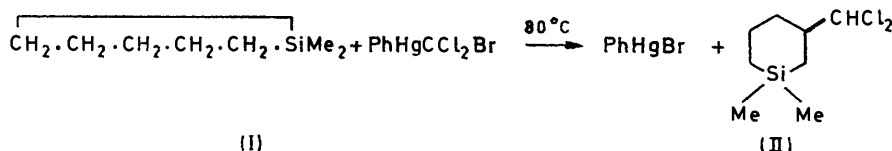


## Organosilicon Chemistry. Part XIV.<sup>1</sup> Insertion of 1,2,2-Trifluoroethylidene into C-H Bonds of Tetra-alkylsilanes: a Novel Alkyl Group Rearrangement

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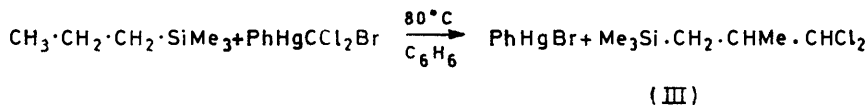
1,2,2-Trifluoroethylidene, generated by pyrolysis of trifluoro-(1,1,2,2-tetrafluoroethyl)silane, inserts (10–30%) into various C-H bonds in the alkyl groups of alkyltrimethylsilanes,  $\text{RSiMe}_3$  (R = Et,  $\text{Pr}^n$ ,  $\text{Pr}^i$ ,  $\text{Bu}^n$ ,  $\text{Bu}^i$ ,  $\text{Bu}^s$ , isopentyl, and cyclopentyl), but does not insert into the primary C-H bonds in tetramethylsilane. The ease of insertion into the C-H bonds is tertiary > secondary > primary, and C-H bonds  $\alpha$  to silicon are somewhat deactivated as compared with those further removed from silicon. In general the  $\alpha$ -insertion products are unstable under the reaction conditions and decompose to give fluorotrimethylsilane; other insertion products are stable. Insertion is also observed into the primary C-H bonds of hexamethyldisilane and hexamethyldisiloxane (ca. 5%). A novel rearrangement of the *s*-butyl group to the *n*-butyl group occurs during the reaction of trichloro-(*s*-butyl)silane with methylmagnesium bromide.

THE reaction of dichlorocarbene with various tetra-alkylsilanes has been investigated previously.<sup>2</sup> Thus the decomposition of (bromodichloromethyl)phenylmercury in benzene solution in the presence of the silane (I)



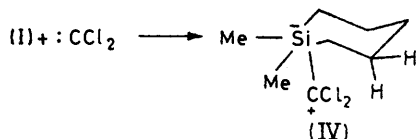
afforded the product (II), formed by exclusive dichlorocarbene insertion into a C-H bond  $\beta$  to the silicon atom.

Exclusive insertion into C-H bonds  $\beta$  to silicon was also observed to occur in the reaction of trimethyl-*n*-propylsilane with dichlorocarbene, although the yield of the insertion product (III) was relatively low (15%).



It was pointed out that the products of insertion into C-H bonds  $\gamma$  to silicon in these silanes should be stable, but that the products of  $\alpha$ -insertion might undergo  $\beta$ -elimination. However, compounds formed by breakdown of  $\alpha$ -insertion products were not detected.

To explain the exclusive insertion of dichlorocarbene into C-H bonds  $\beta$  to silicon in the silane (I) it was suggested that the reaction involved an ylide intermediate (IV) formed by nucleophilic interaction of the carbene



with the silicon atom. The close proximity of the  $\beta$ -C-H bonds in the intermediate (IV) was suggested as the reason for the observed specificity of insertion.

In a previous study<sup>1,3</sup> of the reactions of the carbene  $\text{CHF}_2 \cdot \dot{\text{C}}\text{F}$  (V) with alkylsilanes which contained Si-H

<sup>1</sup> Part XIII, R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, *J.C.S. Perkin I*, 1974, 2391.

<sup>2</sup> D. Seyferth and S. S. Washburne, *J. Organometallic Chem.*, 1966, **5**, 389.

and/or silicon-halogen bonds, carbene insertion was observed to occur with the Si-H and/or silicon-halogen bonds but not with the C-H bonds of the alkyl groups. However, insertion of the carbene (V) into C-H bonds of

alkanes has been observed, and the order of reactivity of the C-H bonds was found to be tertiary > secondary > primary.<sup>4</sup>

An investigation of the reactions of the carbene (V) with tetra-alkylsilanes of the type  $\text{Me}_3\text{SiR}$  (R = Me, Et,  $\text{Pr}^n$ ,  $\text{Pr}^i$ ,  $\text{Bu}^n$ ,  $\text{Bu}^i$ ,  $\text{Bu}^s$ , isopentyl, cyclopentyl,  $\text{SiMe}_3$ ,

and  $\text{OSiMe}_3$ ) was undertaken in order to obtain information as to the effect of the silicon atom on the reactivities of the various C-H bonds towards insertion.

These reactions were studied by means of the gas-phase decomposition of the carbene precursor  $\text{CHF}_2 \cdot \dot{\text{C}}\text{F}_2 \cdot \text{SiF}_3$  (VI) in the presence of the silane at 150 °C using a 1 : 3 molar ratio of carbene precursor (VI) to silane at a maximum total pressure of ca. 0.8 atm. In each case a quantitative yield of silicon tetrafluoride was obtained, indicating complete breakdown of the carbene precursor (VI) to the carbene (V). Also, the expected carbene rearrangement products, trifluoroethylene and the cyclopropanes *cis*- and *trans*- $\text{CHF}_2 \cdot \dot{\text{C}}\text{F} \cdot \text{CHF} \cdot \dot{\text{C}}\text{F}_2$  were observed; in certain cases fluorotrimethylsilane was also isolated and carbonaceous decomposition products were observed in the reaction bulb. The results are shown in Table 1.

The adduct fraction from each reaction was examined by g.l.c. in order to obtain the number and approximate relative percentages of the adducts formed; adduct

<sup>3</sup> R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, *Chem. Comm.*, 1969, 1364.

<sup>4</sup> R. N. Haszeldine and J. G. Speight, *Chem. Comm.*, 1967, 995.

TABLE I  
Products from the reaction of carbene (V) with tetra-alkylsilanes

R in RSiMe <sub>3</sub>	Insertion products	Yield (%)	Statistical yield (%)	Type * of C—bond	Position † of attack
CH <sub>3</sub>	None detected			1y	α
CH <sub>3</sub> ·CH <sub>2</sub>	CHF <sub>2</sub> ·CHF·CHMe·SiMe <sub>3</sub> †	7	3·5	2y	α
	CHF <sub>2</sub> ·CHF·CH <sub>2</sub> ·CH <sub>2</sub> ·SiMe <sub>3</sub>	6	2·0	1y	β
CH <sub>3</sub> ·CH <sub>2</sub> ·CH <sub>2</sub>	CHF <sub>2</sub> ·CHF·CHEt·SiMe <sub>3</sub> §	1	0·5	2y	α
	CHF <sub>2</sub> ·CHF·CHMe·CH <sub>2</sub> ·SiMe <sub>3</sub>	24	12·0	2y	β
(CH <sub>3</sub> ) <sub>2</sub> CH	CHF <sub>2</sub> ·CHF·CMe <sub>2</sub> ·SiMe <sub>3</sub> §	17	17·0	3y	α
	CHF <sub>2</sub> ·CHF·CH <sub>2</sub> ·CHMe·SiMe <sub>3</sub> **	1	0·17	1y	β
CH <sub>3</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> ·CH <sub>2</sub>	CHF <sub>2</sub> ·CHF·CH(Pr <sup>n</sup> )·SiMe <sub>3</sub> §	1	0·5	2y	α
	CHF <sub>2</sub> ·CHF·CHEt·CH <sub>2</sub> ·SiMe <sub>3</sub> ¶	8	4·0	2y	β
	CHF <sub>2</sub> ·CHF·CHMe·CH <sub>2</sub> ·CH <sub>2</sub> ·SiMe <sub>3</sub> ¶¶	12	6·0	2y	γ
(CH <sub>3</sub> ) <sub>2</sub> CH·CH <sub>2</sub>	CHF <sub>2</sub> ·CHF·CMe <sub>2</sub> ·CH <sub>2</sub> ·SiMe <sub>3</sub>	24	24	3y	β
CH <sub>3</sub> ·CH <sub>2</sub> ·CHMe	CHF <sub>2</sub> ·CHF·CMeEt·SiMe <sub>3</sub> §	17	17·0	3y	α
	CHF <sub>2</sub> ·CHF·CHMe·CHMe·SiMe <sub>3</sub>	11	5·5	2y	β
(CH <sub>3</sub> ) <sub>2</sub> CH·CH <sub>2</sub> ·CH <sub>2</sub>	CHF <sub>2</sub> ·CHF·CH(CHMe <sub>2</sub> )·CH <sub>2</sub> ·SiMe <sub>3</sub> **	1	0·5	2y	β
	CHF <sub>2</sub> ·CHF·CMe <sub>2</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> ·SiMe <sub>3</sub>	25	25·0	3y	γ
CH <sub>2</sub> ·[CH <sub>2</sub> ] <sub>3</sub> ·CH	CHF <sub>2</sub> ·CHF·C(SiMe <sub>3</sub> )[CH <sub>2</sub> ] <sub>3</sub> ·CH <sub>2</sub> §	16	16·0	3y	α
	CHF <sub>2</sub> ·CHF·CH·[CH <sub>2</sub> ] <sub>3</sub> ·CH·SiMe <sub>3</sub> ††	6	1·5	2y	β and γ
	CHF <sub>2</sub> ·CHF·CH·[CH <sub>2</sub> ] <sub>2</sub> ·CH(SiMe <sub>3</sub> )·CH <sub>2</sub>				
Me <sub>3</sub> Si	CHF <sub>2</sub> ·CHF·CH <sub>2</sub> ·SiMe <sub>2</sub> ·SiMe <sub>3</sub>	4	0·22	1y	α
Me <sub>3</sub> Si·O	CHF <sub>2</sub> ·CHF·CH <sub>2</sub> ·SiMe <sub>2</sub> ·O·SiMe <sub>3</sub> §	5	0·28	1y	α

\* 1y = primary, 2y = secondary, 3y = tertiary. † Relative to silicon atom. ‡ Partial decomposition of the adduct to Me<sub>3</sub>SiF had occurred. § Complete decomposition of the adduct to Me<sub>3</sub>SiF had occurred. ¶ Adduct ratio estimated from n.m.r. spectra. \*\* Adducts not completely characterised. †† G.l.c. indicated presence of two products in ratio *ca.* 3 : 1, but <sup>19</sup>F n.m.r. spectrum indicated presence of at least five stereoisomers.

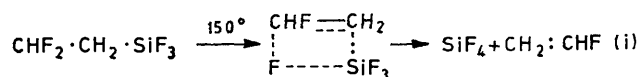
mixtures were separated into their individual components in cases where suitable g.l.c. columns could be found. The ratios of the isomeric C—H insertion products were determined by integration of the appropriate n.m.r. absorptions (*ca.* 10 times).

The <sup>1</sup>H n.m.r. spectra of all the C—H insertion products showed absorption at  $\tau$  *ca.* 4 (1H, tdd, CHF<sub>2</sub>, *J ca.* 56·0, 6·0—8·5, and 5·0 Hz), 5·5—5·8 (1H, dm, CHF, *J ca.* 46·0 Hz), and 8—10 (alkyl groups). The <sup>19</sup>F n.m.r. spectra consisted of absorptions at *ca.* 50 (2F, ABdd, CHF<sub>2</sub>) and 110—140 p.p.m. (1F, complex, CHF) relative to external trifluoroacetic acid. The existence of stereoisomers of certain of the insertion products caused the n.m.r. spectra of these adducts to be more difficult to interpret because of overlapping of bands; in certain cases distinct absorptions, assigned to the CHF groups of the various stereoisomers, were present in the <sup>19</sup>F spectra. In general analysis of the CHF absorption allowed differentiation between isomers, but the chemical shifts and coupling constants observed in the absorptions of the protons of the alkyl groups were also useful in some cases.

The formation of fluorotrimethylsilane in a number of the reactions was shown to be due to the decomposition of the α-C—H insertion products under the reaction conditions (150 °C; 6 h). Complete decomposition of these insertion products occurred in the reactions with the silanes Pr<sup>n</sup>SiMe<sub>3</sub>, Bu<sup>n</sup>SiMe<sub>3</sub>, and (cyclopentyl)SiMe<sub>3</sub>, whereas decomposition of the α-C—H insertion product CHF<sub>2</sub>·CHF·CHMe·SiMe<sub>3</sub> from reaction with the silane EtSiMe<sub>3</sub> was incomplete under the reaction conditions; on further pyrolysis of this α-insertion product (160 °C; 8 h) complete decomposition occurred to afford fluorotri-

methylsilane (100%) and carbonaceous material. Products formed from insertion into β- or γ-C—H bonds were stable under the reaction conditions and so the amount of fluorotrimethylsilane formed was indicative of the amount of the α-insertion product initially produced. In the reactions of the carbene (V) with the silanes Pr<sup>n</sup>SiMe<sub>3</sub> and Bu<sup>n</sup>SiMe<sub>3</sub> small amounts (*ca.* 1%) of fluorotrimethylsilane were detected indicating that some α-insertion by the carbene had taken place.

The decompositions of polyfluoroalkylsilanes which contain fluorine atoms β to silicon have been extensively studied in this department.<sup>5,6</sup> Decomposition takes place by a unimolecular process believed to involve a four-centre transition state [reaction (i)]. The ease of



such decompositions parallels change in the electro-positive nature of the silicon atom, *e.g.* the compound CHF<sub>2</sub>·CH<sub>2</sub>·SiF<sub>3</sub> decomposes at *ca.* 150 °C, and the trichlorosilyl analogue CHF<sub>2</sub>·CH<sub>2</sub>·SiCl<sub>3</sub> decomposes at *ca.* 220 °C.

If this were the only factor involved then β-fluoroalkyl-trimethylsilanes would be expected to decompose at temperatures higher than those at which the trichlorosilyl and trifluorosilyl analogues decompose. However, kinetic studies on β-chloroethylsilanes have shown that the activation energies for β-elimination decrease as chlorine atoms on silicon are replaced by ethyl groups.<sup>7</sup> An early report<sup>8</sup> that the silane CH<sub>2</sub>Cl·CH<sub>2</sub>·SiEt<sub>3</sub> decomposes at *ca.* 80 °C is consistent with this.

<sup>5</sup> R. N. Haszeldine, P. J. Robinson, and R. F. Simmons, *J. Chem. Soc.*, 1964, 1890.

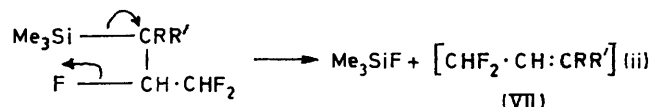
<sup>6</sup> T. N. Bell, R. N. Haszeldine, M. J. Newlands, and J. B. Plumb, *J. Chem. Soc.*, 1965, 2107, and references therein.

<sup>7</sup> I. M. T. Davidson and M. R. Jones, *J. Chem. Soc.*, 1965, 5481.

<sup>8</sup> L. H. Sommer and F. C. Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 485.

The ease of decomposition of such  $\beta$ -chloroalkyltri-alkylsilanes is considered to be due to stabilisation by the alkyl groups of partial positive charge on silicon in the transition state.

It is therefore suggested that the decomposition of the  $\alpha$ -C-H insertion products involves  $\beta$ -elimination initiated by nucleophilic attack of the  $\beta$ -fluorine atom on silicon [reaction (ii)].

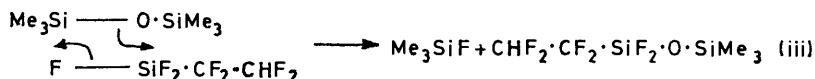


The results obtained indicate that  $\alpha$ -insertion products formed by insertion into a tertiary C-H bond are less thermally stable than those formed by insertion into a secondary C-H bond. This is probably because of the greater release of steric strain on decomposition of compounds of type  $\text{CHF}_2 \cdot \text{CHF} \cdot \text{CRR}' \cdot \text{SiMe}_3$  than those of type  $\text{CHF}_2 \cdot \text{CHF} \cdot \text{CHR} \cdot \text{SiMe}_3$ .

Decomposition of these  $\alpha$ -insertion products by an elimination process involving a  $\gamma$ -fluorine atom is ruled out because silanes containing  $\gamma$ -fluorine atoms are reported to decompose only at high temperature<sup>9</sup> and compounds formed in the present work by  $\beta$ -C-H insertion (which contain  $\gamma$ - and  $\delta$ -fluorine atoms) were stable under the reaction conditions.

Apart from the fluorotrimethylsilane isolated in the decompositions of the  $\alpha$ -C-H insertion products it was expected that olefins of the type  $\text{CHF}_2 \cdot \text{CH} : \text{CRR}'$  (VII) would also be formed. These were not detected although they may have been a major source of the black decomposition products.

Fluorotrimethylsilane (5%) was formed also in the reaction of the carbene (V) with hexamethyldisiloxane, indicating that the insertion product  $\text{CHF}_2 \cdot \text{CHF} \cdot \text{CH}_2 \cdot \text{SiMe}_2 \cdot \text{O} \cdot \text{SiMe}_3$  was initially formed. Although this compound contains an unsubstituted methylene group adjacent to silicon it is probably thermally unstable because of the presence of the Si-O linkage which renders the silicon atom more susceptible to nucleophilic attack by the  $\beta$ -fluorine atom. In support of this, the compound  $\text{CHF}_2 \cdot \text{CHF} \cdot \text{CH}_2 \cdot \text{SiMe}_2 \cdot \text{SiMe}_3$  (see below) was found to be



stable under the same conditions. The formation of fluorotrimethylsilane *via* co-ordination of the silicon atom of the carbene precursor (VI) with the oxygen atom of the disiloxane [reaction (iii)], as suggested for trimethylsilanol,<sup>10</sup> was ruled out because a quantitative yield of silicon tetrafluoride was obtained.

In the attempted reaction of the carbene (V) with tetramethylsilane a C-H insertion product was not detected, but in the reaction with hexamethyldisilane a

<sup>9</sup> R. N. Haszeldine, P. J. Robinson, and R. F. Simmons, *J. Chem. Soc. (B)*, 1967, 1357.

<sup>10</sup> R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, unpublished results.

low yield (4%) of the insertion product  $\text{CHF}_2 \cdot \text{CHF} \cdot \text{CH}_2 \cdot \text{SiMe}_2 \cdot \text{SiMe}_3$  was obtained.

The ease of insertion of the carbene (V) into C-H bonds in tetra-alkylsilanes, tertiary > secondary > primary, is observed regardless of the positions of the C-H bonds relative to the silicon atom. Such insertion is considered to involve a three-centre transition state (VIII) of the type suggested originally<sup>11</sup> for insertion of singlet methylene into C-H bonds. A comparison of the yields obtained by insertion of the carbene (V) into the same type of C-H bond in the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -positions with respect to silicon indicates that the  $\alpha$ -C-H bonds are considerably deactivated. This is shown by the following observations.

(i) The yields of products formed by insertion into tertiary C-H bonds  $\alpha$  to silicon vary little (16--17%) and these yields are distinctly lower than those for insertion into tertiary C-H bonds  $\beta$  (24%) or  $\gamma$  (26%) to silicon.

(ii) Insertion into secondary and even primary C-H bonds  $\beta$  to silicon takes place in the presence of a tertiary C-H bond  $\alpha$  to silicon, but if the tertiary C-H bond is  $\beta$  or  $\gamma$  to silicon almost exclusive insertion into this bond takes place.

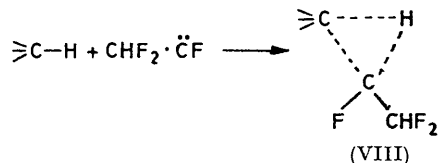
(iii) A secondary C-H bond  $\alpha$  to silicon is only 1.75 times more reactive towards insertion than a primary C-H bond  $\beta$  to silicon, but if a secondary C-H bond  $\beta$  to silicon and a primary C-H bond  $\gamma$  to silicon are present, insertion into the latter bond is not observed.

(iv) The yields of products formed by carbene insertion into secondary C-H bonds  $\alpha$  to silicon in the silanes  $\text{Pr}^n\text{SiMe}_3$  and  $\text{Bu}^n\text{SiMe}_3$  are very low in comparison with the yields of products formed by insertion into the secondary C-H bonds  $\beta$  or  $\gamma$  to silicon.

(v) Products formed by insertion into primary C-H bonds  $\alpha$  to silicon in the tetra-alkylsilanes are not observed, in contrast to the observed insertion into primary C-H bonds  $\beta$  or  $\gamma$  to silicon.

This observed low susceptibility of C-H bonds  $\alpha$  to silicon towards insertion is probably caused in part by (i) steric hindrance by the bulky  $\text{SiMe}_3$  group to approach of the carbene to the  $\alpha$ -C-H bonds and (ii) the electro-positive nature of the adjacent silicon atom which destabilises the three-centre transition state (VIII).

The reaction of the carbene (V) with the silane  $\text{Bu}^n\text{SiMe}_3$  is of interest because a direct comparison of the



reactivities of secondary C-H bonds in the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -

<sup>11</sup> P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, 1956, **78**, 4496; W. von E. Doering and L. H. Knox, *ibid.*, 1961, **83**, 1989.

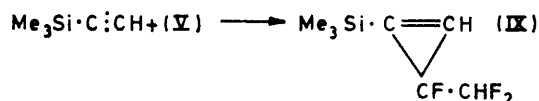
positions can be made. The ratio ( $\alpha : \beta : \gamma$ ) of insertion (1 : 8 : 12) indicates that the  $\alpha$ -C-H bonds are considerably deactivated and that the  $\gamma$ -C-H bonds are 1.5 times more reactive than the  $\beta$ -C-H bonds. The greater susceptibility of the  $\gamma$ -C-H bonds towards insertion is possibly due to such bonds being further removed from the deactivating effect of the silicon atom (see earlier) and to the greater hyperconjugative stabilisation of the transition state for insertion into a C-H bond adjacent to a methyl group than to a methylene group. The second factor is probably dominant because insertion of the carbene (V) into the C-H bonds of n-pentane affords the products  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CHF}\cdot\text{CHF}_2$  (28%) and  $\text{Et}_2\text{CH}\cdot\text{CHF}\cdot\text{CHF}_2$  (9%) indicating that in this alkane a methylene group adjacent to methyl is *ca.* 1.5 times more reactive than the methylene group in the 3-position.<sup>4</sup>

The reaction with cyclopentyltrimethylsilane showed that the tertiary C-H bond  $\alpha$  to silicon was *ca.* 3 times more reactive than the  $\beta$ - and  $\gamma$ -secondary C-H bonds combined. An attempted separation of the  $\beta$ - and  $\gamma$ -C-H insertion products by g.l.c. was unsuccessful although two incompletely resolved peaks (ratio *ca.* 1 : 3) were observed on the g.l.c. trace (possibly due to the  $\beta$ - and  $\gamma$ -insertion products, respectively). However, the <sup>19</sup>F n.m.r. spectrum of the product showed five absorption bands in the CHF region and four bands in the CHF<sub>2</sub> region indicating that at least five of the eight possible stereoisomers resulting from  $\beta$ - and  $\gamma$ -C-H insertion were present.

In the reaction with trimethyl-n-propylsilane, the carbene (V) shows an insertion selectivity comparable to that reported for dichlorocarbene,<sup>2</sup> but a higher yield of insertion product is obtained from the carbene (V).

The observation that  $\alpha$ -,  $\beta$ -, and  $\gamma$ -insertion products can be formed from reaction of the carbene (V) with the various tetra-alkylsilanes studied is evidence against the participation of an ylide mechanism<sup>2</sup> in these reactions.

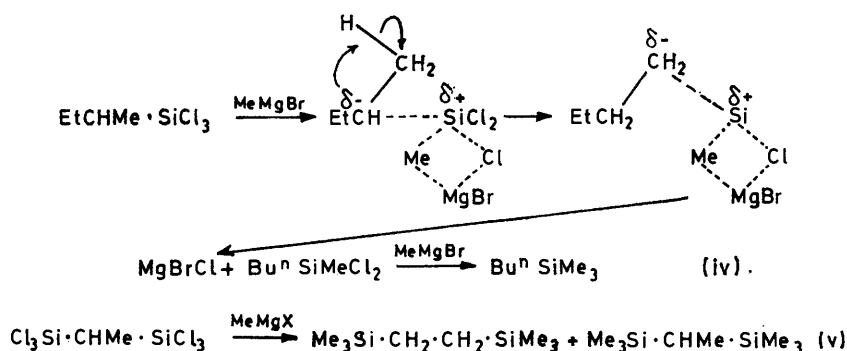
silane (1 : 3 molar ratio) at 150 °C (6 h) afforded unchanged alkyne (66%), silicon tetrafluoride (100%), fluorotrimethylsilane (100%), and a black residue. The quantitative yield of silicon tetrafluoride and the absence of any carbene rearrangement products indicate that the carbene (V) was formed quantitatively and that it then reacted quantitatively with the alkyne to give products, possibly including the cyclopropene (IX), which decomposed to give fluorotrimethylsilane and intractable material.



*Rearrangement of an Alkyl Group during Reaction of an Alkylsilicon Compound with a Grignard Reagent.*—The attempted preparation of the silane  $\text{Bu}^n\text{SiMe}_3$  by addition of trimethylsilane to but-2-ene using various methods of radical initiation was unsuccessful although the trichlorosilyl analogue was prepared (85%) by photochemical addition of trichlorosilane to *trans*-but-2-ene. The reaction of the trichlorosilyl compound so obtained with an excess of methylmagnesium bromide in ether gave the silane  $\text{Bu}^n\text{SiMe}_3$  (62%) and not the expected product  $\text{Bu}^n\text{SiMe}_2$ . It is suggested that the rearrangement observed involves formation of an incipient *s*-butyl carbanion which rearranges to the more stable incipient *n*-butyl carbanion [reaction (iv)]. A comparable rearrangement has been reported<sup>12</sup> to occur to a minor extent (18%) in the methylation of 1,1-bis(trichlorosilyl)ethane [reaction (v)].

The observation that reaction of methylmagnesium bromide with the silane  $\text{Pr}^i\text{SiCl}_3$  gave exclusively the trimethylsilyl analogue  $\text{Pr}^i\text{SiMe}_3$  suggests that steric factors also in part determine whether rearrangement occurs or not.

The silane  $\text{Bu}^n\text{SiMe}_3$ , however, was successfully pre-



The reaction of the carbene precursor (VI) with bromomethyltrimethylsilane gave only a quantitative yield of silicon tetrafluoride and rearrangement products derived from the carbene (V); a  $\text{CH}_2\text{Br}$  group  $\alpha$  to silicon is thus not susceptible to insertion by the carbene (V).

Reaction of the precursor (VI) with ethynyltrimethyl-

pared by the Speier-catalysed addition of trimethylsilane to but-2-yne to afford *cis*-2-trimethylsilylbut-2-ene<sup>13</sup> (98%), followed by quantitative catalytic hydrogenation of the adduct. This compound has been prepared previously by the reaction of *s*-butyl-lithium with chlorotrimethylsilane.<sup>14</sup>

<sup>12</sup> G. Fritz and G. Sonntag, *Z. anorg. Chem.*, 1963, **322**, 41.

<sup>13</sup> J. W. Ryan and J. L. Speier, *J. Org. Chem.*, 1966, **31**, 2698.

<sup>14</sup> A. E. Bey and D. R. Weyenberg, *J. Org. Chem.*, 1965, **30**, 2436.

## EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system in order to avoid contamination with air or moisture. Pure compounds were isolated by repeated fractional condensation *in vacuo* or by preparative scale g.l.c. [Pye 105 or Perkin-Elmer 452 instruments with columns (2–10 m) packed with Silicone SE30 or MS550 oil on Celite]. The identities of products were established by elemental analysis, i.r. spectroscopy (Perkin-Elmer spectrophotometer model 452 with sodium chloride optics), mass spectrometry (A.E.I. MS/2 instrument), and n.m.r. spectroscopy (Perkin-Elmer R10 instrument operating at 60.0 MHz for  $^1\text{H}$  and 56.46 MHz for  $^{19}\text{F}$  or a Varian HA100 spectrometer operating at 100.0 MHz for  $^1\text{H}$  and 94.1 MHz for  $^{19}\text{F}$  with internal tetramethylsilane and external trifluoroacetic acid as the respective references).

Trifluoro-(1,1,2,2-tetrafluoroethyl)silane was prepared by the method reported previously.<sup>5,15</sup> The silanes  $\text{Pr}^n\text{SiMe}_3$ ,  $\text{Bu}^n\text{SiMe}_3$ ,  $\text{Bu}^i\text{SiMe}_3$ , (isopentyl) $\text{SiMe}_3$ , and (cyclopentyl) $\text{SiMe}_3$  were prepared by Speier-catalysed additions ( $\text{H}_2\text{PtCl}_4$ ) of trimethylsilane to the appropriate terminal olefins or cyclopentene and the silanes  $\text{EtSiMe}_3$ ,  $\text{Pr}^i\text{SiMe}_3$ , and

was slowly added (1.5 h) to the stirred solution. The solution was maintained at room temperature (16 h), heated under reflux (6 h), and then cooled and filtered. Removal of the ether by distillation followed by distillation of the residue gave n-butyltrimethylsilane (34.5 g, 0.26 mol, 62%), b.p. 114–116 °C (lit.,<sup>17</sup> 115.3 °C), the i.r. and n.m.r. spectra of which were identical with those of a pure sample prepared by the Speier-catalysed addition of trimethylsilane to but-1-ene at 60 °C;  $\tau$  8.7 (2H, complex,  $\text{MeCH}_2$ ), 8.9 (2H, complex,  $\text{MeCH}_2\text{CH}_2$ ), 9.1 (3H, t,  $J$  6.0 Hz, Me), 9.4 (2H, complex,  $\text{SiCH}_3$ ), and 9.97 (9H, s,  $\text{SiMe}_3$ ).

*Preparation of Trimethyl-(s-butyl)silane.*—A mixture of but-2-yne (5.4 g, 0.10 mol), trimethylsilane (7.4 g, 0.10 mol), and hexachloroplatinic acid (ca. 0.1 g), sealed *in vacuo* in a Pyrex ampoule (ca. 250 ml) and heated at 80 °C (72 h), gave *cis*-2-trimethylsilylbut-2-ene (12.7 g, 98.0 mmol, 98%) (Found: C, 65.3; H, 12.6. Calc. for  $\text{C}_7\text{H}_{16}\text{Si}$ : C, 65.6; H, 12.5%), the i.r. and n.m.r. spectra of which corresponded to those reported.<sup>13</sup>

A solution of the product (10.0 g, 78.0 mmol) in ether (200 ml) was shaken with hydrogen at 75 lb in<sup>-2</sup> in the presence of palladium-carbon (10%, 0.5 g) until the pressure

TABLE 2

Thermal decomposition of trifluoro-(1,1,2,2-tetrafluoroethyl)silane (VI) in the presence of alkylsilanes

Alkylsilane $\text{RSiMe}_3$		(VI) mmol	Products (%) *			
R	mmol		$\text{CF}_2\text{:CHF}$	$\text{CF}_2\text{:CHF}\cdot\text{CF}\cdot\text{CHF}_2$	$\text{Me}_3\text{SiF}$	Insertion products
Me	90.0	30.0	58	42		
Et	90.0	37.0	45	42	5	$\text{CHF}_2\text{:CHF}\cdot\text{CH}_2\text{:CH}_2\cdot\text{SiMe}_3$ , 6 $\text{CHF}_2\text{:CHF}\cdot\text{CHMe}\cdot\text{SiMe}_3$ , 2
$\text{Pr}^n$	90.0	35.9	37	38	1	$\text{CHF}_2\text{:CHF}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{SiMe}_3$ , 24
$\text{Pr}^i$	90.0	30.0	49	33	17	$\text{CHF}_2\text{:CHF}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{SiMe}_3$ , 1
$\text{Bu}^n$	90.0	30.0	51	29	1	$\text{CHF}_2\text{:CHF}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SiMe}_3$ , 11 $\text{CHF}_2\text{:CHF}\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{SiMe}_3$ , 8
$\text{Bu}^i$	90.0	30.0	46	30		$\text{CHF}_2\text{:CHF}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{SiMe}_3$ , 24
$\text{Bu}^s$	90.0	30.0	41	31	17	$\text{CHF}_2\text{:CHF}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{SiMe}_3$ , 11
Isopentyl	90.0	30.0	42	32		$\text{CHF}_2\text{:CHF}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SiMe}_3$ , 25 $\text{CHF}_2\text{:CHF}\cdot\text{CH}(\text{CHMe}_2)\cdot\text{CH}_2\cdot\text{SiMe}_3$ , 1
Cyclopentyl	90.0	30.0	43	35	16	Mixture, 6
$\text{Me}_3\text{Si}$	90.0	30.0	56	40		$\text{CHF}_2\text{:CHF}\cdot\text{CH}_2\cdot\text{SiMe}_2\cdot\text{SiMe}_3$ , 4
$\text{Me}_3\text{Si}\cdot\text{O}$	90.0	30.0	54	41	5	
$\text{CH}_3\text{C}$	90.0	30.0			100	
$\text{CH}_2\text{Br}$ †	36.0	12.0	61	39		

\* Quantitative yield of silicon tetrafluoride and appropriate amount of unchanged reactant alkylsilane also obtained. † Pyrex bulb (2 l) used.

$\text{Me}_3\text{SiC:CH}$  were prepared by appropriate Grignard syntheses. These silanes and commercial samples of tetramethylsilane, hexamethyldisilane, and hexamethyldisiloxane were carefully purified before use.

*Preparation of Trichloro-(s-butyl)silane.*—A mixture of *trans*-but-2-ene (11.2 g, 0.20 mol) and trichlorosilane (27.1 g, 0.20 mol), sealed *in vacuo* in a silica tube (ca. 250 ml) and irradiated (56 g) at a distance of 10 cm from a 500 W medium-pressure u.v. lamp, gave unchanged reactants (6.3 g, 48.0 mmol, 12% recovered) and liquid product which on distillation yielded trichloro-(s-butyl)silane (29.8 g, 0.16 mol, 85%), b.p. 144–145 °C (lit.,<sup>16</sup> 144 °C).

*Reaction of Trichloro-(s-butyl)silane with Methylmagnesium Bromide.*—Bromomethane (142.5 g, 1.5 mol) was added slowly (2 h) to a vigorously stirred suspension of magnesium turnings (43.2 g) in ether (300 ml). The resultant material was decanted under dry nitrogen to remove unchanged magnesium, and trichloro-(s-butyl)silane (83.0 g, 0.43 mol)

drop indicated that reaction was complete (20 h). Distillation of the resultant material yielded trimethyl-(s-butyl)silane (10.1 g, 78.0 mmol, 100%) (Found: C, 64.5; H, 13.6. Calc. for  $\text{C}_7\text{H}_{16}\text{Si}$ : C, 64.6; H, 13.8%), b.p. 113–114 °C (lit.,<sup>14</sup> 114 °C);  $\tau$  8.5 (2H, complex,  $\text{CH}_2$ ), 9.0 (6H, complex, 2Me), 9.4 (1H, complex, CH), and 9.98 (9H, s,  $\text{SiMe}_3$ ); the g.l.c. (4 m SE30 at 70 °C) retention time of a sample was less than that of n-butyltrimethylsilane.

*Thermal Decomposition of Trifluoro-(1,1,2,2-tetrafluoroethyl)silane in the Presence of Trimethylsilyl Compounds.*—All reactions were carried out (150 °C; 6 h) *in vacuo* in a Pyrex bulb (capacity ca. 5 l, unless stated to the contrary) fitted with a side arm and at maximum pressures of ca. 0.8 atm.

(a) *Cyclopentyltrimethylsilane.* A mixture of cyclopentyltrimethylsilane (12.80 g, 90.0 mmol) and the carbene precursor (5.58 g, 30.0 mmol), thermolysed as previously described, gave (i) a mixture (4.18 g, 42.9 mmol) of silicon tetrafluoride and trifluoroethylene (i.r.) which on hydrolysis

<sup>15</sup> W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. and Ind.*, 1961, 789; G. Fishwick, R. N. Haszeldine, C. Parkinson, P. J. Robinson, and R. F. Simmons, *Chem. Comm.*, 1965, 382.

<sup>16</sup> M. G. Voronkov, N. G. Romanova, and G. L. Smirnova, *Chem. listy*, 1958, 52, 640.

<sup>17</sup> A. Bygden, *Ber.*, 1911, 44, 2640.

with water (10 ml, 30 min) *in vacuo* afforded trifluoroethylene (1.06 g, 12.9 mmol, 43%) thus allowing the amount of silicon tetrafluoride originally present to be estimated (3.12 g, 30.0 mmol, 100%); (ii) fluorotrimethylsilane (0.36 g, 4.9 mmol, 16%) (Found: *M*, 92. Calc. for  $C_3H_9FSi$ : *M*, 92), identified by i.r. spectroscopy; (iii) a mixture (0.85 g, 5.2 mmol, 35%) (Found: *M*, 164. Calc. for  $C_4H_9F_3$ : *M*, 164) of *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane, identified by i.r. spectroscopy; (iv) unchanged cyclopentyltrimethylsilane (11.83 g, 83.3 mmol, 92% recovered); and (v) a higher-boiling mixture of carbene insertion products (0.40 g, 1.8 mmol, 6%) (Found: C, 53.5; H, 8.2. Calc. for  $C_{10}H_{19}F_3Si$ : C, 53.6; H, 8.5%), b.p. 210–220° which was indicated by g.l.c. (8 m MS550 oil and 10 m SE30 oil at 185 °C) to contain two components in the ratio *ca.* 3.2 : 1 but which was shown by n.m.r. spectroscopy to be a complex mixture of stereoisomers:  $^{19}F$  n.m.r. bands at 45.5, 49.0, 51.5, and 52.5 p.p.m. (all ddt, total 2F,  $CHF_2$ , *J ca.* 56, 16, and 15 Hz) and 119.5, 126.0, 134.5, 148.0, and 160.5 p.p.m. (all complex, total 1F, CHF) and  $^1H$  n.m.r. bands

† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index issue.

at  $\tau$  *ca.* 4.1 (tm, 1H,  $CHF_2$ ), *ca.* 5.4 (dm, 1H, CHF), 7.1–9.1 (complex, 8H, ring protons), and 9.7–9.9 (s, 9H,  $SiMe_3$ ).

A black residue (*ca.* 0.7 g) remained in the reaction bulb.

(b) *Other trimethylsilyl compounds.* The results obtained from the thermal decomposition of the carbene precursor in the presence of a variety of trimethylsilyl compounds are shown in Table 2. Analytical and b.p. data and n.m.r. spectral data on the new compounds prepared are available as Supplementary Publication No. SUP 21321 (5 pp.).†

*Pyrolysis of Trimethyl-(2,3,3-trifluoro-1-methylpropyl)silane.*—The silane (0.21 g, 1.1 mmol), sealed in a Pyrex ampoule (*ca.* 20 ml) and heated at 160 °C (8 h), gave, as the only volatile product, fluorotrimethylsilane (0.10 g, 1.1 mmol, 100%), identified by i.r. spectroscopy. The black material (*ca.* 0.10 g) which remained in the reaction tube was not investigated further.

*Pyrolysis of Trimethyl-(3,4,4-trifluorobutyl)silane.*—The silane (0.25 g, 1.3 mmol), sealed in a Pyrex ampoule (*ca.* 30 ml) and heated at 320 °C (8 h), gave only unchanged reactant silane (100% recovered).

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