Kinetics of the Reactions of Silicon Compounds. Part 11.[1] Kinetics and Mechanism of the Gas-phase Photochemical Reactions between Trimethylsilane and 1,1-Difluoroethylene

Stuart A. Barker, Robert N. Haszeldine, and Peter J. Robinson*
Department of Chemistry, UMIST, Manchester M60 1QD

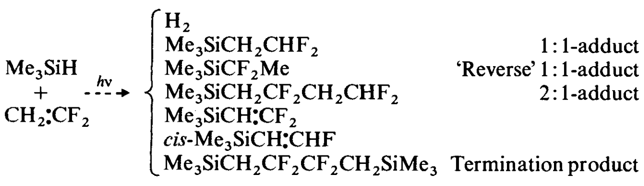
The mercury-photosensitised photolysis of gas-phase mixtures of trimethylsilane and 1,1-difluoroethylene has been studied at 30—80 °C, with reactant ratios from 1:1 to 12:1 and total pressures of 100—600 mmHg, in some cases with added inert gas present. The reaction yields hydrogen (from initiation), the 'normal' and 'reverse' 1:1-adducts (but not in good preparative yield), and the 2:1-adduct, but also two vinyltrimethylsilanes in substantial proportions during the early part of the reaction. A free-radical mechanism is presented, steady-state treatment of which is consistent with the observed quantum yields and kinetic behaviour. The effect of inert gas (CF_4) indicates that the deactivation of excited radicals plays a significant role in determining the product distribution.

The reaction of silanes with alkenes is a well-established route for the synthesis of alkylsilicon compounds. Such addition reactions proceed by free-radical chain mechanisms, which may be initiated by peroxide or transition metal catalysts or photochemically by ultraviolet irradiation.[2] The photochemical reactions have potential advantages in terms of product purity and control of product distribution, and have been extensively studied as synthetic routes. These studies have revealed some curious aspects worthy of mechanistic investigation; for example, irradiation of mixtures of ($Me_3SiH–C_2F_4$), ($Cl_3SiH–C_2F_4$), ($Cl_3SiH–CH_2{:}CF_2$), or ($Cl_3SiH–CF_3CH{:}CH_2$) with a mercury resonance lamp gives good yields of the 1:1-adducts (*e.g.* $CF_3CH_2CH_2SiCl_3$, precursor of the important Silastic rubber), whereas irradiation of ($Cl_3SiH–CF_2{:}CCl_2$) or ($Me_3SiH–CH_2{:}CF_2$) mixtures result in extremely slow reactions and very little of the desired 1:1-adducts.[2–5]

In a previous paper[3] we reported a kinetic study of the 'successful' photochemical reaction of trimethylsilane with tetrafluoroethylene; we now report a corresponding study of the mercury-photosensitised photolysis of trimethylsilane and 1,1-difluoroethylene, which fails to produce good yields of a 1:1-adduct.

Results and Discussion

When trimethylsilane and 1,1-difluoroethylene, containing mercury vapour at its saturated vapour pressure, were irradiated for short periods of time such that the conversion of reactants was less than 1%, the main products shown in Scheme 1 were identified. Typical product formation curves are shown in Figure 1, although the relative proportions of products varied considerably with reaction conditions. It was also shown that the products did not include fluoroethylene, fluoroacetylene, 1,1-difluoroethane, fluorotrimethylsilane, or *trans*-2-fluorovinyltrimethylsilane, and only a trace of hexamethyldisilane was detected.



$$\begin{array}{l} Me_3SiH \\ + \\ CH_2{:}CF_2 \end{array} \xrightarrow{h\nu} \left\{ \begin{array}{ll} H_2 & \\ Me_3SiCH_2CHF_2 & 1{:}1\text{-adduct} \\ Me_3SiCF_2Me & \text{'Reverse' } 1{:}1\text{-adduct} \\ Me_3SiCH_2CF_2CH_2CHF_2 & 2{:}1\text{-adduct} \\ Me_3SiCH{:}CF_2 & \\ cis\text{-}Me_3SiCH{:}CHF & \\ Me_3SiCH_2CF_2CF_2CH_2SiMe_3 & \text{Termination product} \end{array} \right.$$

Scheme 1.

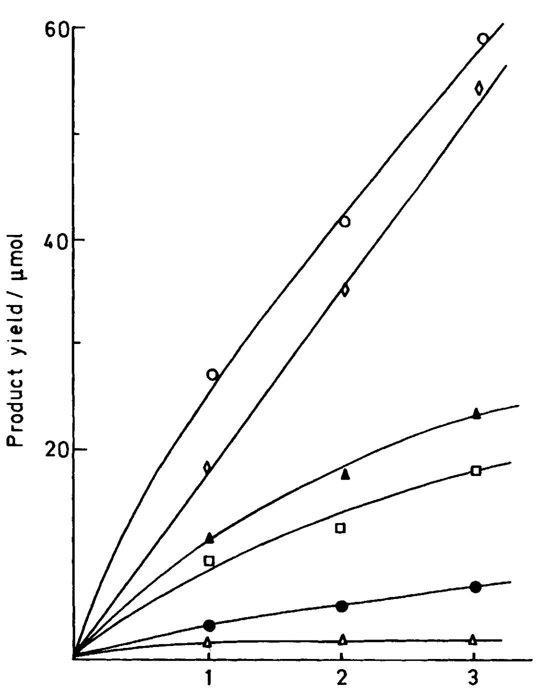


Figure 1. Product formation from trimethylsilane (300 mmHg) and 1,1-difluoroethylene (100 mmHg) absorbing 50 µmol/h of 254 nm radiation at 30 °C: ◇ hydrogen; ○ 1:1-adduct; ● reverse 1:1-adduct; □ 2:1-adduct; △ *cis*-2-fluorovinyltrimethylsilane; ▲ 2,2-difluorovinyltrimethylsilane

When these reaction mixtures were irradiated for longer periods of time, such that most of the reactants were converted into products, then only small amounts (*ca.* 1% of products) of the two vinylsilanes were detected. It thus appears that the vinylsilanes undergo secondary reactions to produce involatile materials which were not detected.

Mechanistic studies were therefore confined to the early stages of the reaction, and quantum yields were determined from the product yields after a standard irradiation time of two hours to give about 1% conversion of reactants to products. During these early stages the yield of hydrogen was linear with time,

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* Department of Chemistry, Manchester Polytechnic, Manchester M1 5GD.

$$\left.\begin{array}{r}\mathrm{Hg6(^1S_0)} + h\nu(254\ \mathrm{nm}) \dashrightarrow \mathrm{Hg6(^3P_1)}\\ \mathrm{Hg6(^3P_1)} + \mathrm{Me_3SiH} \dashrightarrow \mathrm{Hg6(^1S_0)} + \mathrm{Me_3Si^{\bullet}} + \mathrm{H^{\bullet}}\\ \mathrm{H^{\bullet}} + \mathrm{Me_3SiH} \dashrightarrow \mathrm{Me_3Si^{\bullet}} + \mathrm{H_2}\end{array}\right\}\text{Initiation}\qquad\begin{array}{r}(1)\\(2)\\(3)\end{array}$$

$$\left.\begin{array}{r}\mathrm{Me_3Si^{\bullet}} + \mathrm{CH_2{:}CF_2} \dashrightarrow \mathrm{Me_3SiCH_2CF_2^{\bullet}}\\ \mathrm{Me_3SiCH_2CF_2^{\bullet}} + \mathrm{Me_3SiH} \dashrightarrow \mathrm{Me_3SiCH_2CHF_2} + \mathrm{Me_3Si^{\bullet}}\end{array}\right\}\text{Propagation (1:1-adduct)}\qquad\begin{array}{r}(4)\\(5)\end{array}$$

$$\left.\begin{array}{r}\mathrm{Me_3SiCH_2CF_2^{\bullet}} + \mathrm{CH_2{:}CF_2} \dashrightarrow \mathrm{Me_3Si(CH_2CF_2)_2^{\bullet}}\\ \mathrm{Me_3Si(CH_2CF_2)_2^{\bullet}} + \mathrm{Me_3SiH} \dashrightarrow \mathrm{Me_3Si(CH_2CF_2)_2H} + \mathrm{Me_3Si^{\bullet}}\end{array}\right\}\text{Propagation (1:2-adduct)}\qquad\begin{array}{r}(6)\\(7)\end{array}$$

$$\left.\begin{array}{r}\mathrm{2Me_3SiCH_2CF_2^{\bullet}} \dashrightarrow \mathrm{Me_3SiCH_2CF_2CF_2CH_2SiMe_3}\\ \mathrm{2Me_3SiCH_2CF_2^{\bullet}} \dashrightarrow \mathrm{Me_3SiCH{:}CF_2} + \mathrm{Me_3SiCH_2CHF_2}\end{array}\right\}\text{Termination}\qquad\begin{array}{r}(8)\\(9)\end{array}$$

Scheme 2.

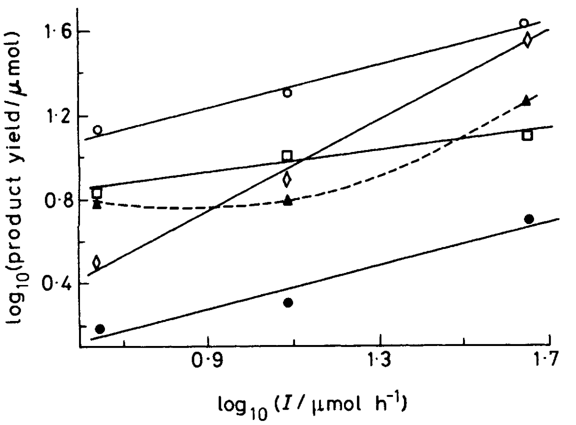

Figure 2. Plots to determine product orders with respect to light absorbed for 300 mmHg trimethylsilane and 100 mmHg 1,1-difluoroethylene irradiated for 2 h at 30 °C: key as Figure 1

but for other materials the rates of production were already decreasing slightly with time (Figure 1). The mechanism shown in Scheme 2 is proposed to account for the results, as discussed in the following paragraphs. The two 1:1 adducts are assumed to be kinetically indistinguishable and are treated as one product except where indicated otherwise.

The formation of hydrogen was found to be linearly dependent on the light intensity $I^{1.0}$ (*e.g.* Figure 2), and increasing the temperature (Figure 3) had little or no effect on the production of hydrogen. This confirms the prediction from known quenching cross-sections[6,7] that initiation by reactions (1)—(3) should be predominant in these systems. The formation of each of the 1:1-adducts was dependent on $I^{0.5}$ and that of the 1:2-adduct on $I^{0.2}$ (Figure 2), and increasing the temperature (Figure 3) raised the yields of these adducts markedly. These observations confirm the reasonable hypothesis that the 1:1- and 2:1-adducts are formed in the chain propagation steps (4)—(7).

From the minimal production of hexamethyldisilane compared with the 'termination products' shown in Scheme 1 it is evident that reaction (4) is faster than reaction (5), and therefore termination proceeds predominantly *via* the larger 1,1-difluoro-2-trimethylsilylethyl radicals. These may presumably combine (8) or disproportionate (9), thus accounting also for the formation of the difluorovinyl compound in (9). A rough estimate for the disproportionation to combination ratio of the radical $\mathrm{Me_3SiCH_2CF_2^{\bullet}}$ can be obtained from the function $\Phi(\mathrm{Me_3SiCH{:}CF_2})/\Phi(\mathrm{H_2}) - \Phi(\mathrm{Me_3SiCH{:}CF_2})$, where Φ is

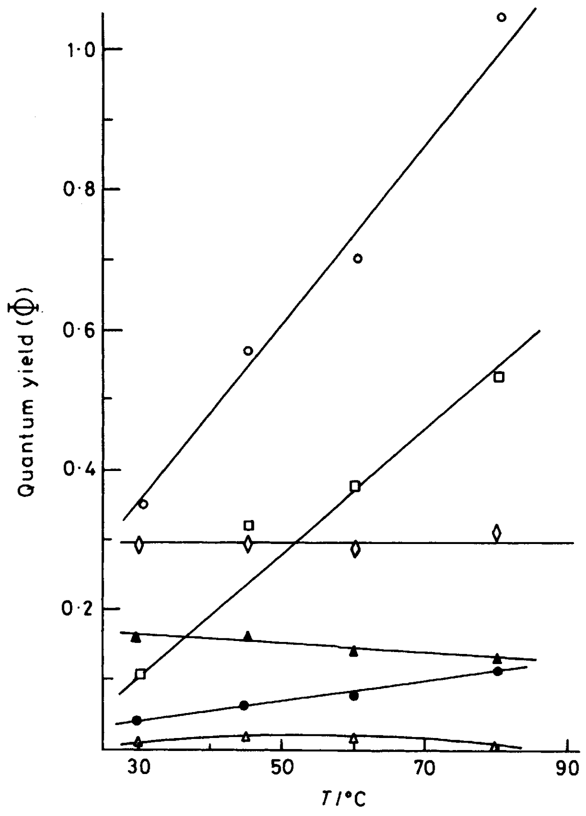

Figure 3. Effect of temperature on product quantum yields from 300 mmHg trimethylsilane and 100 mmHg 1,1-difluoroethylene absorbing 80 μmol of 254 nm radiation over 2 h at 30 °C: key as in Figure 1

quantum yield, and had a value of the order of one. Cross combination of trimethylsilyl and 1,1-difluoro-2-trimethylsilylethyl radicals [reaction (10)] does not seem to occur significantly since (*a*) none of the combination product was detected, and (*b*) its likely decomposition product fluorotrimethylsilane [predicted from reaction (11)][8] was not detected. These arguments presumably also exclude cross disproportionation. Although reactions (10)—(12) could have accounted for the formation of the fluorovinylsilane, another source for this product is evidently needed, and will be discussed later.

$$\mathrm{Me_3SiCH_2CF_2^{\bullet}} + \mathrm{Me_3Si^{\bullet}} \dashrightarrow \mathrm{Me_3SiCH_2CF_2SiMe_3} \qquad (10)$$

$$\mathrm{Me_3SiCH_2CF_2SiMe_3} \dashrightarrow \mathrm{Me_3SiF} + \mathrm{Me_3SiCH_2CF{:}} \quad (11)$$

$$\mathrm{Me_3SiCH_2CF{:}} \dashrightarrow \mathrm{Me_3SiCH{:}CHF} \quad (12)$$

Steady-state treatment of the mechanism shown in Scheme 2 leads to equations (13)—(14) for the formation of the major

$$\frac{\mathrm{d[Me_3SiCH_2CHF_2]}}{\mathrm{d}t} = k_5[\mathrm{Me_3SiH}][2\Phi I/(k_8 + k_9)]^{0.5} + k_9\Phi I/(k_8 + k_9) \quad (13)$$

$$\frac{\mathrm{d[Me_3SiCH_2CF_2CH_2CHF_2]}}{\mathrm{d}t} = k_6[\mathrm{CH_2{:}CF_2}][\Phi I/(k_8 + k_9)]^{0.5} \quad (14)$$

adducts, where Φ is the quantum yield for initiation and I is the number of quanta absorbed per unit time. These are semi-quantitatively consistent with the observed dependence of quantum yields on temperature, light intensity, and reactant composition.

The apparent dependence of 2:1-adduct formation on $I^{0.2}$ rather than $I^{0.5}$ may be due to experimental difficulties, or may be a real effect due to the occurrence of significant termination by reaction (15).

$$\mathrm{Me_3Si(CH_2CF_2)_2^{\cdot}} + \mathrm{Me_3SiCH_2CF_2^{\cdot}} \dashrightarrow \mathrm{Me_3Si(CH_2CF_2)_2CF_2CH_2SiMe_3} \quad (15)$$

Although quenching of the $\mathrm{Hg6(^3P_1)}$ will be predominantly by trimethylsilane [reaction (2)], quenching by difluoroethylene will also be significant,[9] and can account for the formation of 2-fluorovinyltrimethylsilane by reactions (16)—(18). The HF produced in (16) would be expected to give $\mathrm{SiF_4}$ on reaction with glass. However, $\mathrm{SiF_4}$ was not found (i.r. or g.l.c.), and the HF must be reacting in some other way; exclusive formation of the *cis*-isomer is another puzzling feature.

$$\mathrm{Hg6(^3P_1)} + \mathrm{CH_2{:}CF_2} \dashrightarrow \mathrm{Hg6(^1S_0)} + \mathrm{CH{\equiv}CF} + \mathrm{HF} \quad (16)$$

$$\mathrm{Me_3Si^{\cdot}} + \mathrm{CH{\equiv}CF} \dashrightarrow \mathrm{MeSiCH{:}CF^{\cdot}} \quad (17)$$

$$\mathrm{Me_3SiCH{:}CF^{\cdot}} + \mathrm{Me_3SiH} \dashrightarrow \mathrm{Me_3SiCH{:}CHF} + \mathrm{Me_3Si^{\cdot}} \quad (18)$$

The effect of inert gas pressure ($\mathrm{CF_4}$) on the quantum yields is shown in Figure 4. Quenching by $\mathrm{CF_4}$ is insignificant,[7] and the main effect of inert gas is thought to be the deactivation of excited radicals [$\mathrm{Me_3SiCH_2CF_2^{\cdot}}$, $\mathrm{Me_3Si(CH_2CF_2)_2^{\cdot}}$, *etc.*]. Such deactivation will promote addition to the alkene at the expense of hydrogen abstraction (which has the higher activation energy). The effect is therefore to increase the yield of 2:1-adducts and higher products [from reaction (19) *etc.*], at the expense of the 1:1-adducts and the termination products from the 1:1 radicals. Similar effects were observed in the system studied in Part 6.[3]

$$\mathrm{Me_3Si(CH_2CF_2)_2^{\cdot}} + \mathrm{CH_2{:}CF_2} \dashrightarrow \mathrm{Me_3Si(CH_2CF_2)_2CH_2CF_2^{\cdot}} \quad (19)$$

A point of interest in this reaction is the formation of 'reverse 1:1-adduct' ($\mathrm{Me_3SiCF_2Me}$). Quantitative measurements were difficult, but the ratio of normal to reverse 1:1-adduct appeared to change little under the conditions studied, being about 9:1, similar to that found in other additions to 1,1–difluoroethylene.

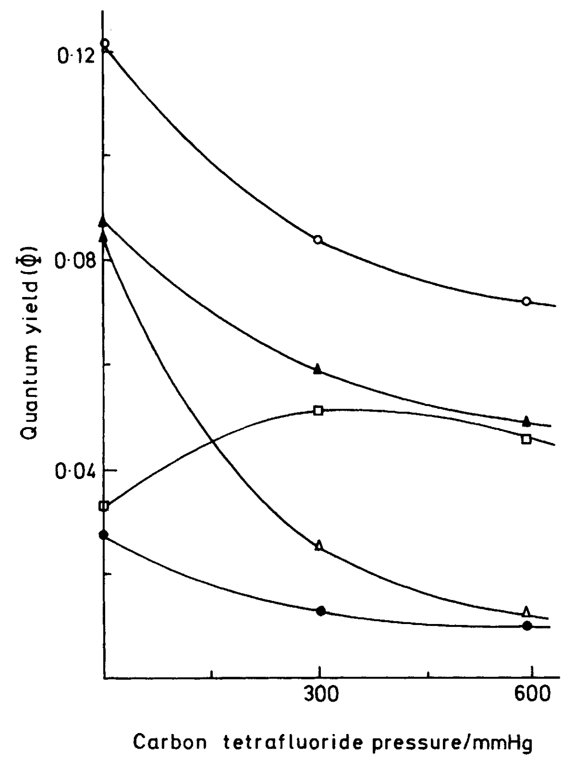

Figure 4. Effect of inert gas ($\mathrm{CF_4}$) on product quantum yields for 50 mmHg trimethylsilane and 50 mmHg of 1,1-difluoroethylene absorbing 80 μmol of 254 nm radiation over 2 h at 30 °C: key as in Figure 1

This study has not revealed any features of the system which are qualitatively different from those of the trimethylsilane–tetrafluoroethylene system studied previously.[3] Although the latter is an efficient preparative reaction, the chain lengths were not high (1—25), and it appears that the inefficiency of the present reaction is attributable merely to a marginally unfavourable balance of various chain steps rather than to any major difference between the two systems. These investigations provide a rational basis for planning photochemical preparations of alkylsilanes. For example, the production of 1:1-adducts is favoured by high silane:alkene ratios at relatively low total pressures and light intensities, but at an elevated temperature.

Experimental

Irradiation of gaseous reactants was carried out in a quartz cell by a low-pressure mercury lamp in an apparatus similar to that described previously.[3] Actinometry was by measurement of mercury-sensitised formation of hydrogen from propane, and variation of light intensity was effected by neutral density filters (Barr and Stroud) whose transmission factors had been measured by spectrophotometry. Hydrogen was separated from the other materials by passing through a U-tube at −196 °C onto activated charcoal at −196 °C, and was then determined by pressure measurement using a spiral gauge. The condensable products were transferred to a sampling bulb and injected by gas syringe into a Pye 104 dual-column flame-ionisation chromatograph. The main products were analysed on a 1 m glass column packed with 10% MS 550 silicone oil and 2.5% polyethylene glycol on silanised Celite at 40 °C and 70 °C; a 40 cm column of silica gel at various temperatures was also used to check for more volatile products. The chromatograph was periodically calibrated for the reaction products using various pressures of these materials in a sampling bulb. Long-chain termination products were not analysed quantitatively because of their low volatility.

Materials.—Trimethylsilane, prepared by lithium aluminium hydride reduction of chlorotrimethylsilane, and 1,1-difluoroethylene (Matheson) were purified by fractional condensation. Carbon tetrafluoride (B.D.H.), 1,1-difluoroethane (Matheson), fluoroethylene (Pennsalt), and propane (Matheson) were thoroughly degassed prior to use. Fluorotrimethylsilane was prepared by passing chlorotrimethylsilane in the vapour phase through a tube containing antimony trifluoride. Silicon tetrafluoride was prepared by heating barium hexafluorosilicate in a silica tube at 500—600 °C and condensing the gas evolved in a trap at −196 °C. All the above materials were shown to be pure by i.r. and g.l.c. Fluoroacetylene was produced (along with tetrafluorosilane) by irradiation of 1,1-difluoroethylene (150 mmHg) in a 200 cm^3 silica cell for 4 h with a low-pressure resonance lamp.

Main reaction products were generated by irradiation of mixtures of trimethylsilane (300 mmHg) and 1,1-difluoroethylene (100 mmHg) in a 200 cm^3 silica cell for 10 h with a lower-pressure mercury resonance lamp. The products from several of these runs were separated by fractional condensation and characterised as follows.

2,2-*Difluoroethyltrimethylsilane* ($CHF_2CH_2SiMe_3$).—The 1:1-adduct isolated by fractional condensation from the above products had vapour pressure 45 mmHg at 25 °C. Found: C, 43.4; H, 8.9; *M*, 138. $C_5H_{12}F_2Si$ requires C, 43.4; H, 8.8%; *M*, 138. The material was shown by g.l.c. and n.m.r. to contain *ca.* 10% of the isomer 1,1-difluoroethyltrimethylsilane (see below). N.m.r. (chemical shift relative to external benzene or trifluoroacetic acid, intensity, band structure, assignment, and coupling constant moduli/Hz quoted): δ_H 1.64 (1 H, tt, CHF_2), 6.32 (2 H, td, CH_2), and 7.46 (9 H, s, $SiMe_3$); δ_F 24.5 [dt, CHF_2, $J(H_\beta F_\beta)$ 58, $J(H_\alpha F_\beta)$ 21, and $J(H_\alpha H_\beta)$ 5 Hz]. The n.m.r. abosrptions arising from the $SiCH_2CHF_2$ grouping were in close agreement with the comparable absorptions in other compounds contained in this group, *e.g.* ref. 4. The i.r. spectrum showed the following main bands (optical density per mmHg pressure in a 10 cm^3 gas cell >0.1 vs; 0.03—0.1 s; 0.003—0.03 m; <0.003, w): 3 000s, 2 920m, 1 430m, 1 390m, 1 260s, 1 210s, 1 110s, 1 080s, 1 050vs, 1 005m, 975s, 905m, 850vs, 760m, and 705m. The mass spectrum showed peaks at *m*/*z* (assignments and relative abundances in parentheses): 43 ($MeSi^+$, 10.6%), 45 ($MeSiH_2^+$, 13.6), 47 (SiF^+, 20.0), 49 (SiH_2F^+, 20.9), 63 ($MeSiHF^+$, 8.5), 73 (Me_3Si^+, 48.5), 77 (Me_2SiF^+, 100), 81 ($MeSiF_2^+$, 15.5), 92 (Me_3SiF^+, 2.1), 97 ($Me_2SiH_2F_2^+$, 4.2), and 103 ($Me_2SiC_2H_2F^+$, 1.5).

1,1-*Difluoroethyltrimethylsilane* ($CH_3CF_2SiMe_3$). The reverse 1:1-adduct was isolated in 60% purity (containing 40% of 2,2-difluoroethyltrimethylsilane) from the previous material by preparative g.l.c. using a 2 m glass column packed with 10% MS 550 silicone oil and 2.5% polyethylene glycol on silanised Celite at 30 °C. δ_H 6.07 (t, Me) and 7.42 (s, $SiMe_3$); δ_F 27.8 [q, CF_2, $J(H_\beta F_\alpha)$ 24 Hz]; *m*/*z* 43 ($MeSi^+$, 8.5%), 45 ($MeSiH_2^+$, 20.9), 47 (SiF^+, 7.9), 49 (SiH_2F^+, 8.2), 63 ($MeSiHF^+$, 3.3), 73 (Me_3Si^+, 100), 77 (Me_2SiF^+, 57.0), and 81 ($MeSiF_2^+$, 26.4).

2,2,4,4-*Tetrafluorobutyltrimethylsilane* ($Me_3SiCH_2CF_2CH_2$-CHF_2). The 2:1-adduct isolated by fractional condensation of the reaction products had a vapour pressure of 5 mmHg at 25 °C. δ_H 1.46 (1 H, tt, CHF_2), 5.04 (2 H, quin. d, γ-CH_2), 6.08 (2 H, t, α-CH_2), and 7.33, (9 H, s, $SiMe_3$); δ_F 4.6 (quin. t, β-CH_2) and 36.4 [dt, CHF_2, $J(H_\delta F_\delta)$ 55, $J(H_\delta H_\gamma)$ 5, $J(H_\alpha H_\beta)$ 22, and $J(F_\beta H_\gamma)$, 16 Hz].

1,4-*Bis*(*trimethylsilyl*)-2,2,3,3-*tetrafluorobutane* (Me_3SiCH_2-$CF_2CF_2CH_2SiMe_3$). This compound isolated from the reaction mixture by fractional condensation, had a vapour pressure of 1 mmHg at 25 °C. ^1H N.m.r. gave a singlet δ 7.28 ($SiMe_3$) and a complex symmetrical band at δ 6.04 assigned to the CH_2 groups. ^{19}F N.m.r. gave a complex symmetrical band at +24.6 p.p.m. assigned to the CF_2 groups. Complex bands are expected since the molecule is symmetrical.[8]

2,2-*Difluorovinyltrimethylsilane* ($CF_2{:}CHSiMe_3$). This compound was prepared in 80% yield by heating an equimolar mixture of tri-n-butyltin hydride and trifluorovinyltrimethylsilane[9,10] in a sealed tube at 100 °C for 24 h, and had a vapour pressure of 178 mmHg at 25 °C. δ_H 3.25 (1 H, dd, CH) and 6.78 (9 H, s, $SiMe_3$); δ_F −4.0 [1 F, dd, F(*cis*)] and −14.0 [1 F, dd, F(*trans*)] [$J(FH_{cis})$ 9.7, $J(FH_{trans})$ 42.0, and J(FF) 25.8 Hz]; $\nu_{max.}$ 2 940s, 2 890m, 1 700s, 1 620m, 1 400m, 1 290s, 1 260s, 1 130s, 1 070m, 952m, 850s, 785m, and 706m; *m*/*z* 43 ($MeSi^+$, 11.5%), 45 ($MeSiH_2^+$, 7.1), 47 (SiF^+, 24.7), 49 (SiH_2F^+, 18.4), 59 (Me_2SiH^+, 4.8), 60.5 ($Me_2SiCH{:}CF_2^{2+}$, 0.6), 63 ($MeSiHF^+$, 7.8), 73 (Me_3Si^+, 10.7), 77 ($H_2SiCH{:}CF_2^+$, 1.4), 101 ($Me_2SiC{:}CF_2^+$, 0.9), 105 ($MeSiC{:}CF_2^+$, 1.4), 121 ($Me_2SiCH{:}CF_2^+$, 30.0), and 136 ($Me_3SiCH{:}CF_2^+$, 4.4).

2-*Fluorovinyltrimethylsilane* ($CHF{:}CHSiMe_3$). This compound was prepared in 81% yield, as a mixture of the *cis*- and *trans*-isomers, by heating an equimolar mixture of tri-n-butyltin hydride and 2,2-difluorovinyltrimethylsilane in a sealed tube at 120 °C for 3 days.

trans-2-*Fluorovinyltrimethylsilane* was isolated from the above mixture by preparative g.l.c. using a 10 m glass column packed with 3% QF1 on silanised Celite at 35 °C, and had a vapour pressure of 120 mmHg at 25 °C. Found C, 50.8; H, 9.3; *M*, 116. $C_5H_{11}FSi$ requires C, 50.8; H, 9.4%; *M*, 118. δ 0.62 (1 H, dd, β-H), 1.92, (1 H, dd, α-H), and 6.96 (9 H, s, $SiMe_3$); δ_F 12.2 [dd, CHF, $J(H_\alpha H_\beta)$ 12.7, $J(FH_\alpha)$ 36, and $J(FH_\beta)$ 92 Hz]; $\nu_{max.}$ 3 070w, 2 965s, 2 910m, 2 140w, 1 740w, 1 625s, 1 410w, 1 325m, 1 255s, 1 190s, 1 075s, 930s, 865s, 840s, 785w, and 690m; *m*/*z* 43 ($MeSi^+$, 17.5%), 45 ($MeSiH_2^+$, 6.8), 47 (SiF^+, 28.4), 49 (SiH_2F^+, 22.4), 51.5 ($Me_2SiCH{:}CHF_2^+$, 0.1), 63 ($MeSiHF^+$, 8.0), 73 (Me_3Si^+, 14.9), 77 (Me_2SiF^+, 96.3), 81 ($MeSiF_2^+$, 1.8), 83 ($Me_2SiC{:}CH^+$, 3.5), 87 ($MeSiCH{:}CF^+$, 3.1), and 103 ($Me_2SiCH{:}CHF^+$, 100).

cis-2-*Fluorovinyltrimethylsilane*, similarly isolated, had *M*, 116; $C_5H_{11}FSi$ requires 118. δ_H 0.25 (1 H, 33, β-H), 2.39 (1 H, dd, α-H), and 6.91 (9 H, s, $SiMe_3$); δ_F 18.8 [dd, CHF, $J(H_\alpha H_\beta)$ 6.8, $J(FH_\alpha)$ 69, and $J(FH_\beta)$ 97 Hz]; $\nu_{max.}$ 3 070m, 2 965s, 2 910m 1 695m, 1 620s, 1 260s, 1 195m, 1 085m, 1 000s, 850s, 775m, and 695m; *m*/*z* 43 ($MeSi^+$, 9.4%), 45 ($MeSiH_2^+$, 5.1), 47 (SiF^+, 20.6), 49 (SiH_2F^+, 20.1), 51.5 ($Me_2SiCH{:}CHF^+$, 0.1), 63 ($MeSiHF^+$, 6.9), 73 (Me_3Si^+, 12.3), 77 (Me_2SiF^+, 100), 81 ($MeSiF_2^+$, 1.0), 83 ($Me_2SiC{:}CH^+$, 0.9), 87 ($MeSiCH{:}CF^+$, 1.2), and 103 ($Me_2SiCH{:}CHF^+$, 27.1).

Acknowledgements

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