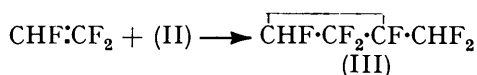
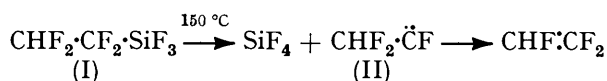


## Organosilicon Chemistry. Part XIII.<sup>1</sup> Insertion Reactions of 1,2,2-Trifluoroethylidene into Silicon-Hydrogen and Silicon-Halogen Bonds <sup>2</sup>

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1,2,2-Trifluoroethylidene, generated by the pyrolysis of 1,1,2,2-tetrafluoroethyltrifluorosilane, inserts exclusively into the silicon-hydrogen bond of trialkylsilanes  $R_3SiH$  ( $R_3 = Et_3, Et_2Me, \text{ or } Me_3$ ) or the silicon-deuterium bond of the silane  $Me_3SiD$  to afford the silanes  $CHF_2 \cdot CHF \cdot SiR_3$  (98–99%) or  $CHF_2 \cdot CDF \cdot SiMe_3$  (88%). With silanes  $X_3SiCl$  ( $X_3 = Cl_3, Cl_2Me, ClMe_2, \text{ or } Me_3$ ) or  $Me_3SiBr$  insertion occurs into the silicon-halogen bond to give the silanes  $CHF_2 \cdot CFCl \cdot SiX_3$  or  $CHF_2 \cdot CBr \cdot SiMe_3$  (2–15%). The silane  $Me_2ClSiH$  reacts exclusively by Si-H insertion (96%) but both Si-H and Si-Cl insertion (total *ca.* 55%) are observed with the silanes  $Cl_3SiH$  and  $MeCl_2SiH$ . Reaction of the carbene with dimethylvinylsilane and allyldimethylsilane gives products (99%) resulting from both Si-H insertion and double-bond addition (ratios 93 : 7 and 67 : 33, respectively), but with trichlorovinylsilane only addition to the double bond takes place (66%).

THERMAL decomposition of 1,1,2,2-tetrafluoroethyltrifluorosilane (I) at 150 °C takes place *via* an  $\alpha$ -elimination process to afford silicon tetrafluoride and 1,2,2-trifluoroethylidene (II).<sup>3,4</sup> In the absence of a reactive substrate, *e.g.* an olefin, the carbene (II) rearranges to trifluoroethylene,<sup>4</sup> and addition of unchanged carbene (II) to trifluoroethylene then affords *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (III). The amount of silicon tetrafluoride formed in reactions



involving thermal decomposition of the silane (I) provides an accurate measure of the extent of formation of the carbene (II).

Previous studies have shown that the carbene (II) reacts with olefins to give cyclopropanes in high yield,<sup>5,6</sup> inserts into the Si-H bond of  $Me_3SiH$  to give  $CHF_2 \cdot CHF \cdot SiMe_3$ ,<sup>6</sup> and inserts into the C-H bonds of alkanes in the order of reactivity tertiary > secondary > primary.<sup>6</sup> The carbene (II), formed as described above, reacts in the singlet state, as shown by (i) exclusive stereospecific addition to both *cis*- and *trans*-but-2-ene<sup>6</sup> and (ii) insertion into the tertiary C-H bond of the optically active ether  $L\text{-CH}_3[\text{CH}_2]_5\text{CHMe}\cdot\text{OMe}$  with complete retention of configuration.<sup>7</sup> Theoretical calculations of the preferred conformations<sup>8</sup> for the related series of carbenes  $\ddot{\text{C}}\text{F}_2$ ,  $\ddot{\text{C}}\text{HF}$ ,  $\text{CF}_3\cdot\ddot{\text{C}}\text{H}$ , and  $(\text{CF}_3)_2\ddot{\text{C}}$  have indicated singlet states with  $R-\ddot{\text{C}}-R$  bond angles of *ca.* 110°.

In the present work the reactions of the carbene (II) with the silanes  $R_3SiH$  ( $R_3 = Et_3, Et_2Me, \text{ or } Me_3$ ),  $Me_3SiD$ ,  $X_3SiCl$  ( $X_3 = Cl_3, Cl_2Me, ClMe_2, \text{ or } Me_3$ ),  $Me_3SiBr$ ,  $X_3SiH$  ( $X_3 = Cl_3, Cl_2Me, \text{ or } ClMe_2$ ),  $X_3Si\cdot\text{CH}\cdot$

<sup>1</sup> Part XII, R. N. Haszeldine, R. V. Parish, and R. J. Taylor, *J.C.S. Dalton*, 1974, 2311.

<sup>2</sup> Preliminary communication, R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, *Chem. Comm.*, 1969, 1364.

<sup>3</sup> W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. and Ind.*, 1961, 789; R. N. Haszeldine, P. J. Robinson, and R. F. Simmons, *J. Chem. Soc.*, 1964, 1890.

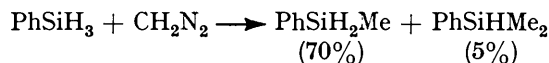
<sup>4</sup> G. Fishwick, R. N. Haszeldine, C. Parkinson, P. J. Robinson, and R. F. Simmons, *Chem. Comm.*, 1965, 382.

$\text{CH}_2$  ( $X_3 = Cl_3 \text{ or } Me_2H$ ), and  $Me_2SiH\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$  have been investigated.

*Reaction of the Carbene (II) with Trialkylsilanes.*—The thermal decomposition of the carbene precursor (I) at 150 °C in the presence of triethylsilane, diethylmethylsilane, or trimethylsilane (1 : 3 molar ratio) afforded silicon tetrafluoride (100%), unchanged trialkylsilane (67% recovered), trifluoroethylene (1–2%), and products of the type  $CHF_2 \cdot CHF \cdot SiR_3$  (IV) ( $R_3 = Et_3, Et_2Me, \text{ or } Me_3$ ) (98–99%), formed by insertion into the Si-H bonds. Products formed by the insertion of (II) into C-H bonds were not detected.

The products (IV) were identified by n.m.r. spectroscopy; the low-field region of the <sup>1</sup>H n.m.r. spectra showed two absorptions of equal intensity centred at  $\tau$  3.97–4.02 ( $\text{CHF}_2$ ) and 5.40–5.55 ( $\text{CHF}$ ), and the high-field region showed absorptions ( $\tau$  8.8–9.8) for methylene and methyl protons in the methyl and ethyl groups. The <sup>19</sup>F n.m.r. spectra showed absorptions at *ca.* 47 ( $\text{CHF}_2$ ) and *ca.* 165 p.p.m. ( $\text{CHF}$ ) to high field of trifluoroacetic acid. The adjacent asymmetric centre makes the two fluorine nuclei of the  $\text{CHF}_2$  group magnetically non-equivalent; consequently they exhibit an AB pattern. However, the outer bands of the AB pattern were not observed and so  $J_{AB}$  could not be determined. The chemical shifts of the hydrogen and fluorine nuclei of the  $\text{CHF}_2 \cdot \text{CHF} \cdot \text{Si}$  group and the observed coupling constants are in agreement with previously determined values.<sup>9</sup>

The insertion of methylene, formed by decomposition of diazomethane, into Si-H bonds was reported in



1962.<sup>10</sup> Since then Seyferth and his co-workers have

<sup>5</sup> R. N. Haszeldine and J. G. Speight, unpublished results; J. Lee, C. Parkinson, P. J. Robinson, and J. G. Speight, *J. Chem. Soc. (B)*, 1967, 1125.

<sup>6</sup> R. N. Haszeldine and J. G. Speight, *Chem. Comm.*, 1967, 995.

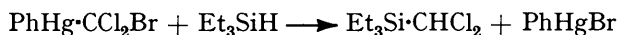
<sup>7</sup> J. M. Birchall, R. N. Haszeldine, and T. K. Dempsey, unpublished results.

<sup>8</sup> R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, 1968, 90, 1485.

<sup>9</sup> D. Cooper, R. N. Haszeldine, and M. J. Newlands, unpublished results.

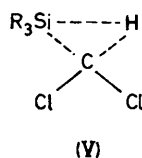
<sup>10</sup> K. Kramer and A. N. Wright, *J. Chem. Soc.*, 1963, 3604.

studied extensively the synthetic and mechanistic aspects of the insertion of mercurial-derived dihalogenocarbenes into the Si-H bonds of trialkyl- and aryl-silanes,<sup>11,12</sup> e.g.



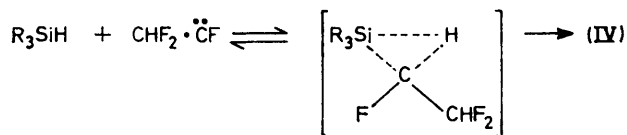
Diphenylcarbene and ethoxycarbonylcarbene, formed by the decomposition of the corresponding diazo-compounds, also insert into Si-H bonds.<sup>13</sup>

It has been suggested<sup>12</sup> that the insertion of dichlorocarbene into Si-H bonds takes place by a one-step reaction involving a slightly polar transition state of the type (V), formed by electrophilic attack of the carbene on the



Si-H bond, which collapses to give the observed products. Evidence for a transition state of type (V) has been provided by the retention of configuration observed in the products from insertion of the carbenes  $\ddot{\text{C}}\text{Cl}_2$  and  $\ddot{\text{C}}\text{Br}_2$  into the Si-H bond of the optically active methyl-(1-naphthyl)phenylsilane.<sup>14</sup> In contrast the insertion of triplet diphenylcarbene into the Si-H bond of this silane results in racemic products formed *via* a two-step mechanism.<sup>14</sup>

It is considered probable that insertion of the carbene (II) into the Si-H bonds of the trialkylsilanes studied to give the products (IV) also takes place *via* an analogous one-step mechanism (Scheme 1).



SCHEME 1

The observation that the carbene (II) inserts into the tertiary C-H bond of isobutane in only 61% yield under analogous conditions<sup>6</sup> indicates a lower reactivity of the tertiary C-H bond towards carbene (II) insertion than of the Si-H bond in trimethylsilane (99% yield). Products formed by insertion into the primary C-H bonds of the methyl groups were not observed in either case.

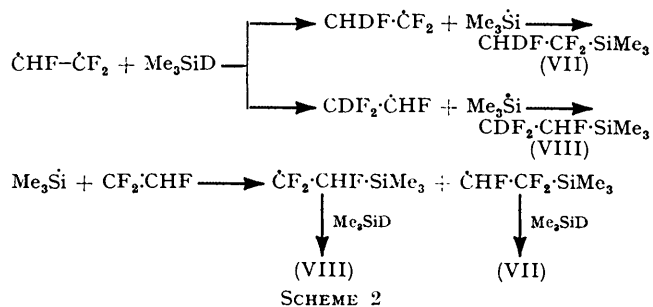
The silane  $\text{CHF}_2\cdot\text{CHF}\cdot\text{SiMe}_3$ , together with the isomeric silane  $\text{CH}_2\text{F}\cdot\text{CF}_2\cdot\text{SiMe}_3$  (ratio *ca.* 60:40), has previously been obtained by the photochemical addition of trimethylsilane to trifluoroethylene.<sup>9</sup> It was therefore considered possible that the Si-H insertion products (IV) were formed *via* reaction of an excited trifluoroethylene species generated by rearrangement of the carbene (II).

<sup>11</sup> D. Seyferth and J. M. Burlitch, *J. Amer. Chem. Soc.*, 1963, **85**, 2667.

<sup>12</sup> D. Seyferth, R. Damrauer, J. Yick-Pui Mui, and T. J. Jula, *J. Amer. Chem. Soc.*, 1968, **90**, 2944.

In order to determine if this were the case, decomposition of the carbene precursor (I) in the presence of an excess of deuteriotrimethylsilane was investigated. This gave silicon tetrafluoride (100%), trifluoroethylene (12%), and a single adduct (88%). The adduct was identified as having the structure  $\text{CHF}_2\cdot\text{CDF}\cdot\text{SiMe}_3$  (VI) on the basis of its <sup>1</sup>H and <sup>19</sup>F n.m.r. spectra; <sup>1</sup>H n.m.r. bands at  $\tau$  4.03 (1H, td,  $\text{CHF}_2$ ) and 9.83 (9H,  $\text{SiMe}_3$ ) and <sup>19</sup>F n.m.r. bands at 47.0 (2F, ABdd,  $\text{CHF}_2\text{F}_2$ ) and 162.5 p.p.m. (1F, tdt, CDF) to high field of trifluoroacetic acid. The absence of a <sup>1</sup>H n.m.r. band for a CHF system and the observation that the <sup>19</sup>F 162.5 p.p.m. band exhibited a 1:1:1 triplet splitting (*J* 10.0 Hz), assigned to geminal F-D coupling, showed conclusively that the adduct had structure (VI).

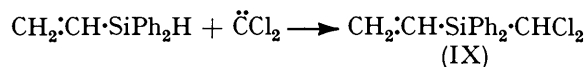
If an activated trifluoroethylene species were involved, the silanes (VII) and (VIII) would be expected to be formed by the sequence shown in Scheme 2. Since



adduct (VI) [and not adduct (VII) or (VIII)] was formed the reaction with both Si-D and Si-H bonds is considered to involve the carbene (II) as the reactive intermediate and not an activated trifluoroethylene species.

The yield of adduct (VI) (88%) is lower than that of adduct (IV) (99%) obtained from insertion into the Si-H bond of trimethylsilane. This indicates that, as expected, insertion into an Si-D bond is slightly less favourable than insertion into an Si-H bond.

*Reactions of the Carbene (II) with Dimethylvinylsilane and Allyldimethylsilane.*—The decomposition of the mercurial  $\text{PhHg}\cdot\text{CCl}_2\text{Br}$  in a mixture of triethylsilane and cyclohexene has indicated that the Si-H bond is only 0.8 times as reactive as the olefinic double bond towards attack by dichlorocarbene.<sup>12</sup> Reaction of diphenylvinylsilane with dichlorocarbene afforded only the Si-H insertion product (IX), indicating that a double bond adjacent to silicon is considerably deactivated towards carbene attack.<sup>15</sup>



The present study of the comparative reactivities of the Si-H and C=C bonds in the silanes  $\text{CH}_2\cdot\text{CH}\cdot\text{SiMe}_2\text{H}$  and

<sup>13</sup> A. Ritter and L. H. Sommer, International Symposium on Organosilicon Chemistry, *Sci. Comm. Prague*, 1965, 279.

<sup>14</sup> L. H. Sommer, L. A. Ulland, and A. Ritter, *J. Amer. Chem. Soc.*, 1968, **90**, 4486.

<sup>15</sup> D. Seyferth, J. M. Burlitch, H. Dertouzos, and H. D. Simmons, *J. Organometallic Chem.*, 1967, **7**, 405.

$\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{-SiMe}_2\text{H}$  towards carbene (II) attack has shown (Table 1) that in both cases Si-H insertion is the

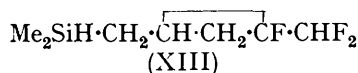
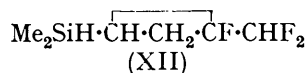
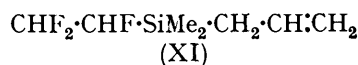
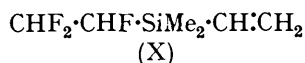
TABLE 1

Reaction of the carbene  $\text{CHF}_2\cdot\ddot{\text{C}}\text{F}$  with vinylsilanes

Silane	Products (% yield) *	
	Si-H Insertion	C=C Addition
$\text{CH}_2\text{:CH}\cdot\text{SiMe}_2\text{H}$	(X) (93)	(XII) (7)
$\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{-SiMe}_2\text{H}$	(XI) (67)	(XIII) (33)

\* Determined by repeated integration of  $^1\text{H}$  and  $^{19}\text{F}$  n.m.r. spectra ( $\pm 3\%$ ).

predominant, though not exclusive, reaction. The products (X)—(XIII) were characterised by  $^1\text{H}$  and  $^{19}\text{F}$  n.m.r. spectroscopy since g.l.c. columns suitable for the complete separation of the products were not found. The cyclopropanes (XII) and (XIII) were both shown by



n.m.r. to be present as mixtures of *cis*- and *trans*-isomers (ratio 1 : 2) and, on the basis of the identified products from previously reported additions of carbene (II) to olefins,<sup>5</sup> the *trans*-isomers are presumed to be the major components.

Since the carbene (II) rearrangement products were not detected in these reactions it is probable that the reactivities of the Si-H bonds towards insertion are of the

cess. Such an explanation has been proposed previously to account for the low reactivity of the olefinic double bonds in trialkylvinylsilanes towards dichlorocarbene addition.<sup>16,17</sup> These effects are greatest when the double bond is adjacent to silicon and decrease as the number of intervening  $\text{CH}_2$  groups increases.

*Reaction of the Carbene (II) with the Silanes  $\text{Me}_n\text{SiCl}_{4-n}$  ( $n = 0-3$ ) and  $\text{Me}_3\text{SiBr}$ .*—Decomposition of the carbene precursor (I) in the presence of an excess of each of the silanes  $\text{SiCl}_4$ ,  $\text{MeSiCl}_3$ ,  $\text{Me}_2\text{SiCl}_2$ ,  $\text{Me}_3\text{SiCl}$ , and  $\text{Me}_3\text{SiBr}$  yielded products formed by insertion of the carbene (II) into a silicon-halogen bond (Table 2). In addition quantitative yields of silicon tetrafluoride together with the carbene rearrangement products trifluoroethylene and *cis*- and *trans*-(III) were obtained. Products arising from the insertion of carbene (II) into the C-H bonds of the chloromethylsilanes and bromotrimethylsilane were not detected.

The  $^1\text{H}$  n.m.r. spectra of the insertion products all showed absorption at  $\tau$  ca. 4.0 ( $\text{CHF}_2$ ) and those which contained methyl groups showed absorptions in the region  $\tau$  9.0—9.95. The  $^{19}\text{F}$  n.m.r. spectra all showed absorption at ca. 46 p.p.m. ( $\text{CHF}_2$ , AB pattern) and absorption at either 73.5—74.5 ( $\text{CFCl}$ ) or 77.0 p.p.m. ( $\text{CFBr}$ ). The chemical shifts and coupling constants were in agreement with those determined previously for the same groups in similar compounds.<sup>18,19</sup>

The silane  $\text{CHF}_2\cdot\text{CFCl}\cdot\text{SiCl}_3$  has been observed to undergo rearrangement on pyrolysis at 160 °C (20 h) to afford the silane  $\text{CHF}_2\cdot\text{CCl}_2\cdot\text{SiFCl}_2$  (85%).<sup>20</sup> In the present work, however, no rearrangement by Cl-F exchange of this or any other adduct containing Si-Cl bonds shown in Table 2 was observed under the conditions employed (150 °C; 6 h).

The statistical yields of Si-Cl insertion products provide an indication of the relative reactivity of the Si-Cl

TABLE 2

Reaction of the carbene  $\text{CHF}_2\cdot\ddot{\text{C}}\text{F}$  with halogenosilanes

Silane	Products (% yield)			Insertion product	Statistical yield of insertion product *	
	$\text{SiF}_4$	$\text{CF}_2\cdot\text{CHF}$	(III)			
$\text{SiCl}_4$	100	50	46	$\text{CHF}_2\cdot\text{CFCl}\cdot\text{SiCl}_3$	4	1
$\text{MeSiCl}_3$	100	45	45	$\text{CHF}_2\cdot\text{CFCl}\cdot\text{SiCl}_2\text{Me}$	10	3.3
$\text{Me}_2\text{SiCl}_2$	100	45	40	$\text{CHF}_2\cdot\text{CFCl}\cdot\text{SiClMe}_2$	15	7.5
$\text{Me}_3\text{SiCl}$	100	54	44	$\text{CHF}_2\cdot\text{CFCl}\cdot\text{SiMe}_3$	2	2
$\text{Me}_3\text{SiBr}$	100	54	38	$\text{CHF}_2\cdot\text{CFBr}\cdot\text{SiMe}_3$	8	8

\* Based on the number of silicon-halogen bonds available for insertion.

same order as those of Si-H bonds in trialkylsilanes. The olefinic double bonds, however, show less reactivity towards addition by carbene (II) than those in hydrocarbon olefins. This is probably due mainly to a decrease in the nucleophilicity of the olefinic double bond caused by overlap of the  $\pi$ -cloud with vacant *d* orbitals on silicon and also to the destabilising effect of the electropositive silicon atom on the transition state of the addition pro-

<sup>19</sup> J. Cudlin and V. Chvalovský, *Coll. Czech. Chem. Comm.*, 1962, **27**, 1658; 1963, **28**, 3088.

<sup>17</sup> D. Seyferth and H. Dertouzos, *J. Organometallic Chem.*, 1968, **11**, 263.

bonds in the individual silanes towards insertion by (II). This order was found to be  $\text{Me}_2\text{SiCl}_2 > \text{MeSiCl}_3 > \text{Me}_3\text{SiCl} > \text{SiCl}_4$ , and the Si-Br bond in bromotrimethylsilane was found to be ca. 4 times more reactive towards insertion than the Si-Cl bond in chlorotrimethylsilane.

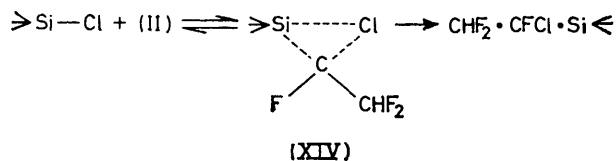
Mechanisms involving a radical abstraction process or

<sup>18</sup> W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, unpublished results.

<sup>19</sup> J. Dyer and J. Lee, *Spectrochim. Acta*, 1970, **26A**, 1045.

<sup>20</sup> T. L. Cottrell, 'The Strengths of Chemical Bonds,' 2nd edn., Butterworths, London, 1958.

initial nucleophilic attack on the silicon atoms of the halosilanes are unlikely because the expected order of reactivity for both processes,  $\text{SiCl}_4 > \text{MeSiCl}_3 > \text{Me}_2\text{SiCl}_2 > \text{Me}_3\text{SiCl}$ , was not observed. It is thus probable that the insertions involve initial electrophilic attack by carbene (II) at the chlorine atom followed closely by interaction of the filled  $sp^2$  orbital of the singlet carbene with the  $d$  orbital system of the silicon atom to afford a three-centre transition state (XIV).



The activation energy for formation of the transition state (XIV) would be expected to be greater than that for formation of the corresponding  $\text{>Si-H}$  transition state on account of the higher Si-Cl bond strength (ca. 91

which breaks down to afford the observed products.<sup>22,25</sup> In addition many of these reactions were carried out in the presence of copper powder or copper salts and it has recently been reported that the intermediacy of a free carbene is doubtful in such reactions.<sup>26</sup>

*Reaction of the Carbene (II) with Silanes containing both Si-H and Si-Cl Bonds.*—The insertion products obtained from decomposition of the carbene precursor (I) at 150 °C (6 h) in the presence of a 2.5 : 1 molar ratio of dimethylchlorosilane, methylchlorosilane, or trichlorosilane are shown in Table 3. In all cases a quantitative yield of silicon tetrafluoride and products resulting from rearrangement of the carbene (II) was also obtained.

Differentiation between products containing the grouping  $\text{CHF}_2 \cdot \text{CFCl} \cdot \text{Si}$ , i.e. Si-Cl insertion products, and those containing the grouping  $\text{CHF}_2 \cdot \text{CHF} \cdot \text{Si}$ , i.e. Si-H insertion products, was achieved by n.m.r. and i.r. spectroscopy. The former products showed a strong i.r. absorption at ca. 4.6  $\mu\text{m}$  (Si-H str.) and characteristic  $^{19}\text{F}$  n.m.r. absorption at ca. 76 p.p.m. (relative to trifluoroacetic

TABLE 3

Reaction of the carbene (II) with silanes containing both Si-H and Si-Cl bonds

Silane	Insertion products				Statistical ratio of insertion products (Si-H : Si-Cl) *
	Si-H	%	Si-Cl	%	
$\text{Me}_2\text{ClSiH}$	$\text{CHF}_2 \cdot \text{CHF} \cdot \text{SiClMe}_2$	96		†	$\infty$
$\text{MeCl}_2\text{SiH}$	$\text{CHF}_2 \cdot \text{CHF} \cdot \text{SiCl}_2\text{Me}$	29	$\text{CHF}_2 \cdot \text{CFCl} \cdot \text{SiHClMe}$ ‡	29	2 : 1
$\text{Cl}_3\text{SiH}$	$\text{CHF}_2 \cdot \text{CHF} \cdot \text{SiCl}_3$	10	$\text{CHF}_2 \cdot \text{CFCl} \cdot \text{SiHCl}_2$	43	0.8 : 1

\* Based on number of Si-H and Si-Cl bonds available. † Less than 2% would have been detected. ‡ Two isomers present in ratio 1 : 1.

kcal mol<sup>-1</sup>) as compared with the Si-H bond strength (ca. 76 kcal mol<sup>-1</sup>).<sup>20</sup>

The anomalous position of chlorotrimethylsilane in the reactivity order is difficult to explain. The covalent radii of the chlorine atom and the methyl group are approximately the same<sup>21</sup> and so the factors determining the low reactivity are probably the exact Si-Cl bond strength and the Cl-Si-Me bond angle; detailed information on these is not available. Although the Si-Br bond in bromotrimethylsilane is ca. four times more reactive towards insertion by the carbene (II) than the Si-Cl bond in chlorotrimethylsilane, the relatively low Si-Br bond strength<sup>22</sup> (ca. 74 kcal mol<sup>-1</sup>) would be expected to result in a much higher yield of insertion product than observed.

The reactions of diazomethane with a variety of metal halides have been reported previously, and with the chlorosilanes investigated products formed by insertion of a  $\text{CH}_2$  group into the Si-Cl bond were isolated.<sup>23</sup> Similar results were later obtained by other workers,<sup>22,24</sup> but it is probable that these reactions do not involve free methylene but rather a diazomethane-silicon complex

acid) assigned to the CFCl group, whereas the latter showed no i.r. absorption band at ca. 4.6  $\mu\text{m}$  but the  $^{19}\text{F}$  n.m.r. spectra showed an absorption at ca. 157 p.p.m. assigned to CHF ( $J_{\text{FH}}$  ca. 45.5 Hz).

The reactivity of the Si-H bond in the silanes decreases as methyl groups are successively replaced by chlorine. It is interesting that the silane  $\text{Me}_2\text{ClSiH}$  affords only the Si-H insertion product and the yield of this compound (96%) indicates that a single chlorine atom does not appreciably deactivate the Si-H bond towards insertion by carbene (II) as compared with the trialkylsilanes studied (yields 98–99%). However, when two or three chlorine atoms are present, i.e. in the silanes  $\text{MeCl}_2\text{SiH}$  and  $\text{Cl}_3\text{SiH}$ , considerable deactivation of the Si-H bond towards insertion is observed. This deactivation is probably due to (i) the strong  $-I$  inductive effect of chlorine which decreases the electron density at the Si-H bond, thus rendering it less susceptible to electrophilic attack by the carbene (II) and (ii) increased steric inhibition to attack on Si-H.

As the reactivity of the Si-H bond towards insertion decreases, a corresponding increase in the reactivity of the Si-Cl bonds towards insertion is observed. The

<sup>21</sup> L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

<sup>22</sup> R. A. Shaw, *J. Chem. Soc.*, 1957, 2831.

<sup>23</sup> A. Ya. Yakubovich, S. P. Makarov, V. A. Ginsburg, G. I. Gavrilo, and E. N. Merkulova, *Doklady Akad. Nauk S.S.S.R.*, 1950, **72**, 69; A. Ya. Yakubovich and V. A. Ginsburg, *J. Gen. Chem. (U.S.S.R.)*, 1952, **22**, 1783.

<sup>24</sup> D. Seyferth and E. G. Rochow, *J. Amer. Chem. Soc.*, 1955, **77**, 907; K. Kramer and A. N. Wright, *Chem. Ber.*, 1963, **96**, 1877.

<sup>25</sup> D. Seyferth, *Chem. Rev.*, 1955, **55**, 1155.

<sup>26</sup> E. Muller, H. Kessler, and B. Zech, *Fortschr. Chem. Forsch.*, 1966, **7**, 128; W. R. Moser, *J. Amer. Chem. Soc.*, 1969, **91**, 1135 and 1141.

yields of Si-Cl insertion products obtained with the silanes  $\text{MeCl}_2\text{SiH}$  and  $\text{Cl}_3\text{SiH}$  (29 and 43%, respectively) are appreciably higher than those obtained from silanes  $\text{Me}_{4-n}\text{SiCl}_n$  containing only Si-Cl and Si-Me linkages (2–15%). The replacement of a methyl group or a chlorine atom by the smaller hydrogen atom thus apparently enables the carbene (II) to approach the Si-Cl bond more easily and also results in a decrease in steric hindrance in the transition state. These factors thus allow insertion into the Si-Cl bond to compete effectively with insertion into the deactivated Si-H bond in the silanes  $\text{MeCl}_2\text{SiH}$  and  $\text{Cl}_3\text{SiH}$ .

The observation that carbene (II) inserts into both the Si-H and Si-Cl bonds of dichloro(methyl)silane and trichlorosilane is in contrast to the copper-catalysed decomposition of diazomethane in the presence of trichlorosilane which afforded the Si-Cl insertion product only.<sup>25</sup>

*Reaction of the Carbene (II) with Trichloro(vinyl)silane.*

—This reaction was investigated in order to determine whether Si-Cl insertion by the carbene (II) could compete successfully with carbene addition to the olefinic double bond. Decomposition of the carbene precursor (I) at 150 °C (6 h) in the presence of an excess of trichloro(vinyl)silane (3 : 1 molar ratio) gave silicon tetrafluoride (100%), trifluoroethylene (34%), and a mixture of *cis*- and *trans*-1-difluoromethyl-1-fluoro-2-trichlorosilylcyclopropane (66%) in the ratio 1 : 2. Products formed by insertion of the carbene (II) into an Si-Cl bond were not detected. The assignments of the *cis*- and *trans*-structures to the separated isomers were made on the basis of the <sup>19</sup>F n.m.r. spectra: the absorption of the tertiary fluorine in the *cis*-isomer is at considerably lower field (110.8 p.p.m.) than that in the *trans*-isomer (127.5 p.p.m.) because of the greater deshielding effect of the trichlorosilyl group when it is *cis* to the fluorine. The observed *cis* : *trans* ratio of 1 : 2 compares well with the same ratio of *cis*- and *trans*-cyclopropanes formed in the reaction of the carbene (II) with the but-2-enes<sup>5</sup> and with dimethylvinylsilane and allyldimethylsilane.

The yield of cyclopropanes obtained in the present reaction (66%) is considerably lower than those obtained from reactions of the carbene (II) with hydrocarbon olefins.<sup>5</sup> This deactivation of the double bond towards carbene (II) addition is probably due to the same factors as put forward to explain the decreased reactivities of dimethylvinylsilane and allyldimethylsilane (see earlier).

#### EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum system in order to avoid contamination with air or moisture. Reactions involving the decomposition of 1,1,2,2-tetrafluoroethyltrifluorosilane (I), were carried out in Pyrex bulbs (capacity *ca.* 2, 3, or 5 l) fitted with a side arm, at pressures of *ca.* 1 atm. Pure compounds were isolated by repeated fractional condensation *in vacuo* or by preparative scale g.l.c. [Pye 105 or Perkin-Elmer 452 instrument with 2–10 m columns packed with Silicone SE 30 or MS 550 oil, dinonyl phthalate, or Apiezon L grease

(10–25%) on Celite or Chromosorb W]. 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 <sup>1</sup>H and 56.46 MHz for <sup>19</sup>F, or a Varian HA100 spectrometer operating at 100.0 MHz for <sup>1</sup>H and 94.1 MHz for <sup>19</sup>F). Tetramethylsilane was used as reference for <sup>1</sup>H spectra and trifluoroacetic acid as reference for <sup>19</sup>F spectra. For compounds marked with an asterisk, detailed n.m.r. and i.r. data are available in Supplementary Publication No. SUP 21095 (12 pp., 1 microfiche).† A double asterisk indicates that n.m.r. data only are available.

1,1,2,2-Tetrafluoroethyltrifluorosilane was prepared by the method reported previously.<sup>3,4</sup> Other starting materials not available commercially were prepared *via* literature methods and were carefully purified before use.

*Decomposition of 1,1,2,2-Tetrafluoroethyltrifluorosilane (I) in the Presence of Silanes.*—(a) *Triethylsilane.* A mixture of triethylsilane (10.40 g, 90.0 mmol) and the silane (I) (5.58 g, 30.0 mmol), heated at 150° (6 h), gave (i) silicon tetrafluoride (3.12 g, 30.0 mmol, 100%), (ii) trifluoroethylene (0.05 g, 0.60 mmol, 2%), (iii) unchanged triethylsilane (7.0 g, 60.5 mmol, 67% recovered), and (iv) *triethyl-(1,2,2-trifluoroethyl)silane* \* (5.82 g, 29.4 mmol, 98%) (Found: C, 48.1; H, 8.4.  $\text{C}_8\text{H}_{17}\text{F}_3\text{Si}$  requires C, 48.4; H, 8.6%), b.p. 169–170°.

(b) *Diethylmethylsilane.* A mixture of diethylmethylsilane (10.20 g, 90.0 mmol) and the silane (I) (5.58 g, 30.0 mmol), heated at 150° (6 h), gave (i) silicon tetrafluoride (3.12 g, 30.0 mmol, 100%), (ii) trifluoroethylene (0.05 g, 0.60 mmol, 2%), (iii) unchanged diethylmethylsilane (6.16 g, 60.5 mmol, 67% recovered), and (iv) *diethylmethyl-(1,2,2-trifluoroethyl)silane* \* (5.42 g, 29.4 mmol, 98%) (Found: C, 45.7; H, 8.2.  $\text{C}_7\text{H}_{15}\text{F}_3\text{Si}$  requires C, 45.6; H, 8.2%), b.p. 142°.

(c) *Trimethylsilane.* A mixture of trimethylsilane (6.67 g, 90.0 mmol) and the silane (I) (5.58 g, 30.0 mmol), heated at 150° (6 h), gave (i) silicon tetrafluoride (3.12 g, 30.0 mmol, 100%), (ii) trifluoroethylene (0.02 g, 0.30 mmol, 1%), (iii) unchanged trimethylsilane (4.44 g, 60.0 mmol, 67% recovered), and (iv) *trimethyl-1,2,2-trifluoroethylsilane* \*\* (4.64 g, 29.7 mmol, 99%) (Found: C, 38.6; H, 6.9. Calc. for  $\text{C}_5\text{H}_{11}\text{F}_3\text{Si}$ : C, 38.4; H, 7.0%), b.p. 82–83°, the i.r. spectrum of which was identical with that of a previously prepared sample.<sup>9</sup>

(d) *Deuteriotrimethylsilane.* A mixture of deuteriotrimethylsilane (1.72 g, 23.0 mmol) and the silane (I), heated at 150° (6 h), gave (i) silicon tetrafluoride (2.49 g, 23.0 mmol, 100%), (ii) trifluoroethylene (0.23 g, 2.8 mmol, 12%), (iii) unchanged deuteriotrimethylsilane (0.21 g, 2.8 mmol, 12% recovered), and (iv) *1-deuterio-1,2,2-trifluoroethyltrimethylsilane* \* (3.17 g, 20.2 mmol, 88%) (Found: C, 38.2; H + D, 7.7.  $\text{C}_5\text{H}_{10}\text{DF}_3\text{Si}$  requires C, 38.2; H + D, 7.7%), b.p. 95°.

(e) *Dimethyl(vinyl)silane.* A mixture of dimethyl(vinyl)silane (7.74 g, 90.0 mmol) and the silane (I) (6.94 g, 37.3 mmol), heated at 150° (6 h), gave (i) silicon tetrafluoride (3.88 g, 37.3 mmol, 100%), (ii) unchanged dimethyl(vinyl)silane (4.55 g, 52.9 mmol, 59% recovered), and (iii) a fraction (6.42 g, 37.1 mmol, 99.5%) (Found: C, 43.1; H, 6.6. Calc.

† For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1973, Index issue.

for  $C_6H_{11}F_3Si$ : C, 42.8; H, 6.5%) which was shown by g.l.c. and n.m.r. spectroscopy to consist of a major component A (93%) and two isomeric compounds B and C (7%). The components could not be separated completely by preparative-scale g.l.c. on a number of different columns. Component A was identified by n.m.r. spectroscopy as dimethyl-(1,2,2-trifluoroethyl)vinylsilane.\*\* Components B and C were identified as the *cis*- and *trans*-isomers\*\* of 1-difluoromethyl-2-dimethylsilyl-1-fluorocyclopropane in the ratio 1:2.

(f) *Allyldimethylsilane*. A mixture of allyldimethylsilane (9.0 g, 90.0 mmol) and the silane (I) (6.94 g, 37.3 mmol), heated at 150° (6 h), gave (i) silicon tetrafluoride (3.88 g, 37.3 mmol, 100%), (ii) unchanged allyldimethylsilane (5.30 g, 53.0 mmol, 59% recovered), and (iii) a fraction (6.73 g, 37.0 mmol, 99%) (Found: C, 46.1; H, 7.2. Calc. for  $C_7H_{13}F_3Si$ : C, 46.1; H, 7.2%) which was shown by g.l.c. and n.m.r. spectroscopy to consist of a major component D (66.5%) and two isomeric compounds E and F (32.5%); an attempted separation of the components by preparative-scale g.l.c. on a variety of columns was unsuccessful. Component D was identified as allyldimethyl-(1,2,2-trifluoroethyl)silane.\*\* Components E and F were identified as *cis*- and *trans*-1-difluoromethyl-2-(dimethylsilylmethyl)-1-fluorocyclopropane,\*\* respectively, and were present in the ratio 1:2.

(g) *Silicon tetrachloride*. A mixture of silicon tetrachloride (15.30 g, 90.0 mmol) and the silane (I) (6.96 g, 37.5 mmol), heated at 150° (6 h), gave (i) silicon tetrafluoride (3.79 g, 37.5 mmol, 100%), (ii) trifluoroethylene (1.51 g, 18.4 mmol, 50%), (iii) a mixture (1.38 g, 8.4 mmol, 46%) of *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane which was identified by a comparison of its i.r. spectrum with that of an authentic sample of the mixture of isomers, (iv) unchanged silicon tetrachloride (15.10 g, 88.5 mmol, 98% recovered), and (v) trichloro-(1-chloro-1,2,2-trifluoroethyl)silane (0.36 g, 1.4 mmol, 4%) (Found: C, 9.4; H, 0.5. Calc. for  $C_2HCl_4F_3Si$ : C, 9.5; H, 0.4%), b.p. 119° (lit.,<sup>27</sup> 116—118°), identified by a comparison of its <sup>1</sup>H and <sup>19</sup>F n.m.r. spectra with those reported.<sup>18,19</sup>

(h) *Trichloro(methyl)silane*. A mixture of trichloro(methyl)silane (13.45 g, 90.0 mmol) and the silane (I) (6.50 g, 35.0 mmol), heated at 150° (6 h), gave (i) silicon tetrafluoride (3.64 g, 35.0 mmol, 100%), (ii) trifluoroethylene (1.29 g, 15.7 mmol, 45%), (iii) a mixture of *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (1.30 g, 7.9 mmol, 45%), (iv) unchanged trichloro(methyl)silane (12.9 g, 86.5 mmol, 96% recovered), and (v) *dichloro*-(1-chloro-1,2,2-trifluoroethyl)methylsilane\* (0.79 g, 3.4 mmol, 10%) (Found: C, 15.2; H, 1.8.  $C_3H_4Cl_3F_3Si$  requires C, 15.5; H, 1.7%), b.p. 115°.

(j) *Dichlorodimethylsilane*. A mixture of dichlorodimethylsilane (11.60 g, 90.0 mmol) and the silane (I) (6.96 g, 37.5 mmol), heated at 150° (6 h), gave (i) silicon tetrafluoride (3.90 g, 37.5 mmol, 100%), (ii) trifluoroethylene (1.39 g, 16.9 mmol, 45%), (iii) a mixture of *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (1.23 g, 7.5 mmol, 40%), (iv) unchanged dichlorodimethylsilane (10.90 g, 84.4 mmol, 93% recovered), and (v) *chloro*-(1-chloro-1,2,2-trifluoroethyl)dimethylsilane\* (1.19 g, 5.6 mmol, 15%) (Found: C, 22.7; H, 3.5.  $C_4H_7Cl_2F_3Si$  requires C, 22.8; H, 3.3%), b.p. 135°.

(k) *Chlorotrimethylsilane*. A mixture of chlorotrimethylsilane (9.76 g, 90.0 mmol) and the silane (I) (6.53 g, 35.1 mmol), heated at 150° (6 h), gave (i) silicon tetrafluoride

(3.65 g, 35.1 mmol, 100%), (ii) trifluoroethylene (1.55 g, 19.0 mmol, 54%), (iii) a mixture of *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (1.26 g, 7.7 mmol, 44%), (iv) unchanged chlorotrimethylsilane (9.66 g, 89.0 mmol, 99% recovered), and (v) (1-chloro-1,2,2-trifluoroethyl)-trimethylsilane\* (0.15 g, 0.75 mmol, 2%) (Found: C, 31.8; H, 5.4.  $C_5H_{10}ClF_3Si$  requires C, 31.5; H, 5.3%), b.p. 128°.

(l) *Bromotrimethylsilane*. A mixture of bromotrimethylsilane (13.80 g, 90.0 mmol) and the silane (I) (6.80 g, 36.6 mmol), heated at 150° (6 h), gave (i) silicon tetrafluoride (3.80 g, 36.6 mmol, 100%), (ii) trifluoroethylene (1.62 g, 19.7 mmol, 54%), (iii) a mixture of *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (1.15 g, 7.0 mmol, 38%), (iv) unchanged bromotrimethylsilane (13.32 g, 87.2 mmol, 97% recovered), and (v) (1-bromo-1,2,2-trifluoroethyl)-trimethylsilane\* (0.64 g, 2.7 mmol, 8%) (Found: C, 26.0; H, 4.7.  $C_5H_{10}BrF_3Si$  requires C, 25.5; H, 4.3%), b.p. 145°.

(m) *Chlorodimethylsilane*. A mixture of chlorodimethylsilane (8.60 g, 90.0 mmol) and the silane (I) (6.96 g, 37.5 mmol), heated at 150° (6 h), gave (i) silicon tetrafluoride (3.90 g, 37.5 mmol, 100%), (ii) trifluoroethylene (0.14 g, 1.7 mmol, 4.5%), (iii) unchanged chlorodimethylsilane (5.12 g, 54.2 mmol, 60% recovered), and (iv) *chlorodimethyl*-(1,2,2-trifluoroethyl)silane\* (6.32 g, 35.8 mmol, 95.5%) (Found: C, 27.4; H, 4.7.  $C_4H_8ClF_3Si$  requires C, 27.2; H, 4.5%), b.p. 109°.

(n) *Dichloro(methyl)silane*. A mixture of dichloro(methyl)silane (10.35 g, 90.0 mmol) and the silane (I) (6.96 g, 37.5 mmol), heated at 150° (6 h), gave (i) silicon tetrafluoride (3.90 g, 37.5 mmol, 100%), (ii) trifluoroethylene (0.65 g, 8.0 mmol, 21%), (iii) a mixture of *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (0.56 g, 3.4 mmol, 18%), (iv) unchanged dichloro(methyl)silane (7.83 g, 68.0 mmol, 76% recovered), and (v) a fraction (4.30 g, 21.8 mmol, 58%) which was separated by g.l.c. (8 m Silicone MS 550 at 98°) into its two components, identified as (a) dichloro(methyl)-1,2,2-trifluoroethylsilane\*\* (2.15 g, 10.9 mmol, 29%) (Found: C, 17.8; H, 2.4. Calc. for  $C_3H_5Cl_2F_3Si$ : C, 18.3; H, 2.5%), b.p. 114° (lit.,<sup>9</sup> b.p. 113—114°) and (b) *chloro*-(1-chloro-1,2,2-trifluoroethyl)methylsilane\* (2.15 g, 10.9 mmol, 29%) (Found: C, 18.1; H, 2.2%), b.p. 104—105°, and present as two stereoisomers in the ratio 6:5 (n.m.r.).

(o) *Trichlorosilane*. A mixture of trichlorosilane (12.2 g, 90.0 mmol) and the silane (I) (6.95 g, 37.4 mmol), heated at 150° (6 h), gave (i) silicon tetrafluoride (3.88 g, 37.4 mmol, 100%), (ii) trifluoroethylene (0.76 g, 9.3 mmol, 25%), (iii) a mixture of *cis*- and *trans*-1-difluoromethyl-1,2,2,3-tetrafluorocyclopropane (0.67 g, 4.1 mmol, 22%), (iv) unchanged trichlorosilane (9.50 g, 70.0 mmol, 78% recovered), and (v) a fraction (4.31 g, 19.8 mmol, 53%) which was separated by g.l.c. (8 m Silicone MS 550 at 90°) into its two components, identified as (a) *dichloro*-(1-chloro-1,2,2-trifluoroethyl)silane\* (3.48 g, 16.0 mmol, 43%) (Found: C, 10.9; H, 1.1.  $C_2H_2Cl_3F_3Si$  requires C, 11.0; H, 0.9%), b.p. 97°, and (b) trichloro-1,2,2-trifluoroethylsilane (0.83 g, 3.8 mmol, 10%) (Found: C, 11.3; H, 1.1%), b.p. 104° (lit.,<sup>9</sup> 104°), i.r. and n.m.r. spectra identical with those previously found.<sup>18,19</sup>

(p) *Trichloro(vinyl)silane*. A mixture of trichloro(vinyl)silane (9.70 g, 60.0 mmol) and the silane (I) (3.90 g, 21.0 mmol), heated at 150° (6 h), gave (i) silicon tetrafluoride (2.18 g, 21.0 mmol, 100%), (ii) trifluoroethylene (0.59 g, 7.2 mmol, 34%), (iii) unchanged trichloro(vinyl)silane (6.30 g,

<sup>27</sup> G. W. R. Puerekhauer, *Diss. Abs.*, 1957, 17, 40.

39.0 mmol, 65% recovered), and (iv) a fraction (3.35 g, 13.8 mmol, 66%) which was separated by g.l.c. (8 m Silicone MS 550 at 135°) into its two components (a) *trans*-1-difluoro-1-methyl-1-fluoro-2-trichlorosilylcyclopropane\* (2.23 g, 9.2 mmol, 44%) (Found: C, 20.1; H, 1.9.  $C_4H_4Cl_3F_3Si$  re-

quires C, 19.7; H, 1.7%), b.p. 153°, and (b) *cis*-1-difluoro-1-methyl-1-fluoro-2-trichlorosilylcyclopropane\* (1.12 g, 4.6 mmol, 22%) (Found: C, 20.1; H, 2.0%), b.p. 156°.

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