

## Polyfluoroalkyl Compounds of Silicon. Part XI.<sup>1</sup> Reactions of Trichloro- and of Trimethyl-silane with Tetrafluoro- and with 3,3,3-Trifluoropropyne

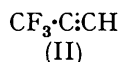
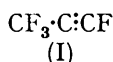
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Photochemical reaction of trichlorosilane with tetrafluoropropyne gives a relatively low yield (65%) of a mixture of the 1 : 1 adducts. 1,3,3,3-tetrafluoroprop-1-enyltrichlorosilane and 2-fluoro-1-trifluoromethylvinyltrichlorosilane in the ratio 31 : 69; trimethylsilane affords a high yield of the trimethylsilyl analogues in the ratio 86 : 14. Similar reactions of trichlorosilane and trimethylsilane with 3,3,3-trifluoropropyne give, in both cases, high yields of the corresponding 3,3,3-trifluoroprop-1-enyl- and 1-trifluoromethylvinyl-silanes in the ratio 72 : 28. Fluorination of the mixture of tetrafluoropropyne-trichlorosilane adducts affords a mixture of the trifluorosilyl analogues which is stable at 300° *in vacuo*.

PHOTOCHEMICAL reaction of silanes  $\text{Me}_n\text{Cl}_{3-n}\text{SiH}$  ( $n = 0-3$ ) with fluoro-olefins has been extensively studied, and with olefins such as  $\text{CF}_2\text{:CHF}$ ,  $\text{CF}_3\text{:CF:CF}_2$ , and  $\text{CF}_3\text{:CH:CHF}$ , two 1 : 1 adducts are formed *via* bidirectional addition of a silyl radical.<sup>2</sup>

Free-radical additions of silanes to unsubstituted alkynes have also been widely investigated, and peroxide-initiated reaction of trichlorosilane with various terminal acetylenes gives the terminal trichlorosilyl 1 : 1 adducts, with the products formed by *trans*-addition generally predominating (*cis* : *trans* addition, *ca.* 1 : 3).<sup>3</sup> Additions to fluorinated acetylenes have been less widely studied; thermal reaction of trimethylsilane with hexafluorobut-2-yne yields the 1 : 1 adduct by *trans*-addition.<sup>4</sup>

Photochemical reactions of trichlorosilane and trimethylsilane with tetrafluoropropyne (I) and 3,3,3-trifluoropropyne (II) have now been carried out to determine whether bidirectional radical addition takes place, and whether *cis*- or *trans*-addition is preferred.



*Tetrafluoropropyne* (I).—The photochemical reaction of trichlorosilane with the acetylene (I) (3·8 : 1 molar ratio), using a low-resonance u.v. lamp, gave telomeric material and a mixture of four 1 : 1 adducts, (*Z*)- (III) (36%) and (*E*)-2-fluoro-1-trifluoromethylvinyltrichlorosilane (IV) (9%), and (*Z*)- (V) (16%) and (*E*)-1,3,3,3-tetrafluoroprop-1-enyltrichlorosilane (VI) (4%).

Photochemical reaction of trimethylsilane with the acetylene (I) (3·7 : 1 molar ratio) under comparable conditions gave the 1 : 1 adducts, (*Z*)- (IX) (66%) and (*E*)-1,3,3,3-tetrafluoroprop-1-enyltrimethylsilane (X) (16%), and (*Z*)- (VII) (10%) and (*E*)-2-fluoro-1-trifluoromethylvinyltrimethylsilane (VIII) (4%).

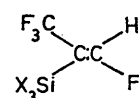
A mixture of the olefins (V), (VI), and (*Z*)- and (*E*)-2-chloro-3,3,3-trifluoropropenyltrichlorosilane,  $\text{CF}_3\text{:CCl:CH:SiCl}_3$  (ratio 6 : 29 : 7 : 2) has also been obtained by the dehydrohalogenation of 2-chloro-1,3,3,3-tetrafluoropropyltrichlorosilane with quinoline.<sup>5</sup>

<sup>1</sup> Part X, D. H. Coy, F. Fitton, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J.C.S. Dalton*, 1974, 1852.

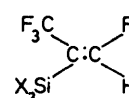
<sup>2</sup> D. Cooper, R. N. Haszeldine, and M. J. Newlands, *J. Chem. Soc. (A)*, 1967, 2098, and references cited therein; unpublished results from this department.

The n.m.r. coupling constants which established the structures of adducts (III)–(X) and the assignments made are shown in Table 1.

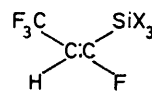
The magnitudes of the coupling constants are in agreement with the proposed structures, *i.e.* in the ranges previously observed, except for the assigned



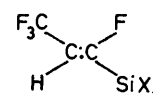
(III) X = Cl  
(VII) X = Me



(IV) X = Cl  
(VIII) X = Me



(V) X = Cl  
(IX) X = Me



(VI) X = Cl  
(X) X = Me

*cis*-H-F and geminal  $\text{CF}_3$ -H couplings for structures (V) and (IX) which are of greater magnitude than expected (especially the H-F couplings). However, these  $\text{CF}_3$ -H couplings cannot be other than geminal couplings, since  $J_{\text{gem}} > J_{\text{cis}} > J_{\text{trans}}$ .

The structures of the isomeric pairs (V) and (VI) and (IX) and (X) are assigned on the basis that *trans*-H-F > *cis*-H-F and *cis*- $\text{CF}_3$ -F > *trans*- $\text{CF}_3$ -F couplings.

In both reactions *trans* addition predominates over *cis* and the *cis* : *trans* ratios observed [1 : 4 for (IV) : (III), (VI) : (V), and (X) : (IX), and 1 : 2·5 for (VIII) : (VII)] are in close agreement with those found previously (*ca.* 1 : 3) for peroxide-initiated additions of trichlorosilane to various terminal olefins.<sup>3</sup> Compounds (V) and (IX) are thus formed preferentially relative to compounds (VI) and (X) even though they are the most sterically hindered isomers.

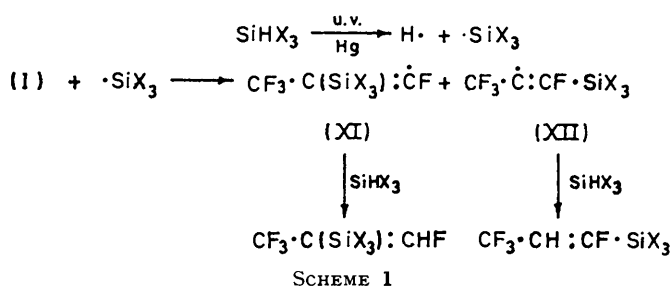
The products are consistent with the reaction pathway in Scheme 1.

<sup>3</sup> R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *J. Amer. Chem. Soc.*, 1961, **83**, 4385.

<sup>4</sup> W. R. Cullen and G. E. Styan, *J. Organometallic Chem.*, 1966, **6**, 117.

<sup>5</sup> R. N. Haszeldine, C. R. Pool, and A. E. Tipping, unpublished results.

The telomeric material observed in the trichlorosilane reaction products probably arises *via* further reaction



of the intermediate radicals (XI) and (XII) (X = Cl) with the acetylene (I).

In both reactions the 1:1 adducts are formed *via* bidirectional addition of the  $\cdot\text{SiCl}_3$  or  $\cdot\text{SiMe}_3$  radicals to (I). The ratios of bidirectional addition observed in

directional additions observed indicate that the two intermediate radicals produced by silyl radical attack are of comparable stability in each case. The  $\cdot\text{SiCl}_3$  radical is expected to be highly electrophilic relative to the  $\cdot\text{SiMe}_3$  radical and the change from mainly central carbon atom attack by the former radical to mainly terminal carbon atom attack by the latter radical is probably due largely to the differences in electrophilicity of the radicals<sup>6</sup> and the possible consequent polar effects in the transition states leading to the intermediate radicals.

Antimony trifluoride converted the mixture of trichlorosilane adducts (III)–(VI) into a mixture of the corresponding trifluorosilyl compounds,  $\text{CF}_3\cdot\text{CH}:\text{CF}\cdot\text{SiF}_3$  and  $\text{CF}_3\cdot\text{C}(\text{SiF}_3):\text{CHF}$ , in the ratio 26:12. This mixture was almost quantitatively recovered (99%) when heated at 300° (24 h), and  $\alpha$ - or  $\beta$ -elimination of silicon tetrafluoride thus does not occur readily in contrast to the

TABLE 1

N.m.r. coupling constants and assignments

Compound	H-F			CF <sub>3</sub> -F		CF <sub>3</sub> -H			H-H	
	<i>gem</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>gem</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
(III)	80.0				8.5		1.1			
(VII)	87.6				8.4		2.0			
(IV)	84.6			15.0				ca. 0.5		
(VIII)	84.0			14.0				†		
(V)		27.0			9.0	9.0				
(IX)		31.5			9.6	9.6				
(VI)			40.0	17.5		7.9				
(X)			42.9	16.9		7.8				
(XIII)							1.8	ca. 0.5		
(XVI)							2.0	†		
(XIV)						4	1.5			ca. 20
(XVII)						5.4	1.3			ca. 20
(XV)						7.0		†	ca. 14.5	
(XVIII)						7.0		ca. 0.5	ca. 13	
Reported range*	69.1–89.9	0–22	10.9–52.4	17.2–25.4	5.8–13.4	6.3–7.8	0.6–2.2	0–0.9		

\* M. G. Barlow, in 'Fluorocarbons and their Derivatives,' ed. R. E. Banks, 2nd edn., Macdonald, London, 1970, pp. 232–235.

† Not observed.

these reactions are compared in Table 2 with those found previously for photochemical reaction of the silanes with hexafluoropropene<sup>2</sup> and 1,3,3,3-tetrafluoropropene.<sup>5</sup>

TABLE 2

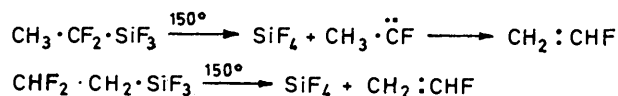
Reactions of trichlorosilyl and trimethylsilyl radicals

Unsaturated compound	Silyl radical	Ratio of attack, terminal : central carbon
CF <sub>3</sub> ·C:CF	·SiCl <sub>3</sub>	31 : 69
CF <sub>3</sub> ·CF:CF <sub>2</sub>	·SiCl <sub>3</sub>	35 : 65
CF <sub>3</sub> ·CH:CHF	·SiCl <sub>3</sub>	26 : 74
CF <sub>3</sub> ·C:CF	·SiMe <sub>3</sub>	86 : 14
CF <sub>3</sub> ·CF:CF <sub>2</sub>	·SiMe <sub>3</sub>	85 : 15

The ratio obtained for reaction of  $\cdot\text{SiCl}_3$  radicals with the acetylene (I) must be treated with caution because the yield of 1:1 adducts obtained is low (65%). However, on a qualitative basis the three ratios for  $\cdot\text{SiCl}_3$  radical addition compare well. With the two  $\cdot\text{SiMe}_3$  radical additions high yields of 1:1 adducts were obtained and the ratios are very similar. The bi-

<sup>6</sup> R. Fields, H. Goldwhite, R. N. Haszeldine, and J. Kirman, *J. Chem. Soc. (C)*, 1966, 2075, and unpublished results.

corresponding eliminations from polyfluoroalkyltrifluorosilanes which take place at *ca.* 150° (Scheme 2).<sup>7</sup>



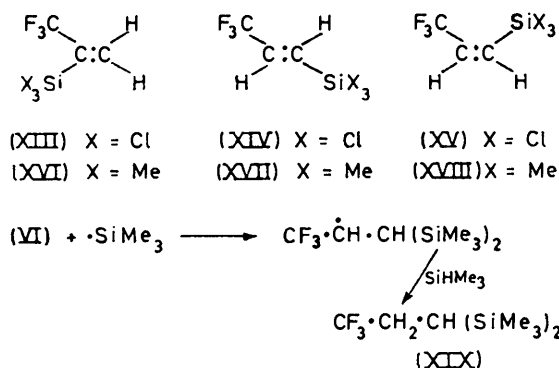
SCHEME 2

**3,3,3-Trifluoropropyne (II).**—The photochemical reaction of trichlorosilane with the acetylene (II) (4:1 molar ratio), using a medium-pressure u.v. lamp, gave the 1:1 adducts 1-trifluoromethylvinyltrichlorosilane (XIII) (27%), and (*E*)- (XIV) (55%) and (*Z*)-3,3,3-trifluoroprop-1-enyltrichlorosilane (XV) (15%).

Similarly, photochemical reaction of trimethylsilane with the acetylene (II) (5:1 molar ratio), but using the low-pressure lamp, gave the 1:1 adducts 1-trifluoromethylvinyltrimethylsilane (XVI) (26%), and (*E*)- (XVII) (47%) and (*Z*)-3,3,3-trifluoroprop-1-enyltri-

<sup>7</sup> For a review see R. N. Haszeldine, in 'New Pathways in Inorganic Chemistry,' eds. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, 1968.

methylsilane (XVIII) (21%) in high yield but low conversion. A reaction (6.5:1 molar ratio), using the medium-pressure lamp, gave mainly telomeric material together with the 1:1 adducts (XVI) (6%) and (XVII) (12%), and a compound tentatively identified as 1,1,1-trifluoro-3,3-bis(trimethylsilyl)propane (XIX) (2%) on the basis of a triplet splitting ( $J$  10.5 Hz) observed in the  $^{19}\text{F}$  n.m.r. spectrum for the  $\text{CF}_3$  group; the *cis*-olefin (XVIII) was not detected. Compound (XIX) is probably formed *via* further  $\cdot\text{SiMe}_3$  radical attack on olefin (VI).



The n.m.r. coupling constants observed in the spectra of adducts (XIII)—(XVIII) and the assignments made are shown in Table 1.

The assignments of *cis*- and *trans*-structures to the 3,3,3-trifluoropropenyl compounds (XIV), (XV), (XVII), and (XVIII) were based on (i) the apparent H-H couplings (*trans* > *cis*) and (ii) the presence or absence of *cis*- $\text{CF}_3$ -H couplings. The geminal  $\text{CF}_3$ -H couplings for compounds (XIV) and (XVII) are somewhat smaller than expected, but are much greater than such *cis*- or *trans*-couplings. The structures (XIII) and (XVI) were assigned on the basis of an absence of geminal  $\text{CF}_3$ -H and *cis*- or *trans*-H-H couplings and the presence of *cis*- $\text{CF}_3$ -H couplings.

The *cis*:*trans* ratios (XIV):(XV) = 3.7:1 and (XVII):(XVIII) = 2.2:1, show that *cis* addition is preferred, in contrast to the additions of the same silanes to the acetylene (I) and the predominant *trans* additions of trichlorosilane to unsubstituted terminal acetylenes under free-radical conditions.<sup>3</sup> The reason for these preferred *cis* additions is not known although the major adducts (XIV) and (XVII) are the least sterically hindered isomers.

Bidirectional radical addition of both the  $\cdot\text{SiCl}_3$  and  $\cdot\text{SiMe}_3$  radicals to the acetylene (II) is observed, in contrast to the unidirectional additions of silane<sup>8</sup> and trichlorosilane<sup>9</sup> to the olefin  $\text{CF}_3\cdot\text{CH}:\text{CH}_2$ . However, *N*-bromobis(trifluoromethyl)amine,  $(\text{CF}_3)_2\text{NBr}$ , gives unidirectional  $(\text{CF}_3)_2\text{N}\cdot$  radical addition to this olefin (attack on the terminal  $\text{CH}_2$  group), but bidirectional addition to the acetylene (II).<sup>10</sup>

<sup>8</sup> T. N. Bell, R. N. Haszeldine, M. J. Newlands, and J. B. Plumb, *J. Chem. Soc.*, 1965, 2107.

<sup>9</sup> A. M. Geyer, R. N. Haszeldine, R. N. Leedham, and R. J. Marklow, *J. Chem. Soc.*, 1957, 4472.

## EXPERIMENTAL

Techniques used were as described in earlier papers. An 8 m Silicone MS 550 oil g.l.c. column was used.  $^1\text{H}$  and  $^{19}\text{F}$  N.m.r. chemical shifts are relative to internal tetramethylsilane and external trifluoroacetic acid, respectively. Photochemical reactions were carried out in silica tubes (ca. 250 ml) 15 cm from a Hanovia S500 medium-pressure lamp or 10 cm from a Thermal Syndicate (type T/M5/534C/2) low-pressure mercury resonance lamp. The low-pressure lamp was used unless the rate of reaction was then too slow, in which case the medium-pressure lamp was used; no effect was noted on the type of product produced.

**Reactions of Tetrafluoropropyne.**—(a) *With trimethylsilane.* A mixture of trimethylsilane (5.94 g, 80.0 mmol) and tetrafluoropropyne<sup>11</sup> (2.41 g, 21.5 mmol), when irradiated with the low-pressure lamp (120 h), gave unchanged trimethylsilane (ca. 4.5 g, ca. 77% recovered) and a higher-boiling 1:1 adduct fraction (3.85 g, 20.3 mmol, 96%) (Found:  $M$ , 185. Calc. for  $\text{C}_6\text{H}_{10}\text{F}_4\text{Si}$ :  $M$ , 187) shown by g.l.c. (column at 75°) and n.m.r. spectroscopy to contain four components in the ratio 17:69:10:4. The major component was separated (g.l.c.) and identified as (*Z*)-1,3,3,3-tetrafluoroprop-1-enyltrimethylsilane (IX) (2.65 g, 14.2 mmol, 66%) (Found: C, 38.9; H, 5.7%;  $M$ , 187.  $\text{C}_6\text{H}_{10}\text{F}_4\text{Si}$  requires C, 38.9; H, 5.4%;  $M$ , 187), b.p. (Siwoloboff) 92°,  $\lambda_{\text{max}}$  6.00m and 6.10m (C:C str)  $\mu\text{m}$ ,  $\tau$  4.0 (1H, dq, vinylic H) and 9.85 (9H, s,  $\text{SiMe}_3$ );  $^{19}\text{F}$   $\delta$  -21.6 (3F, t,  $\text{CF}_3$ ) and 16.6 p.p.m. (1F, dq, vinylic F). The three other components of the mixture were not separated but were identified by n.m.r. spectroscopy as (i) (*E*)-1,3,3,3-tetrafluoroprop-1-enyltrimethylsilane (X) (0.64 g, 3.35 mmol, 16%),  $\tau$  4.70 (1H, dq, vinylic H) and 9.80 (9H, s,  $\text{SiMe}_3$ ),  $^{19}\text{F}$   $\delta$  -19.2 (3F, dd,  $\text{CF}_3$ ) and 22.0 p.p.m. (1F, dq, vinylic F); (ii) (*Z*)-2-fluoro-1-trifluoromethylvinyltrimethylsilane (VII) (0.40 g, 2.1 mmol, 10%),  $\tau$  2.6 (1H, dq, vinylic H) and 9.8 (9H, s,  $\text{SiMe}_3$ ),  $^{19}\text{F}$   $\delta$  -19.8 (3F, dd,  $\text{CF}_3$ ) and 25.1 p.p.m. (1F, dq, vinylic F); and (iii) (*E*)-2-fluoro-1-trifluoromethylvinyltrimethylsilane (VIII) (0.16 g, 0.9 mmol, 4%),  $\tau$  2.9 (1H, d, vinylic H) and 9.7 (9H, s,  $\text{SiMe}_3$ ),  $^{19}\text{F}$   $\delta$  -21.3 (3F, d,  $\text{CF}_3$ ) and 23.1 p.p.m. (1F, dq, vinylic F).

(b) *With trichlorosilane.* A mixture of trichlorosilane (15.0 g, 0.11 mol) and tetrafluoropropyne (4.38 g, 39.3 mmol), irradiated with the low-pressure lamp (97 h), gave (i) unchanged acetylene (0.35 g, 3.14 mmol, 8% recovered), (ii) unchanged trichlorosilane (ca. 11 g, ca. 73% recovered), (iii) a 1:1 adduct fraction (5.72 g, 23.3 mmol, 65%) (Found: C, 14.7; H, 0.7%;  $M$ , 250. Calc. for  $\text{C}_3\text{HCl}_3\text{F}_4\text{Si}$ : C, 14.5; H, 0.4%;  $M$ , 249.5), b.p. (Siwoloboff) 102–103°, and (iv) a non-volatile residue (ca. 2.3 g). The 1:1 adduct fraction was shown by g.l.c. (column at 95°) to contain four components in the ratio 56:14:24:6 (n.m.r. ratio 54:14:25:7) and these were identified by n.m.r. spectroscopy as (i) (*Z*)-2-fluoro-1-trifluoromethylvinyltrichlorosilane (3.14 g, 12.8 mmol, 36%),  $\tau$  3.65 (dq, vinylic H),  $^{19}\text{F}$   $\delta$  -20.5 (3F, dd,  $\text{CF}_3$ ) and 14.1 p.p.m. (1F, dq, vinylic F); (ii) (*E*)-2-fluoro-1-trifluoromethylvinyltrichlorosilane (0.80 g, 3.26 mmol, 9%),  $\tau$  3.4 (dq, vinylic H),  $^{19}\text{F}$   $\delta$  -24.1 (3F, dd,  $\text{CF}_3$ ) and 21.0 p.p.m. (1F, dq, vinylic F); (iii) (*Z*)-1,3,3,3-tetrafluoroprop-1-enyltrichlorosilane (1.40 g, 5.7 mmol, 16%),  $\tau$  2.6 (dq, vinylic H),  $^{19}\text{F}$   $\delta$  -21.0 (3F, t,

<sup>10</sup> J. Freear and A. E. Tipping, *J. Chem. Soc. (C)*, 1968, 1096; 1969, 1848.

<sup>11</sup> R. E. Banks, M. G. Barlow, W. D. Davies, R. N. Haszeldine, K. Mullen, and D. R. Taylor, *Tetrahedron Letters*, 1968, 3909.

$\text{CF}_3$ ) and 18.1 p.p.m. (1F, dq, vinylic F); and (iv) (*E*)-1,3,3,3-tetrafluoroprop-1-enyltrichlorosilane (0.37 g, 1.53 mmol, 4%),  $\tau$  2.8 (dq, vinylic H),  $^{19}\text{F}$   $\delta$  -18.5 (3F, dd,  $\text{CF}_3$ ) and 31.0 p.p.m. (1F, dq, vinylic F).

*Fluorination of the Isomeric Trichlorosilane-Tetrafluoropropyne 1:1 Adducts.*—A mixture (4.0 g, 16.1 mmol) of the foregoing isomeric adducts, when passed repeatedly *in vacuo* through a column (20 cm) containing antimony trifluoride and a small amount of antimony pentachloride (*ca.* 5% by weight), gave a trace of silicon tetrafluoride and a higher-boiling fraction (1.2 g, 6.1 mmol, 38%) (Found: *M*, 196. Calc. for  $\text{C}_3\text{HF}_7\text{Si}$ : *M*, 198), b.p. (Siwoloboff) 54°, which was shown by g.l.c. (column at 40°) and n.m.r. spectroscopy to contain four components present in the ratio 55:13:25:7 considered to be (*Z*)- (0.66 g, 3.36 mmol, 21%) and (*E*)-2-fluoro-1-trifluoromethylvinyltrifluorosilane (0.16 g, 0.78 mmol, 5%), and (*Z*)- (0.30 g, 1.55 mmol, 9%) and (*E*)-1,3,3,3-tetrafluoroprop-1-enyltrifluorosilane (0.08 g, 0.42 mmol, 3%).

*Reactions of 3,3,3-Trifluoropropyne.*—(a) *With trimethylsilane; experiment 1.* A mixture of trimethylsilane (9.6 g, 0.13 mol), and the acetylene (1.94 g, 20.6 mmol), when irradiated with the low-pressure lamp (120 h), gave (i) unchanged 3,3,3-trifluoropropyne (1.79 g, 19.0 mmol, 92% recovered), (ii) unchanged trimethylsilane (9.48 g, 0.128 mol, 98% recovered), and (iii) a higher-boiling fraction (0.26 g, 1.5 mmol, 94%) (Found: *M*, 170. Calc. for  $\text{C}_8\text{H}_{11}\text{F}_3\text{Si}$ : *M*, 168), shown by n.m.r. spectroscopy to consist of 1-trifluoromethylvinyltrimethylsilane (XVI) (0.07 g, 0.42 mmol, 26%),  $^{19}\text{F}$   $\delta$  -15.6 p.p.m. (d,  $\text{CF}_3$ ),  $\tau$  2.6—3.4 (2H, complex, vinylic H) and 9.7 (9H, s,  $\text{SiMe}_3$ ); (*E*)-3,3,3-trifluoroprop-1-enyltrimethylsilane (XVII) (0.13 g, 0.75 mmol, 47%),  $^{19}\text{F}$   $\delta$  -10.6 p.p.m. (dd,  $\text{CF}_3$ ),  $\tau$  3.1—3.8 (2H, two complex dm, vinylic H) and 9.8 (9H, s,  $\text{SiMe}_3$ ); and (*Z*)-3,3,3-trifluoroprop-1-enyltrimethylsilane (XVIII) (0.06 g, 0.33 mmol, 21%),  $^{19}\text{F}$   $\delta$  -8.5 p.p.m. (dd,  $\text{CF}_3$ ),  $\tau$  3.2—4.2 (2H, two complex dm, vinylic H) and 9.8 (9H, s,  $\text{SiMe}_3$ ).

(b) *With trimethylsilane; experiment 2.* A mixture of trimethylsilane (9.8 g, 0.13 mol) and the acetylene (1.94 g, 20.6 mmol) irradiated with the medium-pressure lamp (130 h), gave (i) unchanged 3,3,3-trifluoropropyne (*ca.* 15 ml

gas, *ca.* 0.7 mmol, *ca.* 4% recovered), (ii) unchanged trimethylsilane (5.74 g, 72.5 mmol, 60% recovered), and (iii) a higher-boiling fraction (0.70 g, 4.2 mmol, 21%) (Found: C, 43.1; H, 6.9%; *M*, 171. Calc. for  $\text{C}_8\text{H}_{11}\text{F}_3\text{Si}$ : C, 42.8; H, 6.6%; *M*, 168) which was shown by n.m.r. spectroscopy to contain 1-trifluoromethylvinyltrimethylsilane (XVI) (0.22 g, 1.3 mmol, 7%), (*E*)-3,3,3-trifluoropropenyltrimethylsilane (XVII) (0.41 g, 2.4 mmol, 12%), and a compound tentatively identified as 1,1,1-trifluoro-3,3-bis(trimethylsilyl)propane (XIX) (0.07 g, 0.4 mmol, 2%),  $^{19}\text{F}$   $\delta$  -8.8 p.p.m. (t,  $\text{CF}_3$ ),  $\tau$  8.2—9.4 (3H, complex,  $\text{CH}_2$  and CH) and 9.9 (18H, s, 2  $\text{SiMe}_3$ ). A telomeric liquid (*ca.* 5 g) was recovered from the reaction tube.

(c) *With trichlorosilane.* A mixture of trichlorosilane (21.6 g, 0.16 mol) and the acetylene (3.79 g, 40.2 mmol), irradiated with the medium-pressure lamp, gave (i) unchanged propyne (2.50 g, 26.4 mmol, 66% recovered), (ii) unchanged trichlorosilane (*ca.* 20 g, *ca.* 90% recovered), and (iii) a higher-boiling fraction (3.0 g, 13.1 mmol, 97%) (Found: *M*, 242. Calc. for  $\text{C}_3\text{H}_2\text{F}_3\text{Cl}_3\text{Si}$ : *M*, 239.5), which was shown by g.l.c. (column at 125°) and n.m.r. spectroscopy to contain three components in the ratio 57:15:28 and from which the two major components were separated (g.l.c.) and identified as (*E*)-3,3,3-trifluoroprop-1-enyltrichlorosilane (XIV) (1.70 g, 7.44 mmol, 55%) (Found: C, 16.0; H, 1.2%; *M*, 231.  $\text{C}_3\text{H}_2\text{F}_3\text{Cl}_3\text{Si}$  requires C, 15.7; H, 0.9%; *M*, 229.5),  $\lambda_{\text{max}}$  6.18  $\mu\text{m}$  and 6.24  $\mu\text{m}$  (C:C str.)  $\mu\text{m}$ ,  $^{19}\text{F}$   $\delta$  -10.2 p.p.m. (3F, dd,  $\text{CF}_3$ ),  $\tau$  2.8—3.2 (two complex dm, vinylic H) and 1-trifluoromethylvinyltrichlorosilane (XIII) (0.86 g, 3.66 mmol, 27%) (Found: C, 15.6; H, 1.0%; *M*, 232),  $^{19}\text{F}$   $\delta$  -18.4 p.p.m. (dd,  $\text{CF}_3$ ),  $\tau$  2.8—3.3 (complex, vinylic H).

The third component was not separated but was identified as (*Z*)-3,3,3-trifluoroprop-1-enyltrichlorosilane (0.48 g, 2.09 mmol, 15%),  $^{19}\text{F}$   $\delta$  -15.4 p.p.m. (d,  $\text{CF}_3$ ),  $\tau$  3.2—3.5 (two complex dm, vinylic H).

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