2\text{Cl}\cdot\text{CHF}\cdot\text{SiF}_3$ decomposes by an α -elimination process. The reason for the preferred internal nucleophilic attack on silicon by fluorine, rather than by chlorine, is probably due to the bond-energy difference, $D(\text{Si-F}) - D(\text{C-F})$ being greater than $D(\text{Si-Cl}) - D(\text{C-F})$. At present, however, it is not clear why compounds of the type $>\text{CF}\cdot\text{CHF}\cdot\text{Si}\leq$ decompose by β elimination while those of types $>\text{CF}\cdot\text{CF}_2\cdot\text{Si}\leq$ and $>\text{CF}\cdot\text{CFCl}\cdot\text{Si}\leq$ decompose by α elimination.

EXPERIMENTAL

Techniques used were as described previously.¹ Trichloro(1-chlorovinyl)silane, (I), was prepared by chlorination of trichloro(vinyl)silane (87%) followed by dehydrochlorination of the adduct with quinoline (83%).⁶ (1-Bromovinyl)trichlorosilane, (II), was prepared similarly in 76% overall yield.¹³ Spectral details for compounds marked with an asterisk are in Supplementary Publication No. SUP 21470 (6 pp.).*

* 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).

Fluorination of (I).—Silane (I) (27.3 g, 0.139 mol), passed repeatedly *in vacuo* through a column (20 cm) packed with antimony trifluoride and a small amount of antimony pentachloride (5% by weight), gave (1-chlorovinyl)trifluorosilane, (III) * (15.3 g, 0.105 mol, 75%) (Found: C, 16.4; H, 1.35%; *M* 147. $C_2H_2ClF_3Si$ requires C, 16.4; H, 1.4%; *M* 146.5), b.p. (Siwoloboff) 85.5 °C.

Pyrolysis of (I).—(a) *Alone.* Silane (I) (1.46 g, 10.0 mmol), sealed in a Pyrex ampoule (*ca.* 250 cm³) and heated at 245 °C (200 h), gave a mixture (0.08 g, 1.0 mmol, 5% decomp.) of acetylene and mixed halogenosilanes and unchanged (I) (1.37 g, 9.4 mmol, 94% recovered).

A second pyrolysis of (I) (1.46 g, 10.0 mmol) at 280 °C (50 h) gave unchanged reactant (0.96 g, 6.50 mmol, 65% recovered) and a mixture (0.50 g, 7.0 mmol) of acetylene, silicon tetrafluoride, and silicon tetrachloride (*i.r.*) and which on hydrolysis with water (5 cm³) *in vacuo* afforded acetylene (0.09 g, 3.4 mmol, 97%) (Found: *M* 26. Calc. for C_2H_2 : *M* 26).

(b) *In the presence of tetramethylethylene.* A mixture of (I) (1.21 g, 8.30 mmol) and the olefin (1.83 g, 21.8 mmol), sealed in a Pyrex ampoule (*ca.* 250 cm³) and heated at 280 °C (50 h) gave (i) a mixture (0.42 g) (Found: *M* 57. Calc. for 4 : 3 mixture of C_2H_2 and SiF_4 : *M* 59) of acetylene and SiF_4 , (ii) unchanged olefin (1.80 g, 21.4 mmol, 99% recovered) shown to be contaminated with a small amount of $SiCl_4$ (*i.r.*), and (iii) unchanged (I) (0.85 g, 5.81 mmol, 70% recovered).

(c) *In the presence of trimethylsilane.*—A mixture of (I) (1.21 g, 8.30 mmol) and trimethylsilane (1.62 g, 22.0 mmol), heated (as before) at 280 °C (100 h), gave (i) a mixture (0.49 g; Found: *M* 58) of acetylene and SiF_4 in the ratio 4 : 3, (ii) unchanged Me_3SiH (1.60 g, 21.7 mmol, 99% recovered), and (iii) unchanged (I) (0.79 g, 5.41 mmol, 65% recovered).

Fluorination of (II).—Silane (II) (5.0 g, 20.8 mmol), treated with SbF_3 (containing 5% by weight of SbF_5), gave (i) SiF_4 (*ca.* 1 mmol), (ii) (1-bromovinyl)trifluorosilane, (IV) * (1.64 g, 8.45 mmol, 78%) (Found: C, 12.5; H, 1.1%; *M* 189. $C_2H_2BrF_3Si$ requires C, 12.7; H, 1.1%; *M* 191), b.p. (Siwoloboff) 115 °C, and (iii) unchanged (II) (2.40 g, 9.95 mmol, 48% recovered).

Pyrolysis of (IV).—Silane (IV) (3.1 g, 16.3 mmol), sealed in a Pyrex ampoule (*ca.* 250 cm³) and heated at 280 °C (40 h), gave a mixture (0.31 g) of acetylene and SiF_4 and a thick black tar which was not further investigated. At 220 °C pyrolysis of (IV) gave only unchanged material (99%).

Reaction of Trichlorosilane with cis-1,2-Difluoroethylene.—A mixture of trichlorosilane (27.0 g, 0.198 mol) and the olefin (3.2 g, 50.0 mmol), sealed in a silica tube (*ca.* 250 cm³) and irradiated at a distance of 15 cm from a Hanovia S500 u.v. lamp (70 h), gave (i) unchanged olefin (0.76 g, 10.8 mmol, 22% recovered), (ii) unchanged $HSiCl_3$ (21.8 g, 0.161 mol, 82% recovered), and (iii) trichloro(1,2-difluoroethyl)silane, (VI) * (6.6 g, 33.0 mmol, 85%) (Found: C, 12.2; H, 1.6%; *M* 199. $C_2H_3Cl_3F_2Si$ requires C, 12.0; H, 1.5%; *M* 199.5), b.p. (Siwoloboff) 122—123 °C.

Reactions of (VI).—(a) *Pyrolysis.* Silane (VI) (2.0 g, 10.0 mmol), sealed in a Pyrex ampoule (*ca.* 250 cm³) and heated at 150 °C (17 h), gave (i) a mixture (1.22 g) of vinyl chloride, vinyl fluoride, and mixed halogenosilanes which, after hydrolysis with aqueous sodium hydroxide (10% w/v, 10 cm³) *in vacuo*, gave a mixture (0.36 g, 6.3 mmol; *M* 59) of vinyl chloride (0.27 g, 4.3 mmol, 48%) and vinyl fluoride (0.08 g, 2.0 mmol, 22%), and (ii) a mixture (0.70 g, 3.5 mmol,

35%) (Found: *M* 202. Calc. for $C_2H_3Cl_3F_2Si$: *M* 199.5) which was shown by *i.r.* spectroscopy and g.l.c. (4m Silicone MS550 oil at 130 °C) to contain unchanged (VI) (0.20 g, 1.0 mmol, 10% recovered) and dichloro(1-chloro-2-fluoroethyl)fluorosilane, (XIII) * (0.50 g, 2.5 mmol, 28%).

(b) *Attempted dehydrofluorination.* A mixture of (VI) (8.0 g, 40.0 mmol) and quinoline (6.5 g, 50.8 mmol) was slowly warmed from 0 to 60 °C under nitrogen and the volatile products collected in traps cooled to -78 and -130 °C; a thick black tar was also formed which was not investigated further. The products were vinyl fluoride (0.6 g, 13.0 mmol, 43%) and unchanged (VI) (1.9 g, 9.5 mmol, 24%). Reaction of (VI) with excess of dry sodium fluoride at 25 °C gave unchanged silane (85%) and a mixture of tetrahalogenosilanes (*ca.* 20%) contaminated with a trace of vinyl fluoride (*i.r.*), while reaction at 100 °C gave unchanged silane (40%) and a complex mixture of tetrahalogenosilanes and vinyl fluoride.

(c) *Fluorination.* Silane (VI) (5.0 g, 25.0 mmol), passed repeatedly *in vacuo* through a column (25 cm) packed with SbF_3 and a small amount of SbF_5 (5% by weight), gave (i) a mixture (0.20 g, 4%) of vinyl fluoride and SiF_4 , (ii) unchanged silane (1.20 g, 6.0 mmol, 24% recovered), and (iii) (1,2-difluoroethyl)trifluorosilane, (XI) * (2.1 g, 14.1 mmol, 74%) (Found: C, 15.9; H, 2.0%; *M* 148. $C_2H_3F_5Si$ requires C, 16.0; H, 2.0%; *M* 149), b.p. (Siwoloboff) 54 °C.

Pyrolysis of (XI).—(a) *Alone.* Silane (XI) (1.0 g, 6.7 mmol), sealed in a Pyrex ampoule (*ca.* 250 cm³) and heated at 150 °C (15 h), gave a 1 : 1 mixture (0.97 g, 13.2 mmol, 97%) (Found: *M* 75. Calc. for 1 : 1 mixture of C_2H_3F and SiF_4 : *M* 75) of vinyl fluoride and SiF_4 and also a trace amount of unchanged reactant.

(b) *In the presence of tetramethylethylene.* A mixture of the olefin (2.80 g, 33.2 mmol) and (XI) (1.0 g, 6.7 mmol), pyrolysed as in the previous experiment (17 h), gave a mixture (0.97 g, 13.0 mmol, 97%) of SiF_4 and vinyl fluoride, and unchanged olefin (2.77 g, 33.1 mmol, 99% recovered).

Reaction of $HSiCl_3$ with 1-Chloro-2-fluoroethylene.—A mixture of $HSiCl_3$ (135.5 g, 1.0 mol) and the olefin (15.5 g, 0.192 mol), sealed in a silica ampoule (*ca.* 250 cm³) and irradiated (as before) (100 h), gave, on distillation through a column (30 cm), (i) unchanged $HSiCl_3$ (109 g, 0.81 mol, 81% recovered), b.p. 32—33 °C, (ii) $SiCl_4$ (1.70 g, 10.0 mmol, 5%), b.p. 60—65 °C, (iii) a mixture (1.67 g, 9.2 mmol, 5%), b.p. 100—130 °C, shown by *i.r.* spectroscopy and g.l.c. (2 m Silicone column at 95 °C) to contain trichloro(1-fluoroethyl)silane (0.90 g, 5.0 mmol, 3%) and trichloro(2-fluoroethyl)silane (0.77 g, 4.2 mmol, 2%), (iv) a mixture (21.1 g, 97.5 mmol, 51%), b.p. 145—150 °C, shown by *i.r.* spectroscopy and g.l.c. (4 m Silicone column at 110 °C) to consist of trichloro(1-chloro-2-fluoroethyl)silane, (IX) (6.97 g, 32.1 mmol, 17%) and trichloro(2-chloro-1-fluoroethyl)silane, (VIII) (14.2 g, 65.4 mmol, 34%), present in the ratio 33 : 67, and (v) a residue (*ca.* 10 g), b.p. >200 °C.

Fractional distillation of the mixture of the trichloro-(chlorofluoroethyl)silanes at atmospheric pressure through a spinning-band column gave (i) a mixture (7.1 g, 32.8 mmol, 17%), b.p. 148—149 °C, shown by g.l.c. (4 m Silicone column at 110 °C) to consist of (VIII) and (IX) in the ratio 8 : 92 and (ii) a mixture (13.4 g, 62.0 mmol, 32%), b.p. 151—152 °C, shown by g.l.c. (as before) to consist of (VIII) and (IX) in the ratio 9 : 1 and which, on refractionation through the spinning-band column, gave (VIII) (*ca.* 10 g),

b.p. 152 °C, as shown by g.l.c. and by comparison of its i.r. and n.m.r. spectra with those obtained previously.⁸

Reaction of (VIII) with Quinoline.—A mixture (6.0 g, 27.8 mmol) of (VIII) (5.4 g, 25.0 mmol) and (IX) (0.6 g, 2.8 mmol) present in the ratio 9:1 was added dropwise (30 min) to quinoline (4.0 g, 30.0 mmol) kept at 0 °C. The reaction mixture was heated to 50 °C *in vacuo* and the volatile products were identified as a mixture of unchanged reactant silanes (1.4 g, 6.5 mmol, 23% recovered), shown by i.r. spectroscopy to be contaminated with a trace amount of (I) and vinyl fluoride (0.98 g, 21.3 mmol, 100%) contaminated with a trace of vinyl chloride (i.r.).

Reaction of (IX) with Quinoline.—A mixture (6.0 g, 27.8 mmol) of (IX) (5.52 g, 25.6 mmol) and (VIII) (0.48 g, 2.2 mmol), present in the ratio 23:2, was added dropwise (30 min) to quinoline (4.0 g, 30.0 mmol) at room temperature. The reaction mixture was gently warmed *in vacuo* until an exothermic reaction started and the volatile products were collected and identified as vinyl fluoride (trace) and (I) (4.0 g, 20.4 mmol, 74%).

Reactions of (VIII).—(a) **Pyrolysis.** A mixture (1.01 g, 4.65 mmol) of (VIII) (0.90 g, 4.15 mmol) and (IX) (0.11 g, 0.5 mmol), present in the ratio 9:1, when sealed in a Pyrex ampoule (*ca.* 100 cm³) and heated at 170 °C (17 h), gave (i) vinyl chloride (0.03 g, 0.48 mmol, 6%) contaminated with a trace of SiF₄ (i.r.), (ii) SiCl₄ (0.09 g, 0.53 mmol), and (iii) dichloro(1,2-dichloroethyl)fluorosilane, (XIV) * (0.84 g, 3.90 mmol, 93%) (Found: C, 11.1; H, 0.9%; *M* 219. C₂H₃Cl₄-FSi requires C, 11.2; H, 1.4%; *M* 216), b.p. (Siwoloboff) 138 °C.

(b) **Fluorination.** Compound (VIII) (10.0 g, 46.4 mmol), added dropwise to a mixture of SbF₃ and SbF₅ (*ca.* 5% by weight) at a pressure of *ca.* 2 cmHg, gave a mixture (trace) of SiF₄ and vinyl chloride and (2-chloro-1-fluoroethyl)-trifluorosilane, (XII) * (4.95 g, 29.6 mmol, 64%) (Found: C, 14.2; H, 1.9%; *M* 168. C₂H₃ClF₃Si requires C, 14.45; H, 1.8%; *M* 166.5), b.p. (Siwoloboff) 74 °C.

Pyrolysis of (XII).—(a) **Alone.** Silane (XII) (0.85 g, 5.1 mmol), sealed in a Pyrex ampoule (*ca.* 250 cm³) and heated at 170 °C (17 h), gave an equimolar mixture (0.84 g, 10.1 mmol, 99%) (Found: *M* 84. Calc. for 1:1 mixture of C₂H₃Cl and SiF₄: *M* 83) of vinyl chloride and SiF₄.

(b) **With tetramethylethylene.** A mixture of (XII) (0.92 g, 5.50 mmol) and the olefin (2.8 g, 33.2 mmol), sealed in a Pyrex ampoule (*ca.* 250 cm³) and heated at 170 °C (17 h), gave (i) unchanged olefin (2.75 g, 32.8 mmol, 98.5% recovered), (ii) a mixture (0.90 g, 10.8 mmol, 98%) of SiF₄ and vinyl fluoride, and (iii) a small amount (*ca.* 0.05 g) of higher-boiling material which contained a high proportion of C-H bonds (i.r.).

Reaction of n-Butyl-lithium with Vinyl Fluoride in the Presence of Chlorotrimethylsilane.—A solution of n-butyl-lithium (7.26 g, 0.11 mol) in dry diethyl ether (90 cm³) at -78 °C was added dropwise (4 h) to a stirred mixture of chlorotrimethylsilane (14.7 g, 0.135 mol) and vinyl fluoride (5.12 g, 0.150 mol) maintained at -120 °C and the mixture further stirred (2 h) and then allowed to warm to room temperature. This gave unchanged vinyl fluoride (4.74 g, 0.103 mol, 92%) as the only volatile product. The reaction mixture was hydrolysed with water (25 cm³), filtered, and the solution extracted with diethyl ether (2 × 25 cm³), dried (Mg[SO₄]), and distilled to afford n-butyltrimethylsilane (9.10 g, 70.0 mmol, 64%), b.p. 93 °C. A polymeric solid (0.3 g) was also formed in the reaction.

Reaction of 1-Bromo-1-fluoroethylene with SiCl₄ in the Presence of n-Butyl-lithium.—A mixture of the olefin (6.1 g, 50.0 mmol) and diethyl ether (70 cm³) was stirred at -100 °C under nitrogen and a solution of n-butyl-lithium (3.2 g, 50.0 mmol) in a mixture of diethyl ether (15 cm³) and pentane (15 cm³), cooled to -78 °C, was added dropwise (1 h). Then a solution of SiCl₄ (42.5 g, 0.25 mol) in diethyl ether (30 cm³) at -78 °C was added (10 min). Filtration of the product mixture followed by fractional distillation gave (i) a mixture of pentane and diethyl ether (*ca.* 125 cm³) b.p. 33–36 °C, (ii) SiCl₄ (39.9 g, 0.234 mol, 94% recovered), b.p. 51–54 °C, (iii) trichloroethynylsilane (0.4 g, 2.5 mmol, 5%), b.p. 69 °C (lit.,¹⁸ 73 °C), and (iv) n-butyl bromide (6.3 g, 46.0 mmol, 92%), b.p. 97 °C. A polymeric solid (*ca.* 5 g) was also obtained.

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¹⁸ E. A. Chernyshev and G. F. Pavelko, *Izvest. Akad. Nauk S.S.S.R. Otdel. khim. Nauk*, 1966, 2205.