FLUOROALKYLSILICON COMPOUNDS

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Unless otherwise stated the work described is that of the author and has not been previously submitted in whole or in part at this or any other University.

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Summary of the thesis.

The addition reaction of silicon hydrides with fluoro-olefins is a convenient method for the preparation of fluoroalkylsilicon compounds. A study of the free radical addition reaction of silanes with fluoro-olefins indicates that in certain cases bidirectional addition can take place. The object of the present research was to establish cases of bidirectional addition, and in such cases to attempt a correlation between the isomer ratios of the adducts and the structures of the silyl radicals. The addition reactions of trichlorosilane, methyldichlorosilane and trimethylsilane with the olefins vinyl fluoride, trifluoroethylene and 1-chloro-2-fluoroethylene are reported.

The addition reactions of trichlorosilane, methyldichlorosilane and trimethylsilane with vinyl fluoride give exclusive addition at the $=CH_2$ group. This suggests that the intermediate radical $CHF \cdot \overset{\bullet}{C}H_2 \cdot SiX_3$ is more stable than the radical $\overset{\bullet}{C}H_2 \cdot CHF \cdot SiX_3$. The structures of the adducts were determined by means of nuclear magnetic resonance spectroscopy. The absence of the adducts derived from

the less stable radical, e.g., $CH_3 \cdot CHF \cdot SiX_3$, was checked by synthesis of these compounds (X=Cl and Me).

The addition reaction of trichlorosilane with trifluoroethylene gives exclusive addition at the =CHF group, but the addition reactions of methyldichlorosilane and trimethylsilane with this olefin are bidirectional. The isomer ratios indicate that the order of electrophilicity of the radicals is $Cl_3Si > Cl_2MeSi > Me_3Si$.

The structures were determined by nuclear magnetic resonance spectroscopy and were confirmed by synthesis (for adducts with trichlorosilane and with trimethylsilane).

The addition reaction of trichlorosilane with 1-chloro-2-fluoroethylene is bidirectional but the addition reaction of trimethylsilane with this olefin takes place exclusively at the =CHF group. This indicates that the trichlorosilyl radical is more electrophilic than the trimethylsilyl radical, $Cl_3Si > Me_3Si$. Further reaction of the excess of the silane with the adducts takes place. This gives rise to the formation of reduced adducts and consequent alteration of the isomer ratios of the 1:1 adducts.

The hydrolysis, pyrolysis, and in one case, the fluorination reactions of the adducts have been studied as a means of indicating the isomer ratios of the adducts. Chemical evidence of this nature is ambiguous in the absence of nuclear magnetic resonance data.

C O N T E N T S.

INTRODUCTION.

INTRODUCTION

Organosilicon compounds have become well known in the last two decades because of the technological importance of siloxane polymers, but the history of organosilicon chemistry dates back to 1840 when the possible existence of organosilicon compounds was realised by Dumas. Buff and Wohler [1] in 1857 observed the formation of a compound later shown to be trichlorosilane, and Friedel and Crafts [2] later prepared the first organosilicon compound by the reaction of diethylzinc with silicon tetrachloride.

$$2(C_2H_5)_2Zn + SiCl_4 \longrightarrow Si(C_2H_5)_4 + 2ZnCl_2$$
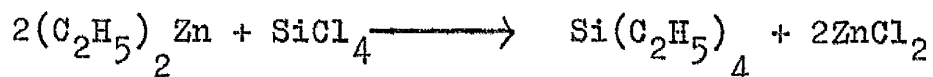
It was soon established that the silicon-chlorine bond was easily broken by water and by ethyl alcohol,[3] and that viscous oils similar in composition to modern silicone fluids were formed by hydrolysis of ethoxysilanes such as diethoxydiethylsilane.[4]

$$(C_2H_5)_2SiCl_2 + 2C_2H_5OH \longrightarrow \left[(C_2H_5)_2Si(OC_2H_5)_2\right] + 2HCl$$

$$n\ (C_2H_5)_2Si(OC_2H_5)_2 \xrightarrow{OH^-} \left[-O-\underset{\underset{C_2H_5}{|}}{\overset{\overset{C_2H_5}{|}}{Si}}-O- \right]_n + 2nC_2H_5OH$$
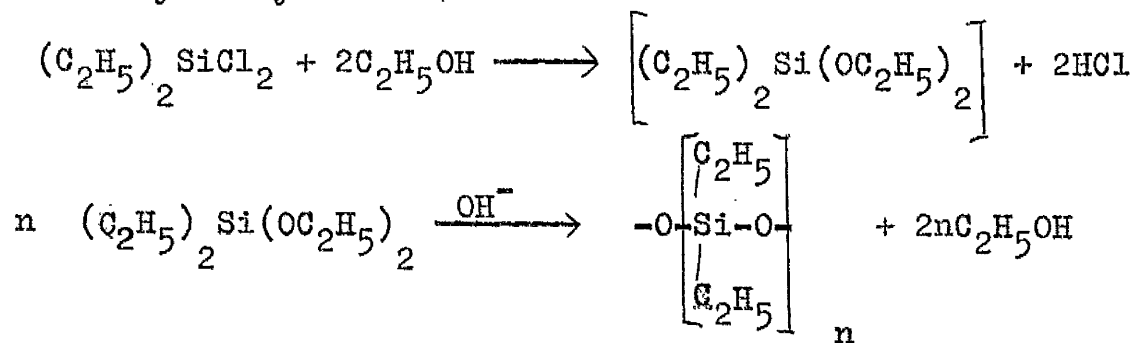
The major contribution to our knowledge of organosilicon chemistry in its pre-industrial era was

made by Professor F.S. Kipping at University College, Nottingham. Kipping published fiftyfour papers covering the synthesis, isolation, and identification of a great number of new organosilicon compounds over a period of fortyfive years in his search for asymmetric tetrasubstituted silicon compounds .[5]

Organosilicon chemistry remained essentially an academic subject until knowledge of the fundamental mechanisms of polymerisation and the properties of macromolecules had been enlarged. This development was due to the industrial interest in thermally stable and non-conducting polymers, and to the pressure of war time demands. The post-war activity in this field can be judged from the fact that over twelve hundred compounds were described in more than five hundred references during the period 1947-1954.[6]

Industrial interests have been concerned mainly with the preparation of siloxanes in the form of "silicone" fluids, elastomers, rubbers and resins; and of their monomer precursors, the haloalkyl-and haloaryl-silanes. Silicones were so called by Kipping in the belief that they were similar to the ketones ($R_2Si:O$ and $R_2C:O$). They are however greatly different from ketones in that their essential linkage is $\left[\begin{array}{c} R \\ | \\ Si-O \\ | \\ R \end{array}\right]$, the siloxane linkage.

The other groups attached to silicon may be either organic

as shown, or additional oxygen atoms which cross-link the

siloxane chain. It is this wide structural variation

which allows the preparation of the diverse range of

commercial siloxanes now available. An indication of the

variation may be obtained by a comparison of the chain -

stopped methylpolysiloxanes $Me_3SiO(SiMe_2O)_n SiMe_3$,[7] (Table 1).

TABLE 1.

Viscosity and boiling point in methylpolysiloxanes.

Value of n	0	1	2	5	14	48	150	210	350
Viscosity at 25° (centistokes)	0.65	1.04	1.53	3.24	10	50	200	350	1000
boiling point/ pressure. cm mercury.	99.5/76	152/76	192/76	165/20	-	-	-	-	-

One has only to consider other possible

structures involving cross-linking to realise the extent of

the variation available,[8] e.g.,
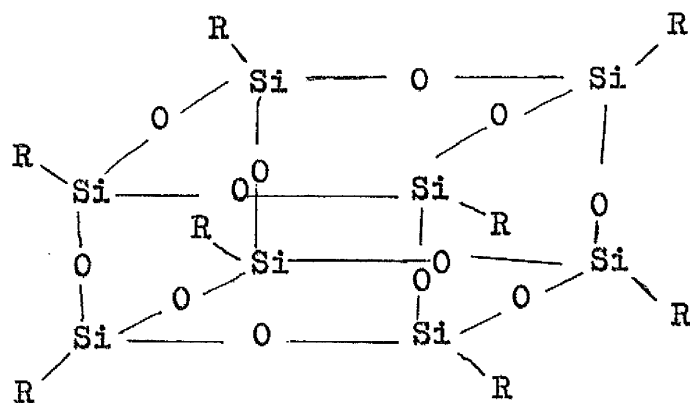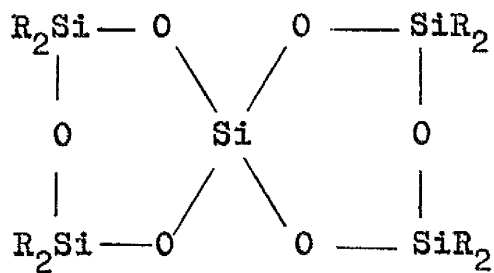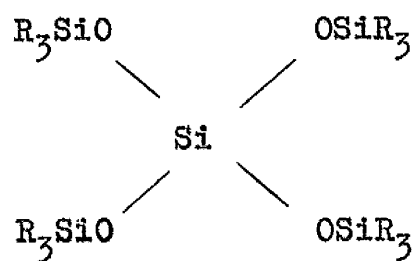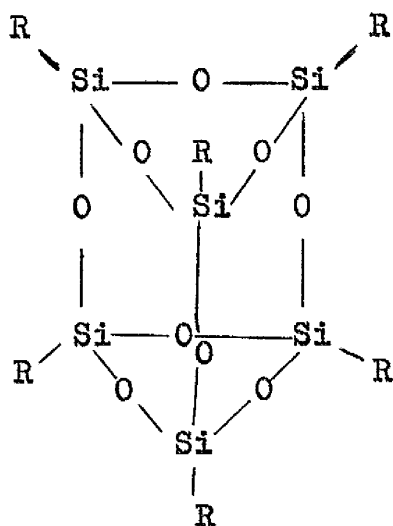
Although carbon functional organosilicon compounds are technically of much less importance than siloxanes at present, the extension of our understanding of organosilicon chemistry undoubtedly depends on these compounds, and continued interest is being shown in them. Thus attempts to combine the properties of the siloxanes with the thermal and chemical stability of the fluorocarbons resulted in an investigation of the preparation and properties of fluoroalkylsilicon compounds. This served as an indication of the important modifications wrought in an alkyl chain by the introduction of a silyl group. An outline of the general methods available for the preparation of organosilicon compounds follows.

Routes to organosilicon compounds.

Methods involving organometallic reagents.

The first organosilicon compounds were prepared by the treatment of silicon tetrachloride with dialkylzinc[2] and by the reaction of aryl halides with silicon tetrachloride and sodium in ether.[9]

$$2Zn(C_2H_5)_2 + SiCl_4 \longrightarrow Si(C_2H_5)_4 + 2ZnCl_2$$

$$SiCl_4 + 4C_6H_5Cl + 8Na \longrightarrow (C_6H_5)_4Si + 8NaCl$$

These methods however have the serious disadvantage of producing the tetrasubstituted silane, even when a deficiency of the organic compound is used. This can be overcome for cases in which the organosodium compound is easily prepared, as in active methylene compounds such as cyclopentadiene,[10] fluorene,[11] and indene[12]. Reaction of the sodio-derivative with silicon tetrachloride can then take place in a stepwise manner.

$$RNa + SiCl_4 \longrightarrow RSiCl_3 + NaCl$$

The most widely applied method for forming silicon-carbon bonds is the Grignard reaction, because silicon-halogen, silicon-alkoxy, and even silicon-hydrogen bonds can be replaced by alkyl, alkenyl, alkynyl, and aryl groups.[13]

This was the method most frequently by Kipping in his search for optically active silicon compounds .[5] Attempts to prepare the silicon analogue of a Grignard reagent, which is thought to be a reaction intermediate,[14] have been unsuccessful[15] although there is evidence for the formation of a similar germanium compound.[16] Stepwise replacement of halogen attached to silicon can be effected, and different groups may be attached to the silicon atom by either isolation of the intermediate halogeno-organosilane followed by reaction with a further Grignard reagent, or by treatment of the reaction mixture from a halide and one Grignard reagent directly with a different Grignard reagent.[17]

$$SiCl_4 + C_2H_5MgBr \longrightarrow C_2H_5SiCl_3 + MgBrCl$$

$$C_2H_5SiCl_3 + C_6H_5MgBr \longrightarrow C_2H_5,C_6H_5SiCl_2 + MgBrCl$$

$$C_2H_5,C_6H_5SiCl_2 + {}^nC_3H_7MgBr \longrightarrow C_2H_5,C_6H_5,{}^nC_3H_7SiCl + MgBrCl$$

$$C_2H_5,C_6H_5,{}^nC_3H_7SiCl + C_6H_5CH_2MgCl \longrightarrow C_2H_5,C_6H_5,{}^nC_3H_7SiCH_2C_6H_5 + MgBrCl$$
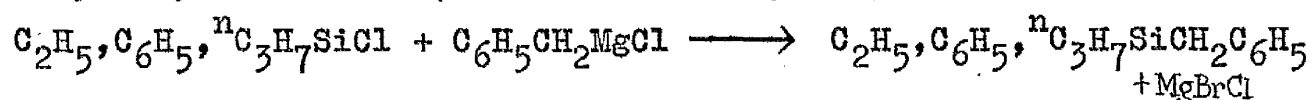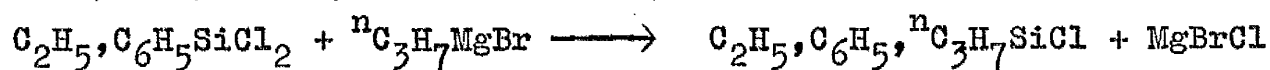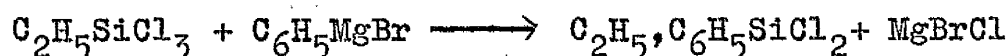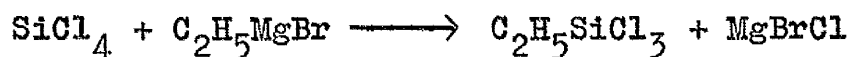
The disadvantages of the method are the increasing difficulty of replacement of successive halogen atoms which is probably of steric origin, and the tendency of magnesium salts to retain organosilicon compounds rather tenaciously.

Organolithium compounds react with silicon compounds more readily than do Grignard reagents, and their use is a recent development which has greatly expanded the scope of the synthesis, as stepwise replacement may sometimes be

achieved.[18,19]

$$SiH_4 + 2C_2H_5Li \longrightarrow (C_2H_5)_2SiH_2$$

The greater ease with which organolithium compounds

attack silicon is clearly seen by the replacement of

four hydrogen atoms attached to silicon by aryl groups[18]

$$SiH_4 + 4C_6H_5Li \longrightarrow (C_6H_5)_4Si \ .$$
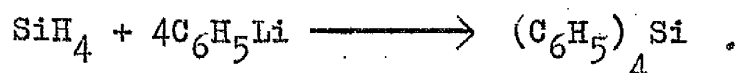
Organoaluminium compounds have also recently been used

to prepare tetraalkylsilanes[20]. Organosilyllithium

compounds R_3SiLi are also known where at least one organic

group is aryl.[21]

Perfluoroalkyllithium compounds and perfluoro-

Grignard reagents have been used to prepare perfluoro-

alkylsilicon- and perfluoroarylsilicon-compounds.[48,49]

The preparation of the reagents and their manipulation is not

easy, and their use normally leads to mixtures of products.

The reaction of silicon halides with diazomethane.

This method has been reviewed by Seyferth[22].
Silicon tetrachloride undergoes methylenation readily
when treated with diazomethane in ether at $-55°$ to $-45°$[23,24].

$$CH_2N_2 + SiCl_4 \longrightarrow Cl_3Si\cdot CH_2Cl + N_2.$$

At room temperature vigorous and explosive decomposition
occurs.

The reaction also takes place with silicon tetrachloride,
but fluoromethylfluorosilane is not formed in the reaction
of diazomethane with silicon tetrafluoride. Introduction
of a second and third group, however, takes place with
increasing difficulty, and a fourth methylene group
cannot be inserted. A similar reluctance of the insertion
reaction to take place is observed with alkylchlorosilanes.
The mechanism was thought to be a polar process [22,25] but
it is now thought to involve a carbon insertion reaction.[18]

The direct synthesis.

The direct synthesis, commercially the most important preparative method, was patented by Rochow in 1945 [26]. In general usage the term direct synthesis is applied to the preparation of organohalo-silanes from elemental silicon and an organic halide. The reaction takes place with commercial silicon (98% Si) but it is much more efficient with a copper catalyst and elevated temperatures $(250-500^{\circ})$. Alkyl and aryl chlorides are usually employed, because the fluorides are relatively unreactive, and the bromides and iodides break down under the reaction conditions to form olefins and hydrogen halides.

Complex mixtures of products are obtained. For example, the reaction of methyl chloride with silicon containing a copper catalyst at $300-400^{\circ}$ may give varying amounts of the following [26,27],

$MeSiCl_3$, Me_2SiCl_2, Me_3SiCl, Me_4Si, $MeSiHCl_2$, Me_2SiHCl, $SiCl_4$, $SiHCl_3$, SiH_2Cl_2, H_2, CH_4, C_2H_6, C_2H_4, $R_xSiCl_{(4-x)}(R>Me)$, $Me_xSi_2OCl_{(6-x)}$, Si_2Cl_6, $Me_xSi_2Cl_{(6-x)}$, $Me_x(SiCH_2Si)Cl_{(6-x)}$, $Me_x(SiCH_2CH_2Si)Cl_{6-x}$, $Me_x(SiCH_2SiCH_2Si)Cl_{6-x}$.
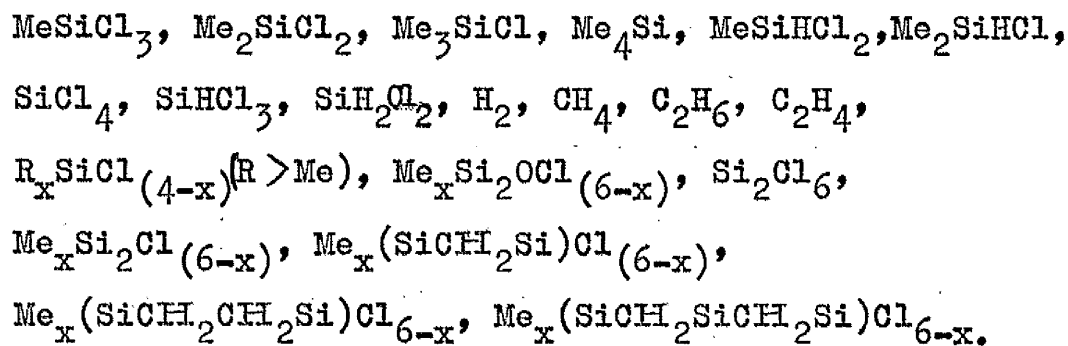
The composition of the product may be controlled to some extent by the choice of temperature, flow-rate of organic halide, and the nature and quality of the catalyst.

The siloxane precursors methyltrichlorosilane, dimethyldichlorosilane, and trimethylchlorosilane are the most valuable products.

Metals other than copper may be used as catalysts, e.g. nickel, tin, antimony, manganese, silver and titanium. Silver is most effective when aryl halides are used, and both tin and nickel are superior to copper as catalysts when vinyl halides are used [28].

Silicon-hydrogen bonds can be introduced into the organosilicon product by the addition of hydrogen gas to the stream of alkyl halide, or by reaction with hydrogen formed in the pyrolysis of the organic halide [29].

$$2RCl + H_2 + Si \longrightarrow RSiHCl_2 + RH$$

Similarly the incorporation of hydrogen chloride into the reaction mixture gives rise to a favourable production of alkyltrichlorosilane [30].

$$RCl + 2HCl + Si \longrightarrow RSiCl_3 + H_2$$

It has been suggested[31] that the reaction involves the formation of methyl copper, since if copper is heated alone in a stream of methyl chloride half the copper is removed in the form of a volatile labile compound whilst the other half remains as copper (I) chloride.

$$2Cu + CH_3Cl \longrightarrow CuCl + (CuCH_3)$$
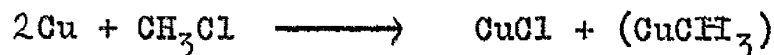
Studies of the reaction of a single crystal of silicon

embedded in copper and exposed to methylchloride at

350° suggest that the silicon and copper form an

intermetallic compound which then polarises the carbon-

chlorine bond when chemisorption occurs by ionic

charges on the lattice.[32]   Thermal decomposition of

methyl copper produces free methyl radicals which may then

react with silicon subchlorides produced by the reaction of

silicon with copper (I) chloride.

$$Si - Cl + \overset{\bullet}{C}H_3 \longrightarrow CH_3SiCl$$
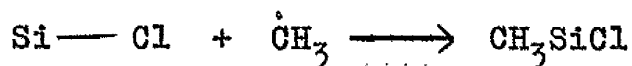
The methyl silicon chlorides so formed can then add on

either more methyl radicals or chlorine atoms to satisfy

the valency of silicon.

The formation and decomposition of methyl copper leads to

a transport of copper from the entrance of the reactor to

the exit during the direct synthesis, and it may even be

found in the condensed organosiliconhalides [33] .

The direct synthesis is of doubtful use for the

preparation of fluoroalkylsilanes as there is conflicting

evidence in the literature. The first attempt using

chlorotrifluoromethane, chloropentafluoroethane and

chloroheptafluorocyclobutane with silicon and a copper

catalyst at 500-100° gave only silicon tetrahalides
and organic breakdown products.[34]   A report that
trifluoromethyl halides react with a silicon-copper
alloy at 400° [35] to form $(CF_3)_n SiX_{(4-n)}$ (where X =
Cl, Br, I;   n = 1 $\longrightarrow$ 3)   could not be repeated by
other workers.[36]   Work carried out in this
department suggests that these claims are unfounded,
and that the products would break down at the temperatures
at which the reactions are carried out.   Trifluoromethyl-
trifluorosilane can probably be prepared in low yield by
this route with short contact times and rapid quenching .[37]

The interaction of hydrocarbons and silicon halides.

Several processes for producing organosilicon compounds from hydrocarbons have appeared in the patent literature and in many Russian publications.

The process is of considerable industrial interest because of the relatively cheap starting materials, and the high yields sometimes obtained[38],

e.g., $$HSiCl_3 + C_6H_6 \xrightarrow[\text{high pressure}]{BCl_3, 275^{\circ}} C_6H_5SiCl_3 \quad (73\%).$$
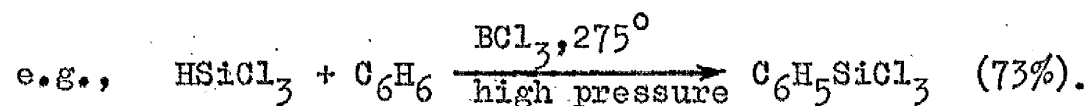
but the process is of little value in the laboratory. There is little information on the mechanism of this process, and apparent contradictions exist in the literature.[39]   The method appears to be largely restricted to aryl and vinyl compounds.

The addition of silicon hydrides to unsaturated compounds.

This method, first reported by Sommer and co-workers[40] and later by other workers[41] in 1947 has rapidly become an important laboratory and industrial process because it provides a method whereby an extensive range of organic radicals containing functional groups may be attached to the silicon atom. The addition reaction may be carried out under conditions usually associated with free radical reactions, or in the presence of tertiary bases, metals, or metal salts, under which conditions the mechanism is complex and is thought to be ionic.[52-54] There has been a report to the contrary for catalysts of platinum and hexachloroplatinic acid[42].

Addition reactions catalysed by peroxides, ultra-violet light and γ- radiation, and thermal addition reactions.

These reactions are thought to proceed via a free radical chain mechanism similar to that proposed by Kharasch and co-workers for the addition of halogeno-methanes to olefins.[43] The mechanism of this process is described more fully in the section concerned with free radicals. The method is versatile in that the major restrictions are the necessity for at least one silicon-

hydrogen bond in the silane and for the lack of
polymerisation of the olefin. Thus chlorosilanes
and alkyl- or aryl-silanes can be added to a wide
range of cyclic and linear olefins[44], and the
preparative value of this method can be extended by
applying the Grignard reaction to the resulting halosilanes.

$$Ph_2HSiCl + CH_2=CH\cdot CH_3 \xrightarrow{160-400} Ph_2ClSi\cdot CH_2\cdot CH_2\cdot CH_3$$

$$SiHCl_3 + CH_2= C(CH_3)_2 \xrightarrow{h\nu} Cl_3Si\cdot CH_2\cdot CH(CH_3)_2$$
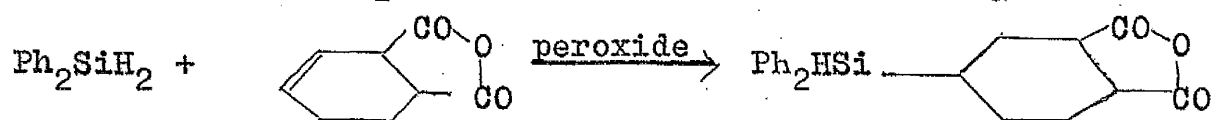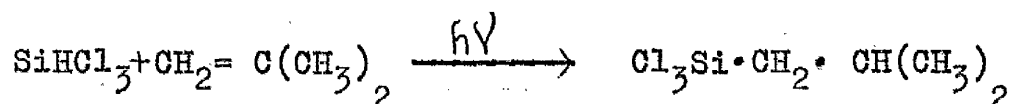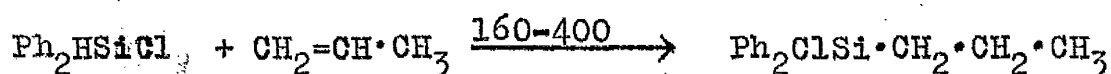
Similarly silicon hydrides add to acetylenes to give
vinylsilanes and disilylethanes[44].

$$SiHCl_3 + CH \equiv CH \xrightarrow{(Bu^t O)_2} Cl_3Si\cdot CH=CH_2$$

$$Cl_3Si\cdot CH=CH_2 + SiHCl_3 \longrightarrow Cl_3Si\cdot CH_2\cdot CH_2\cdot SiCl_3$$
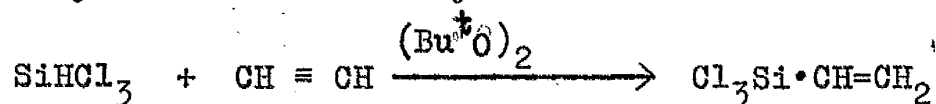
From thermal reaction at $450-510^{\circ}$ ethynyl-vinyl silicon
compounds are formed[44,46] but it is doubtful if this
involves an addition reaction as the only operative
mechanism.

$$SiH_4 + CH{:}CH \longrightarrow SiH_3 \cdot CH{:}CH_2$$

$$SiH_4 + SiH_3 \cdot CH{:}CH_2 \longrightarrow SiH_2(CH{:}CH_2)_2$$

$$SiH_2(CH{:}CH_2)_2 + CH{:}CH \longrightarrow SiH(CH{:}CH_2)_2 C{\equiv}CH. + H_2$$
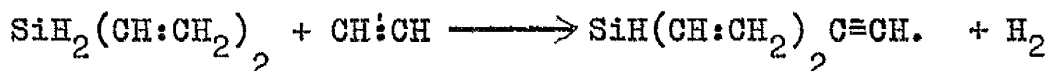
Though dehydrogenation of the vinylsilicon compound may be possible it is more likely that the ethynyl group is formed by a non-radical bimolecular interaction.

The addition of silicon hydrides to olefins of the type $R_2C{=}CR_2$ takes place readily in the presence of peroxides, and under the influence of ultraviolet light, but the use of the latter is less satisfactory, yields being generally much lower. The use of ultraviolet light does, however, avoid some of the complications met with in the use of peroxide initiators, such as addition initiation and dimerisation without initiation. The yields are dependent on the group R (R=alkyl), increased branching decreasing the yield[40b]. The rate of addition has been shown to increase with increasing number of methyl groups on the unsaturated carbon atoms, the order of the rates being the same as that for bromination, and the reverse of that for hydrogenation[47] :

$$Me_2C{:}CMe_2 > Me_2C{:}CHMe > HMeC{:}CHMe > EtHC{:}CH_2 > Me_2C{:}CH_2 > H_2C{:}CH_2$$
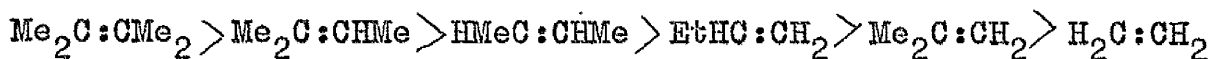
Free radical addition reactions of silicon hydrides to unsaturated ethers[55], esters[56], acyl halides[57],

and acids[58] have been claimed. Polychloroolefins, however, react with silanes to give mainly vinyl silanes by dehydrohalogenation of the normal saturated adduct when the reaction is carried out at elevated temperatures.[45,59,60]

$$HSiCl_3 + CH_2:CHCl \xrightarrow{550 - 650^0} (Cl_3Si \cdot CH_2 \cdot CH_2Cl) \longrightarrow Cl_3Si \cdot CH=CH_2 \quad [45]$$

$$HSiCl_3 + CCl_2= CCl_2 \xrightarrow[or \ (Bu^tO)_2]{600^0, \ or \ h\nu} Cl_3Si \cdot CCl=CCl_2 \quad [60]$$
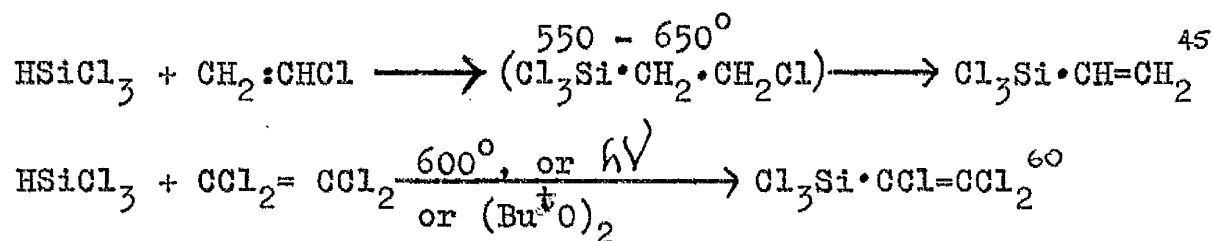
Even at low temperatures only a small amount of the saturated adduct is formed.[60] If the chlorine atoms are removed from the position of unsaturation, however, adducts are formed in good yields.[61] Alkyl silanes do not add to allyl bromide, hydrogen-bromine exchange taking place instead.[62] Triphenyl silane behaves similarly with allyl chloride[63], although in the peroxide catalysed reaction low yields of the adduct are formed.[40] Silicon-hydrogen bonds react preferentially with the hydroxyl or the amino group in allyl alcohol and allyl amine , but the adducts may be prepared when these groups are protected .[64]

In contrast to chloro-olefins, normal saturated adducts are formed with fluoro-olefins .[65-70] The simple 1:1 adducts may be obtained by varying the silane:olefin ratio, and adducts such as $(CH_3)_2SiH(C_2HF_4)$ are produced

in the reaction of dimethylsilane with tetrafluoroethylene.
Because of the high silicon-chlorine bond energy as
compared to that of the carbon-chlorine bond, silyl-
radicals may abstract chlorine atoms from adducts
containing both chlorine and fluorine atoms.   Thus the
reaction of trichlorosilane with chlorotrifluoroethylene
produces not only 1,1,2-trifluoro-2-chloroethyltrichloro-
silane, but as much as 45% of 1,1,2-trifluoroethyltrichloro-
silane.[70]

$$HSiCl_3 + CF_2:CFCl \longrightarrow CFHCl \cdot CF_2 \cdot SiCl_3$$

$$CFHCl \cdot CF_2 \cdot SiCl_3 + HSiCl_3 \longrightarrow CFH_2 \cdot CF_2 \cdot SiCl_3$$

It is of interest to note that the direction of the
addition reaction in this case is consistent with the
formation of the more stable intermediate radical
$-\overset{\bullet}{\underset{|}{C}}FCl.$ This is opposite to that observed for addition
reactions to chlorotrifluoroethylene catalysed by metals.[71]
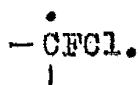
$$HSiCl_3 + CF_2:CFCl \xrightarrow{\text{metal}} CHF_2 \cdot CFCl \cdot SiCl_3.$$
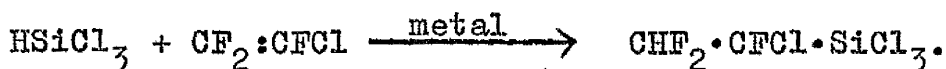
Addition reactions catalysed by transition metals and
by base catalysts.

As the addition of silanes to substituted olefins
gives carbon-functional organosilicon compounds which are
difficult to prepare by organometallic procedures, and
which are particularly interesting as precursors to
silicones, the possible application of catalysts has been

widely investigated.   Platinum and palladium supported

on carbon, γ-alumina, or asbestos have been particularly

useful ,[72,73]and salts such as potassium hexachloroplatinate

(IV) have been used.   Hexachloroplatinic(IV) acid has

also been most effective in catalysing the addition of

silanes to olefins .[73-77] These reactions may be carried

out in the presence of polymerisation inhibitors[52] thus

enabling simple adducts to be obtained from olefins which

rapidly polymerise under free radical conditions:

e.g., $MeSiHCl_2$ + CH_2:CHPh $\longrightarrow$ $MeCl_2Si \cdot CH_2CH_2 \cdot Ph$ 83%.[52]

The mechanism is complex in nature and has been regarded

as essentially an ionic process[52-54]; thus the direction

of addition appears to be controlled by the electron

density at the site at which the incipient siliconium ion

or hydride ion attacks.   This is illustrated by the noble

metal catalysed addition reaction of trichlorosilane to

methylacrylate, and of triethylsilane to methylmethacrylate.

$$SiHCl_3 + CH_2=CH-\overset{O}{\overset{||}{C}}-OCH_3 \longrightarrow CH_3-CH-\overset{O}{\overset{||}{C}}-OCH_3 \qquad 52.$$
$$\underset{\overset{|}{SiCl_3}}{}$$

$$Et_3SiH + CH_2=\overset{CH_3}{\overset{|}{C}}-\overset{O}{\overset{||}{C}}-OCH_3 \longrightarrow Et_3SiCH_2\overset{CH_3}{\overset{|}{CH}}\cdot\overset{O}{\overset{||}{C}}-OCH_3 \qquad 54.$$
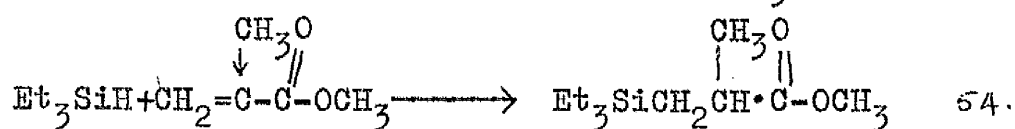
Since minute amounts of the catalyst are effective, it has

been suggested that an ionic chain process may be involved.[52]

Initial nucleophilic attack of an incipient hydride ion on the

double bond to give a carbanion is visualised as the
normal initiation step. In addition reactions with
internal olefins the initial carbanion rearranges by
proton shift to the more stable carbanion, and
consequently <u>normal</u>-alkylsilicon compounds are produced[52,75],
e.g., $SiHCl_3 + CH_3 \cdot CH_2 \cdot CH=CH \cdot CH_3 \longrightarrow Cl_3Si(CH_2)_4 \cdot CH_3$.
Addition of the intermediate carbanions to other
molecules of olefin before the silyl residue is added
may account for the telomerisations which sometimes occur[76].

$$MeSiHCl_2 + 2CF_2 : CF_2 \xrightarrow{H_2PtCl_6} CHF_2 \cdot CF_2 \cdot CF_2 \cdot CF_2SiCl_2Me$$
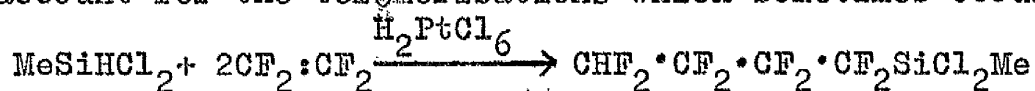
It has been claimed that a platinum catalyst
facilitates the homolysis of the silicon hydrogen bond[77],
as shown by the reaction of silanes with diphenylpicryl-
hydrazyl. On reaction with the silane, the platinum is
believed to release atomic hydrogen which then reacts with
the diphenylpicrylhydrazyl radical. When a catalyst of
platinum/carbon is used it is thought that the reaction
starts on the surface of the carbon as H-D exchange only
takes place in the presence of the catalyst at 150-68°.
This is regarded as evidence for a homolytic reaction[77].
The formation of a platinum-silicon carbon compound has
also been claimed to take place in this reaction[77b].
Trichlorosilane and acrylonitrile however, give the same
product, $CN \cdot CH_2 \cdot CH_2 \cdot SiCl_3$, in the presence of

benzoyl peroxide, pyridine, and platinum/asbestos,[78] but
in the presence of the nickel complex, $Ni(C_5H_5N)_4Cl_2$,
the other isomer, $CH_3 \cdot CH(SiCl_3)CN$, is formed[78a].
It may be possible that under certain catalytic
conditions, both the heterolytic and the homolytic
process can take place side by side.

Organic bases, such as pyridine and the nickel
complex, $Ni(C_5H_5N)_4Cl_2$[78a], and tertiary amines and
phospines[79], have been used to catalyse ionic addition
reactions of silanes to olefins. Amines and phosphines
were found to be ineffective in the absence of a highly
polar solvent,[79] possibly because the abnormal silicon-
hydrogen bond fission required is facilitated in polar
media. Iron pentacarbonyl and certain transition metal
halides have also been used to catalyse these addition
reactions but chromium, manganese, and tungsten carbonyls
were found to be ineffective.[80]

Of the three main routes to organosilicon
compounds, the addition reaction of silanes with
olefins provides the most satisfactory route to
polyfluoroalkylsilicon compounds. The work
described in this dissertation is concerned with the
addition reactions of silyl radicals with fluoro-olefins
with the object of elucidating some of the mechanistic
effects, and of correlating the isomer ratios of the
products with the structure of the attacking radical for
those cases in which bidirectional addition occurs.
A general description of free radicals and a discussion
of the addition mechanism follows.

Reaction of free radicals.

General description:

The separation of two atoms or groups
sharing a σ- molecular orbital can take place in two
distinct ways: one in which the two electrons of the
bonding orbital remain in the atomic orbital of one of
the resultant particles, and the other in which the
electron pair is split, and each resultant atom or group
retains one electron in a half filled orbital. These
latter groups which retain the unpaired electron are
generally called "free radicals" in this context to
distinguish them from classical inorganic radicals, and
the process by which they are formed is known as homolysis.
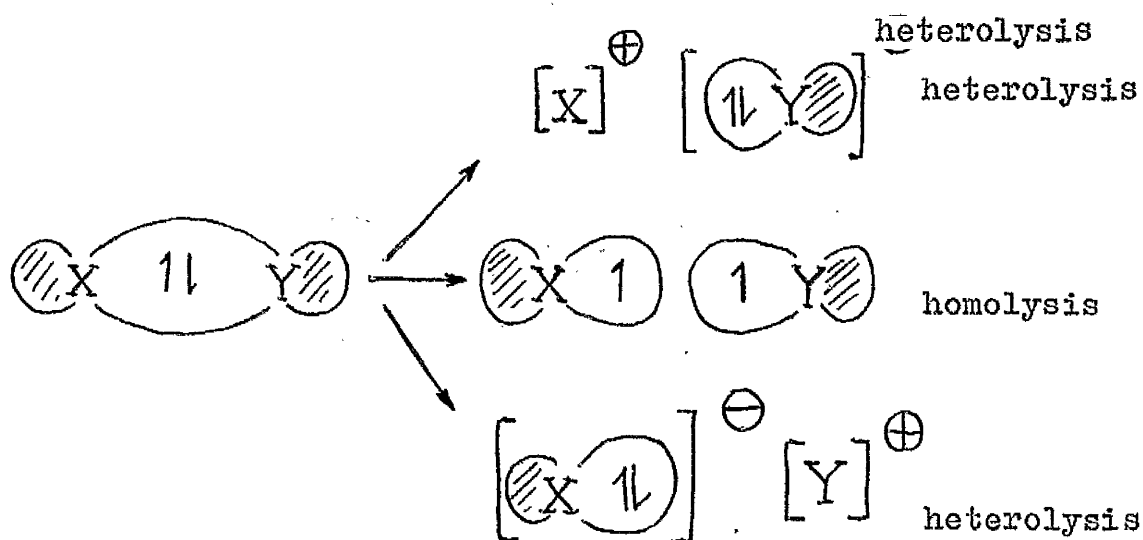
The description of a free radical as a
molecule containing one or more unpaired electrons is

often applied with the exclusion of metal compounds such

as the ferricyanide ion and samarium acetylacetonate:

$$\left[\text{Fe(CN)}_6\right]^{3-} \quad , \quad \text{Sm}^+ \quad -\text{CH} \underset{\text{COCH}_3}{\overset{\text{COCH}_3}{<}} \quad ,$$
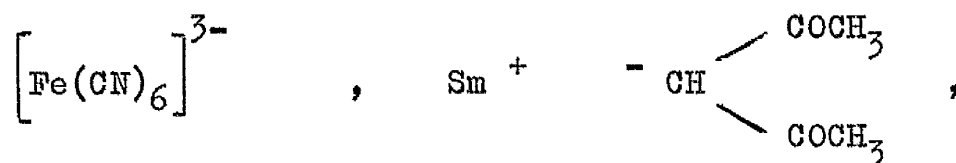
but this is only an arbitrary division as some of the

reactions of these paramagnetic species resemble those of

free radicals. Radicals thus described may be very variable

in their stability. Extreme examples are molecular oxygen,

and diphenylpicrylhydrazyl which are stable under laboratory

conditions, and hydroxyl or amino radicals which are known

only at high temperatures or in systems far from thermo-

dynamic stability.[81] This definition also distinguishes

between diradicals or triplet state molecules, and carbenes

or singlet state molecules with an empty orbital.
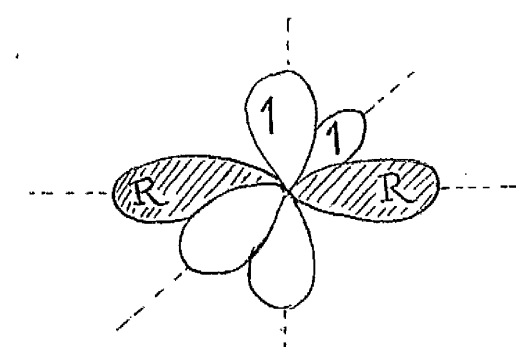
triplet state methylene
sp hybridised
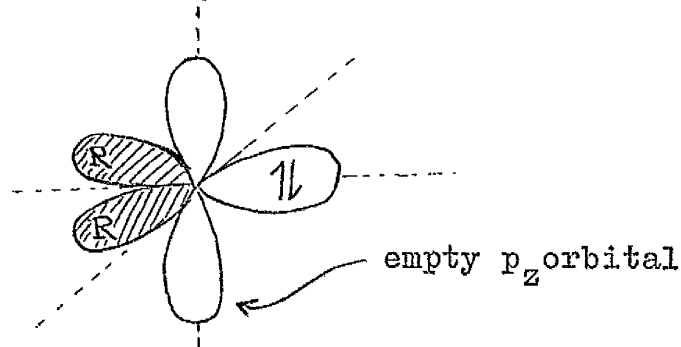
singlet state methylene
sp^2 hybridised.

Speculation about free radicals in the nineteenth

century was the natural result of the recognition that

chemical compounds often contain groups of atoms

of considerable stability which retain their identity

throughout the course of a reaction. The limited

theoretical frame-work within which this speculation

was carried out allowed even the more stable free

radicals to avoid detection until the concept of

valency had been more rigorously defined. Gomberg's

chance discovery of the triphenylmethyl radical [82]

was the first of a series of discoveries of relatively

stable free radicals. These are usually large radicals

containing aromatic groups in which it is now throught

that the radical is resonance stabilised by distribution

of the ψ- function of the free electron over the aromatic

system as a whole:
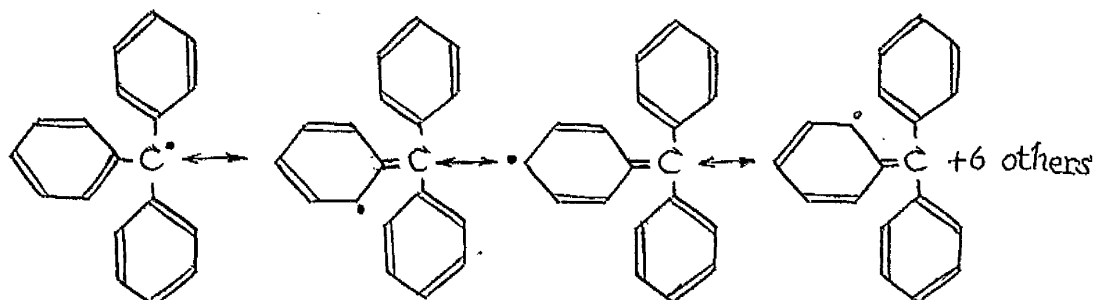
The dissociation of hexaphenylethane has been shown to

be a free radical reaction by the striking independence

of the rate constant from solvent effects, except in cases

where the solvent enters directly into the reaction by being

attacked by a radical[83] . Pentaphenylcyclopentadienyl,
for canonical forms of which the unpaired electron appears
on twenty different carbon atoms, appears to exist
entirely as the free radical in the solid state.[84] Whilst
steric hindrance in this molecule probably decreases the
amount of resonance by preventing coplanarity, it may
assist dissociation by hampering dimerisation.
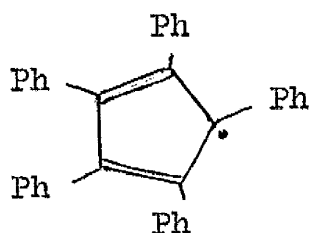
Pentaphenylcyclopentadienyl radical

Radicals which are stabilised by ion formation have also
been prepared:[85]

e.g.
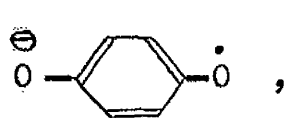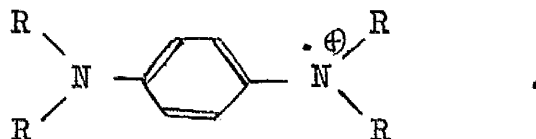
semiquinone ion   Wurster salt.

High temperature vapour density and spectroscopic
work, however, suggested the existence of free atoms, and
the postulation that free atoms took part in chemical
reactions (Nernst 1918) lifted free radicals and atoms
from the level of chemical curiosities.

Paneth's demonstration of the existence of free alkyl radicals (1929) and later Polanyi's development of the diffusion flame technique marked the beginning of studies of small reactive free radicals as species taking part in reactions. The development of comprehensive radical chain theories for the gas phase oxidation of hydrocarbons, and the investigations of the "anti-Markownikoff" addition reactions with olefins formed the major advances in the understanding of free radicals. The commercially important polymerisation of vinyl compounds also received considerable attention.

Evidence for the participation of free radicals is almost always indirect, proof of their existence being dependent on kinetic studies backed up by careful product analysis. The diagnostic tests which are used to detect the presence of radicals in a system may be classified under two headings: those that detect radicals, and those that detect chain reactions involving radicals.

The detection of radicals:

(a) Chemical properties. The reaction of a gas stream containing free radicals with metallic mirrors was the first method to yield good evidence for the formation of radicals.[86] The value of this method has been much increased by the use of radio-active metals so

that the removal of the mirror can be followed more accurately with a Geiger counter than with the older optical methods.[87]   The rates of removal of the mirrors have also been followed by measurement of electrical conductivity [88] and of the weight of the mirror[89] , both of which have the advantage of giving continuous readings.   The rate of "blueing" of films of molybdenum and tungsten oxides,[90]   and the "glow" of zinc sulphide screens[91] have also been used a heterogeneous radical detectors.   The stable coloured free radical diphenylpicrylhydrazyl(DPPH) can be used as a homogenious radical detector by measuring the fading of the colour as the radicals react with it.[92]   Similarly the detection of dibenzyl and dicumyl formed by dimerisation in reactions involving toluene and cumene respectively is regarded as indicating the presence of free radicals.[93]

(b)   Spin-Spin isomerism and isotopic labelling.

In the neighbourhood of the large inhomogeneous magnetic field of a free radical or other paramagnetic species the forbidden para to ortho-hydrogen transition is facilitated. It is thus possible to estimate the radical concentration by the rate of the para- to ortho- conversion, but the concentrations of radicals required are prohibitively high for most reactions.[94]   Hydrogen-deuterium exchange has been used to investigate the primary process in reactions

of amino[95] and alkyl[96] radicals.   Not only deuterium,
but other stable, and radioactive isotopes have been
used, and there are many cases in which "tracer"
techniques can shed light on the primary process.[96]
The use of stable isotopes in complex molecules has the
advantage of establishing the position of the atom
concerned with the aid of mass spectrometry whereas
radioactive isotopes give only a general picture of
the degree of activity.   Both methods using isotopes
have the drawback that some degree of fractionation may
occur during the experiment if the chemical properties of
compounds containing different isotopes are not very
similar.

(c)   _Physical properties_: Diffusion
techniques, thermal conductivity, calorimetry, and
measurement of pressure changes have been used to indicate
the presence of free atoms, but they are very limited in
their application.[96]   Mass spectrometry has been used to
detect the presence of free radicals.[97]   The application
of an electron energy less than the appearance potential
of R^+ but greater than the radical ionisation potential
followed by the detection of a peak at mass R constitutes
proof of the presence of the radical R• .

(d)   _Optical Methods_: Emission spectra
have been used to indicate the presence of excited atoms

and radicals in a few special cases but the method has no general application.[98]   The detection and estimation of free radicals by absorption spectra is without difficulty in principle but the high concentrations needed for this method tend to be prohibitive.[99]   The method has nevertheless been applied to a large number of systems.[100] Ultra-violet and visible absorption spectra have been observed by either using prolific sources of radicals or by isolating them by trapping in a solid matrix.   It is reasonably expected that electronic energy levels of a radical are not so widely separated as those of the parent compound and consequently shifts to the red are observed. These are occasionally sufficient to bring the absorption into the visible region.   Electron spin resonance is the most satisfactory method of detecting unpaired electrons. Not only does it provide a method of detecting radicals and determining their concentration even when they are present in only minute amounts, but it is free from interference by non-radical contaminants and gives much information about the electronic distribution within the molecule by means of hyperfine structure.[101]

The occurrence of a chain mechanism may be deduced from one or more of the following generalisations.

(a)   The probability factor of the Arrhenius equation is greater than unity.   Photochemical reactions, for

example, will have a high quantum yield equal to the product of the quantum yield for the primary act and the average chain length.

(b) The explosion boundary is well defined, i.e., as one parameter, e.g. pressure, is changed the transition from from a steady state reaction to an explosion is abrupt.

(c) The rate of the reaction rises from zero to a maximum.   For a non-chain reaction the rate of disappearance of the reactants is highest at the beginning and falls off with time.   There is evidence to suggest that if the reactant concentration for a chain reaction could be maintained constant, explosion reactions would continuously accelerate, and slow chain reactions would approach a limiting rate asymptotically.[102]

(d) An induction period (i.e., a time lag in an inhibitor-free system) is observed before the onset of the reaction is detected.[103]

(e) The reaction is susceptible to either acceleration or retardation by other substances, e.g., the spontaneous ignition temperature of a 2:1 hydrogen-oxygen mixture is lowered from 580° to 330° by a trace of nitrosylchloride. Nitrosyl chloride can also act as a negative catalyst or inhibitor in the photosynthesis of phosgene from carbon monoxide and chlorine.[104]

(f) Reactions at the surface of the vessel are important in chain reactions. This is shown by the sensitivity of the reaction to changes in the surface to volume ratio.

(g) Chain reactions are rarely of simple order.

The existence of free radical reactions is frequently inferred from the reaction conditions and from the nature of the products, further proof being regarded as unnecessary in many publications. Thus the observation of such things as an induction period, the necessity of initiation by photolysis or by known "radical initiators", the action of inhibitors, and the isolation of products consistent with a free radical mechanism is often regarded as sufficient evidence for a free radical reaction. This approach obviously necessitates the carry-over of much information from one reaction to another, and the current literature indicates that this assumption is, in general, justified. There are indications, however, that in certain cases energy may be carried over from the primary step, and that the "hot" radicals thus formed may react quite differently from similar atoms or radicals in thermal equilibrium with their surroundings.[105]

Free radical addition reactions.

Prior to the 1930's considerable doubt had existed about the explanation of the addition of hydrogen halides to olefins. The existing anomalies were demonstrated by a series of investigations carried out by Kharasch and his collaborators who showed that the addition proceeded according to the Markownikoff rule[106] if the reactants were pure and oxygen was excluded from the system[107], whereas the presence of small amounts of peroxides or oxygen gas caused rapid anti-Markownikoff addition.[107]

$$HBr + CH_2 = CH \cdot CH_2Br \nearrow \searrow$$

CH$_3 \cdot$CHBr$\cdot$CH$_2$Br
Markownikoff

CH$_2$Br$\cdot$CH$_2 \cdot$CH$_2$Br
Anti-Markownikoff
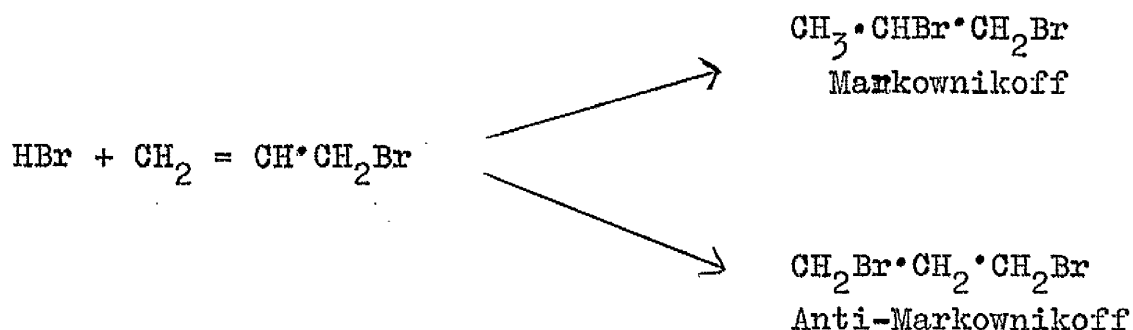
A fast free radical chain process was postulated to explain the anti-Markownikoff addition reaction;[108-110] thus only catalytic quantities of initiator introduced either deliberately or fortuitously are necessary for the reaction to proceed. This may be represented for the general case as follows for (a) peroxide initiation and (b) photochemical initiation.

a) $RO \cdot OR \longrightarrow 2RO \cdot$ (1)

$$RO\cdot + A\cdot B \longrightarrow ROB + A\cdot \qquad (2)$$

$$(b) \qquad A\cdot B \xrightarrow{\quad h\nu \quad} A\cdot + B\cdot \qquad (3)$$

$$A\cdot + CH_2:CHR \longrightarrow ACH_2\cdot CHR \qquad (4)$$

$$ACH_2\cdot CHR + AB \longrightarrow ACH_2\cdot CHBR + A\cdot \qquad (5)$$

$$2A\cdot \longrightarrow A\cdot A \qquad (6)$$

$$2ACH_2\cdot CHR \longrightarrow ACH_2\cdot CHR\cdot CHR\cdot CH_2A \qquad (7)$$

$$A\cdot + ACH_2\cdot CHR \longrightarrow ACH_2\cdot CHAR \qquad (8)$$
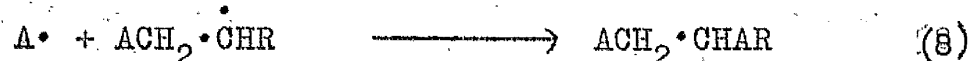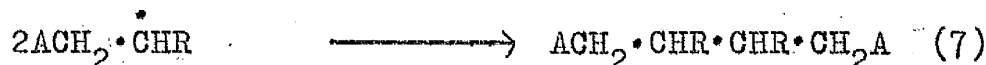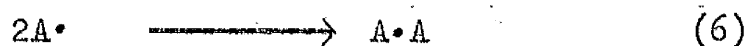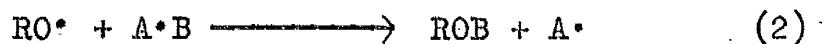
(1), (2) and (3) are initiation steps. (4) and (5) are

propagation steps, variously referred to by different

authors as (4) addition step, or initiation step

(i.e., polymerisation initiation.), and (5) displacement

step, or chain transfer. The terms addition step and

displacement step will be used here for (4) and (5)

respectively; (6), (7) and (8) are termination reactions.

The propagation steps (4) and (5) are the

important steps in determining the products since the

radical A· may be consumed and regenerated many thousands

of times for every radical introduced into the system in

the initiation step. It follows that no more termination

products are produced than chains are started, and

consequently if the chains are long the termination products

contribute little to the reaction, and are infrequently

detected. Termination products become important when the

energetics of the system are such that the kinetic chain

length (i.e., the number of molecules of product formed per molecule initiated) is low, and as bimolecular reactions of the type (6), (7), and (8) almost invariably have high rate constants (10^7 l/mole/sec), the time between initiation and termination is only of the order of a second.[111]   Thus the propagation steps (4) and (5) must be rapid in comparison to all chain terminations for a long kinetic chain length.   If either of these reactions is significantly endothermic, or exothermic but with a high activation energy or highly negative entropy of activation, addition by a chain mechanism is difficult, regardless of the efficiency of the initiation.[112]

The overall addition reaction:

$$A \cdot B + CH_2 = CHR \longrightarrow CH_2A \cdot CHBR,$$

is generally exothermic by about 20 kcal/mole,[111] but the energy must be suitably divided between the addition step (4) and the displacement step (5).   The manner in which this division occurs is determined primarily by the effective resonance energies of the radicals A• and R• which can be calculated from bond dissociation energy data.   Tabulated approximate energies of the propagation steps in free radical addition reactions to propylene (TABLE 2) illustrate this point.[112]   Thus for the addition of water, the reaction does not proceed because the displacement step (5) is significantly endothermic, even though the addition step (4) is

weakly endothermic.

A-B	$A\cdot + CH_2{:}CHCH_3 \longrightarrow$ $A\cdot CH_2\cdot\overset{\bullet}{C}H\cdot CH_3$ (4)	$A\cdot CH_2\overset{\bullet}{C}H\cdot CH_3 + AB$ $\longrightarrow A\cdot CH_2\cdot CHB\cdot CH_3 + \overset{\bullet}{A}$ (5)
HO-H	-36	26
Cl-H	-36	9
Br-H	-9	7
I-H	+3	-23
I-I	+3	-10
CH_3O-H	-20	-7
Cl_3C-Cl	-18	-4

TABLE 2:- Approximate energies of the propagation steps in free radical addition reactions to propene.[112] k cal/mole.

A semiquantitative picture of free radical addition reactions may be obtained by consideration of structural changes which can be discussed in terms of resonance, steric, and polar phenomena, and of the effect of the olefin/addend ratio on the yields. An investigation of the latter effect for a number of addition reactions of halogenomethanes appears to be quite general.[113] At low olefin/addend ratios, the addition step (4) becomes the slow step in propagation and termination occurs through (6) with accumulated A• radicals. At high olefin/addend ratios the slow step becomes the displacement step(5), and termination occurs through reaction(7)

The general result is the observance of a maximum yield at some particular ratio.

At high olefin/addend ratios the competition between the intermediate radical $ACH_2 \cdot \overset{\bullet}{C}HR$ and the adding radical $A^\bullet$ for the excess of the olefin may seriously interfere with the desired chain. Such reactions lead to the formation of telomers.

$$A \cdot CH_2 \cdot \overset{\bullet}{C}HR + CH_2:CHR \longrightarrow A \cdot CH_2 \cdot CHR \cdot CH_2 \cdot \overset{\bullet}{C}HR \qquad (9)$$

$$A \cdot CH_2 \cdot CHR \cdot CH_2 \overset{\bullet}{C}HR + A \cdot B \longrightarrow A \cdot CH_2 \cdot CHR \cdot CHBR + A^\bullet \qquad (10)$$

$$A \cdot CH_2 \cdot CHR \cdot CH_2 \cdot \overset{\bullet}{C}HR + nCH_2:CHR \longrightarrow A(CH_2 \cdot CHR)_n CH_2 \cdot \overset{\bullet}{C}HR \qquad (11)$$

$$A(CH_2 \cdot CHR)_n CH_2 \cdot \overset{\bullet}{C}HR + A \cdot B \longrightarrow A(CH_2 \cdot CHR)_{(n+1)} B + A^\bullet \qquad (12)$$
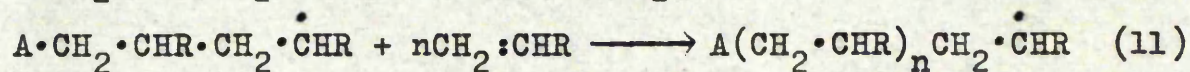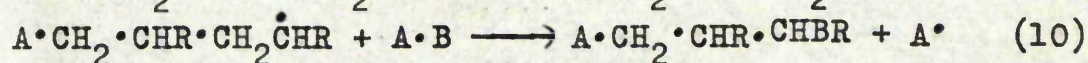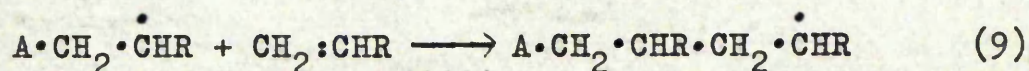
In the case of olefins which do not readily polymerise this is not particularly serious, and only small amounts of low telomers are formed by reactions (9) and (10) in many addition reactions. If, however, the rate constant for reaction (9) is comparable with that of reaction (4) (the addition step), high polymers are obtained through reaction (11) with chain transfer through reaction (12) in this case. This effect is assessed quantitatively in terms of the chain transfer constant C for A-B where:

$$C_{AB}\frac{(A \cdot B)}{(olefin)} = \frac{K_{(5)}(A \cdot B)}{K_{(a)}(olefin)} = \frac{\text{mole fraction of 1:1 adduct,}}{\text{mole fraction of telomers}}$$

and $K_{(5)}$ and $K_{(9)}$ are rate constants for equations (5) and (9). Thus it has been shown that in the addend $A \cdot B$, where A

is organic, the chain transfer constant increases in the order for B $H < Cl < Br < I$, and with substituents in A that increase the resonance stabilisation of A•.   Similarly the reactivity of A•B with constant A varies in the same order, so that observed differences in reactivity do not necessarily reflect a specific property of the radical A•, but may also be related to the displacement step and thus to the undissociated molecule A•B.

The exothermicity of the addition and displacement reactions is not the only important factor since small differences in activation energies or in the pre-exponential factors may lead to large differences in the rate.   These more subtle effects have been studied by the use of competitive reactions, and have been discussed in terms of steric and polar effects.[111] Steric effects are important in the addition step (4), so that non-terminal olefins undergo addition less readily than do terminal olefins[111,114].   As might be expected, radicals with strong electron withdrawing groups show enhanced reactivity with electron-rich olefins, and vice-versa.   This polar effect appears to vary from a simple dipolar interaction to a lowering of the energy of the transition state by contributions from change transfer complexes in extreme cases.[114]

<u>Orientation in free radical addition reactions.</u>

Free radical addition reactions to
simple olefins of the type $RCH:CH_2$ have been shown to
give exclusive addition at the $= CH_2$ group.   In view of
the homolytic nature of the reaction this specificity
is remarkable at first sight, but it has been shown that
both polar and steric effects are relatively unimportant.
In a series of addition reactions of the trifluoromethyl
radical to olefins it has been shown that the rate is
greatly affected, but not the direction of addition,
irrespective of whether R shows inductive effects,
hyperconjugation, is conjugated, or contains large groups.

The olefins $CF_3 \cdot CH:CF_2$ and $CH_3 \cdot CH:CF_2$ show
slow but exclusive addition to the $=CH$ group,[115] and
present evidence indicates that orientation is governed
by the relative stabilities of the intermediate radicals;
thus $X \cdot CH(CF_3) \cdot CF_2$ is more stable than $X \cdot CF_2 \cdot CH \cdot CF_3$.
The basic concept is that replacement of hydrogen attached
to the carbon atom formally carrying the lone electron of
the free radical by any other atom or group causes an
increase in radical stability.[115] This allows the
prediction that the order of radical stabilities will be
tertiary⟩secondary⟩primary, where the terms refer to
groups other than hydrogen, and not necessarily to the

carbon skeleton only.[115-118]   Hyperconjugative

stabilisation may play a less important part when

hydrogen is attached to the carbon atom adjacent to

that carrying the lone electron,

e.g., $(CF_3)_2 \overset{\bullet}{C} \cdot CH_2 \cdot CF_3$ $\Big\rangle$ $(CF_3)_3 C \cdot \overset{\bullet}{C}H_2$

$\updownarrow$

$(CF_3)_2 C : CH \cdot CF_3$

$H^\bullet$
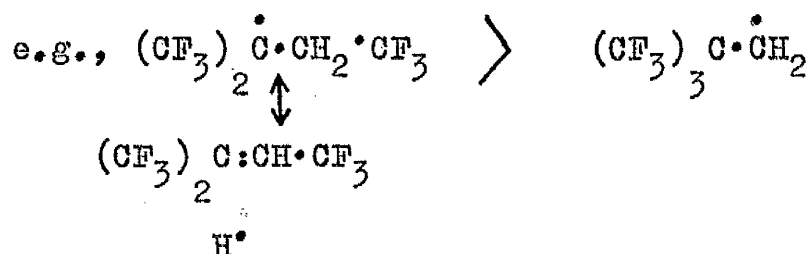
Resonance stabilisation of radicals substituted by halogen

on the α or β carbon atom can also play an important

part in determining the direction of addition,[115,116]

e.g., $RCX_2 \cdot \overset{\bullet}{C}X_2 \longleftrightarrow RCX_2 \cdot \overset{\bullet+}{C}X \overset{-}{X} \longleftrightarrow RCX_2 \cdot \overset{\bullet\bullet}{C}X \overset{\bullet}{X}$.
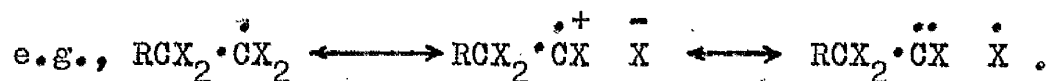
The stabilising effect of halogen substituents has been

found to increase in the order $H \langle F \langle Cl \langle Br$, so that a

strongly stablising substituent may disrupt the basic

tertiary $\rangle$ secondary $\rangle$ primary order.[119] The stability of

the intermediate radical has also been investigated for

a series of addition reactions of bromotrichloromethane

to trans-stilbenes.[120]   The results indicate that polar

effects of substituents in the aromatic rings are small,

and that resonance stabilisation is important, e.g.,

$$\overset{-}{\underset{\underset{O}{\overset{|}{\cdot}}}{O}}\overset{+}{N}\!-\!\!\bigcirc\!\!-CH\cdot CH(CCl_3)\!\!-\!\!\bigcirc \longleftrightarrow NO_2\!\!-\!\!\bigcirc\!\!-\overset{\bullet}{C}H\cdot CH(CCl_3)\!\!-\!\!\bigcirc$$

$$\overset{CH_2}{\underset{\overset{\bullet}{H}}{}}\!\!=\!\!\bigcirc\!\!=CH\cdot CH(CCl_3)\!\!-\!\!\bigcirc \longleftrightarrow CH_3\!\!-\!\!\bigcirc\!\!-\overset{\bullet}{C}H\!-\!CH(CCl_3)\!\!-\!\!\bigcirc$$
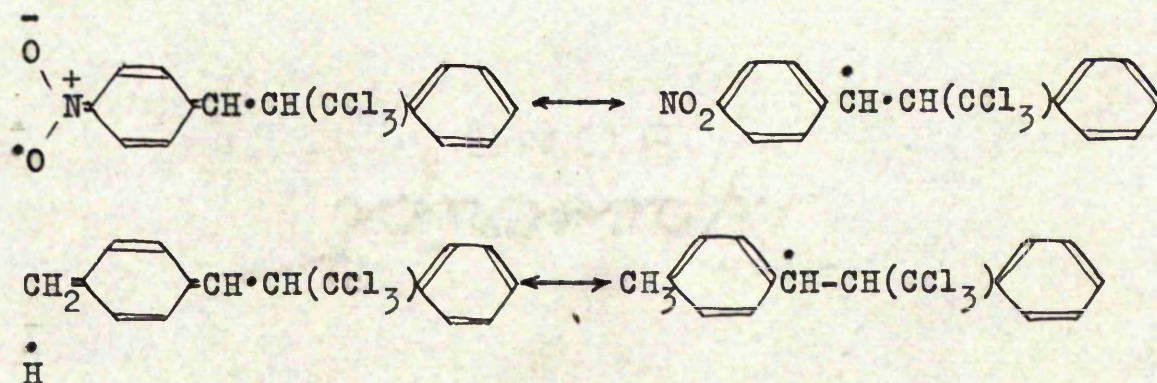
Lovelace and co-authors[121] have suggested an empirical rule which predicts that if RX reacts with an olefin, the radical R$^{\bullet}$ attacks the olefinic carbon atom with the lowest $\sum$ E.A. of its substituents, where

E is the Pauling electronegativity and A is the atomic refraction.

e.g.,
$$CF_2\!:\!CFCl + HSiCl_3 \xrightarrow{h\nu} CHFCl\cdot CF_2\cdot SiCl_3 \qquad [70]$$
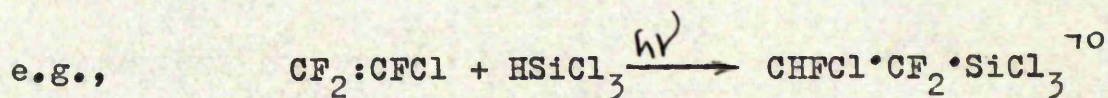
$\sum EA$ = 9.6; 23.6; for $^{\bullet}CF_2$ and $^{\bullet}CFCl$ respectively

An assessment of the stabilities of a series of alkyl iodides has been made by correlating the bathochromic shifts in the ultraviolet absorption spectrum with the ionisation potentials I.P., (e.v.) of the alkyl radical, the dissociation energy (D(R-I)kcal/mole), the calculated, and observed resonance energies of the hydrocarbon radicals R.E., (kcal/mole), and the stabilisation energies S.E., (kcal/mole), Table 3.[115]

TABLE III	Me	Et	^nPr	^iPr	^nBu	^tBu
I.P.,	13.60	10.07	8.67	7.77	-	7.19
D(R-I)	54.0	52.0	50.0	46.5	49.0	45.0
R.E.,(calc)	0	7.05	8.6	14.1	-	21.1
R.E.,(obs)	0	7.2	8.1	12.6	-	16.7
SE.,	0	2	4	7.5	5	9
λ max(mμ)	257	258	258	261	-	270

All these effects point to decreasing radical stability

in the order $Me_3\dot{C} > Me_2\dot{C}H > CH_3\cdot CH_2\cdot \dot{C}H \sim CH_3\cdot \dot{C}H_2 > \dot{C}H_3$

This approach has been extended to cover a series of

other halogen containing radicals, and the relative

stabilities so obtained are in agreement with the stabilities

obtained from chemical evidence.

　　　　All published addition reactions of silanes to

olefins and fluoro-olefins to date (1963) can be explained

by this approach.   The product derived exclusively from the

most stable intermediate radical has been found in all cases,

apart from a brief report of the addition of trichlorosilane

to trifluoroethylene[70] in which the possibility of a

bidirectional addition was indicated from hydolysis data.

The implications of bidirectional addition reactions are considered in the discussion section. The addition reactions of other hetero-radicals derived from the hydrides of germanium, tin, phosphorus, and sulphur generally follow this rule,[111] any variation from it being more a function of the olefin rather than the addend.

Free Radical displacement reactions.

From the discussion of the mechanism of the free radical addition reaction it is evident that one of the steps is a displacement reaction.

$$ACH_2 \cdot \overset{\bullet}{C}HR + AB \longrightarrow ACH_2 \cdot CHRB + \overset{\bullet}{A}$$
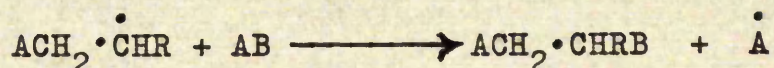
This type of reaction is not necessarily restricted to the addition reaction, and can be stated in general terms,

$$\overset{\bullet}{R} + X-Y \longrightarrow RX + \overset{\bullet}{Y}.$$

The reaction is variously referred to (by different authors) as an abstraction reaction, radical transfer reaction, or a radical displacement reaction. Some consideration of the abstraction reaction is a necessary complement to discussion of the addition reaction, not only because of the displacement step in the addition, but because of the possibility of a further interaction of free radicals with molecules of the product.

The mechanism of the displacement has received considerable attention,[121,122] in particular, the abstraction of hydrogen from aliphatic compounds. Using a development of a method first used by London, Polanyi[122] has developed a system whereby the potential energy of the system R-----X----Y is considered at varying distances of R---X and X---Y. The factors controlling the process are conveniently discussed in terms of potential energy diagrams.[123]

$$R' + XY \rightarrow RX + Y'$$

(a) Potential Energy Surfaces

(b) Potential Energy Profiles

M - N represents X - Y with distant R'. As R' approaches the energy of X - Y increases to P - O, and in the event of reaction not taking place, the energy of X - Y takes the form POP^1. If reaction takes place the transition state is represented by POQ with activation energy E. R - S represents the repulsion between the new molecule R - X and Y', and QQ^1 the similar repulsion when R - X is partly stretched.

Consideration of this model shows that the activation energy E is controlled by four factors:

1) The strength of the bond formed, R-X; this corresponds to a lowering of the energy curve R·S and consequently QQ^1; i.e., a lower activation energy.

2) The strength of the bond broken; this corresponds to a steepening of PP^1, and a higher intersection with QQ^1, i.e. a higher activation energy.

3) Repulsion between the new radical Y' and R - X; this corresponds to a steepening of QQ^1 and a higher intersection with PP^1, i.e., a higher activation energy.

4) Repulsion between the incoming radical R' and the molecule X - Y, causing a raising of PP^1 relative to MN, and hence a higher activation energy.

For example, in the chlorination of saturated alkanes, the strength of the bond formed (H-Cl) by the

reaction $\overset{\bullet}{Cl} + RH \longrightarrow R^{\bullet} + HCl$ is the main factor,
irrespective of the character of R. The nature of R is
important, however, in determining the position of attack,
as explained by the second factor. This effect is
illustrated by the observation that the relative ease
of abstraction from different types of carbon atom is
tertiary $\rangle$ secondary $\rangle$ primary. The nature of the third
and fourth factors controlling the activation is dependent
on the substituents of the radical and of the other
molecule involved,[123,124] but these are of relatively
smaller importance.

Although most of the work has been carried out
on the abstraction of hydrogen, the approach can be applied
to any similar reaction, the determining factors still being
the strength of the bond formed and the nature of the bond
broken. Thus whilst bonded hydrogen atoms are susceptible
to attack by free halogen atoms, leading to the formation of
carbon-halogen bonds, a bonded halogen is also susceptible
to attack by radicals which form strong bonds with halogen,
resulting in the generation of an alkane,
e.g., Attack of a silyl radical on chloroakanes leads to
the formation of the alkane and a chlorosilane.[125]

Free radical rearrangements.

Knowledge of free radical rearrangements is much less extensive than that of rearrangements involving carbonium ions and other species, but it is now evident that at ordinary temperatures free radicals show much less tendency to undergo rearrangements than do more electron deficient species.[126] Aryl, alkyl, and hydrogen migration via 1,2-shifts have been observed, mainly in fairly complex radical systems.[126]

e.g.,

$$Ph-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \cdot \overset{\overset{O}{\|}}{C} \cdot \longrightarrow Ph-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \cdot + CO \qquad (1)$$

$$Ph-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\cdot}{C}H_2 \longrightarrow Ph \cdot CH_2 \cdot \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \cdot \qquad (2)$$

$$Ph-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\cdot}{C}H_2 + Ph-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{/}}{C}}-CH_2 \cdot CHO \longrightarrow Ph-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + Ph-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \cdot \overset{\overset{O}{\|}}{C} \cdot \quad (3)$$

$$Ph-CH_2 \cdot \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \cdot + Ph-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \cdot CHO \longrightarrow Ph \cdot CH_2 \cdot CH(CH_3)_2 + Ph \cdot \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{/}}{C}} \cdot CH_2 \cdot \overset{\overset{O}{\|}}{C} \cdot \quad (4)$$
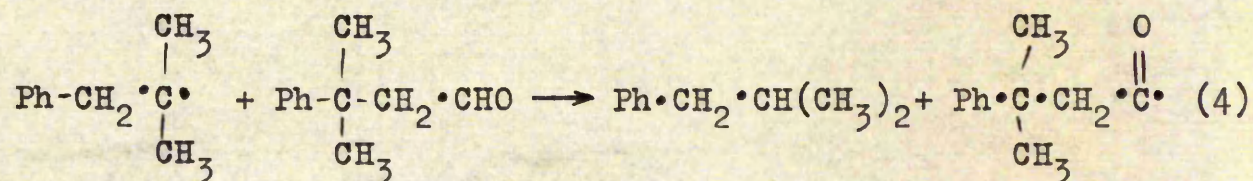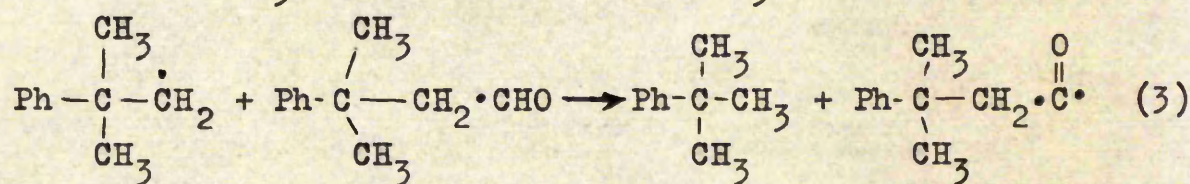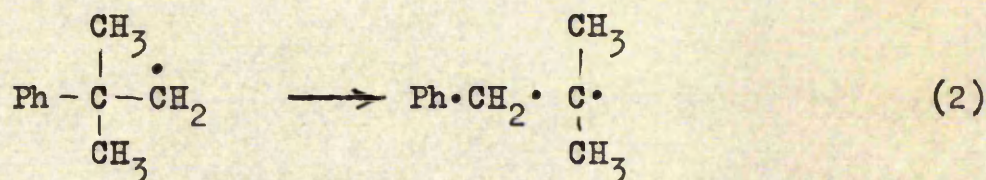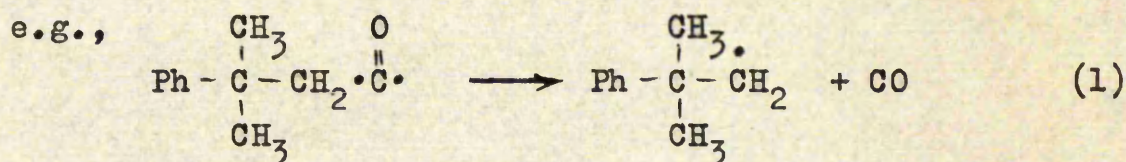
The activation energies of equation (2) and (3) are similar.

Of more relevance to a consideration of addition reactions to simple olefins is the rearrangement of

radicals by halogen migration. This is particularly important when orientation data is derived from analysis based on a non-rearranging radical intermediate. A reinvestigation[127] of the addition reaction of hydrogen bromide with 1,1,1-trichloropropene which was originally thought to give 3-bromo-1,1,1-trichloropropane[128] (equation (5)), showed that the product was in fact 3-bromo-1,1,2-trichloropropane (equations 6,7,) formed by a 1,2-chlorine migration.

$$Br^{\bullet} + CH_2\!:\!CH\cdot CCl_3 \longrightarrow BrCH_2\cdot \overset{\bullet}{C}H\cdot CCl_3 \overset{HBr}{\longrightarrow} BrCH_2\cdot CH_2\cdot \overset{\bullet}{C}Cl_3 + Br \qquad (5)$$

$$Br^{\bullet} + CH_2\!:\!CH\cdot CCl_3 \longrightarrow BrCH_2\cdot \overset{\bullet}{C}H\overset{C}{\overset{\wedge}{Cl_3}} \longrightarrow CH_2Br\cdot CHCl\cdot \overset{\bullet}{C}Cl_2 \qquad (6)$$

$$CH_2Br\cdot CHCl\cdot \overset{\bullet}{C}Cl_2 + HBr \longrightarrow CH_2Br\cdot CHCl\cdot CHCl_2 + \overset{\bullet}{Br} \qquad (7)$$
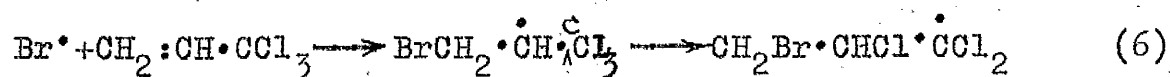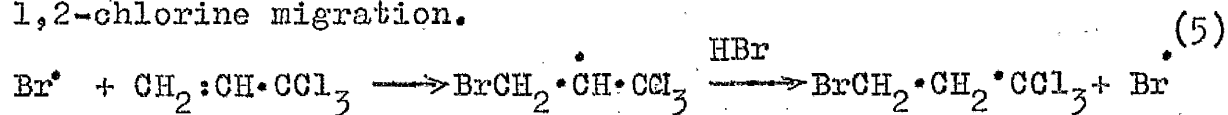
Radical addition reactions of mercaptans, bromine, and bromotrichloromethane to 1,1,1-trichloropropene also give results which can be accounted for on the basis of a radical rearrangement.[129]

The factors influencing the rearrangement appear to be the formation of a more stable radical, and the possibility of forming a bridged transition state;[130]
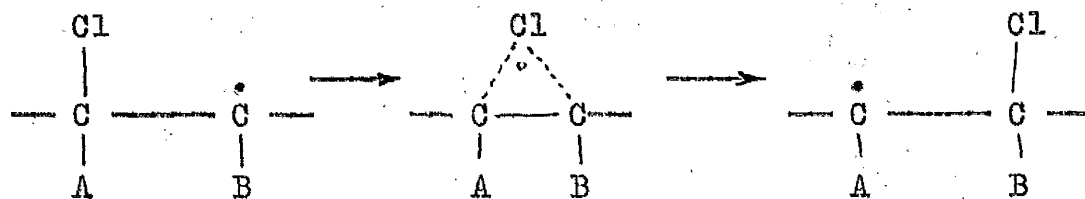
The cyclic transition state must, however, represent a lower energy path than the simple dissociation and subsequent recombination which might be visualised as a reverse addition reaction.[130]

$$
\begin{array}{ccccc}
\overset{\displaystyle X}{\underset{\displaystyle A}{-\,C\,}} - \overset{\displaystyle \bullet}{\underset{\displaystyle B}{C\,}} - & \longrightarrow & \underset{\displaystyle A}{-\,C\,} = \underset{\displaystyle B}{C\,} - & +\; \overset{\bullet}{X} \longrightarrow & \underset{\displaystyle A}{-\,\overset{\bullet}{C}\,} - \overset{\displaystyle X}{\underset{\displaystyle B}{C\,}} -
\end{array}
$$
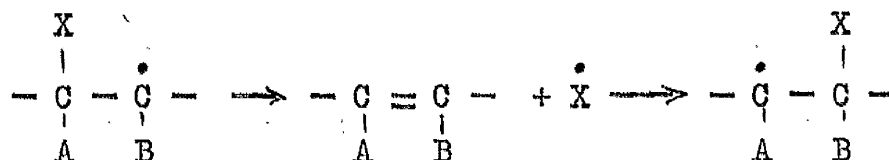
The evidence cited by Walling[126] seems to favour a bridged intermediate, e.g., in mercaptan addition reactions to 1,1,1-trichloropropane, halogen attack on mercaptan should be an extremely rapid competing process if the bridged form is not involved.

$$\overset{\bullet}{Cl} + RSH \longrightarrow \overset{\bullet}{RS} + HCl .$$

The migration of halogen seems to be restricted to chlorine and bromine atoms as migrations of fluorine atoms in normal free radicals have not been observed.

The free radical addition of silanes to olefins, at the most versatile preparative method for fluoroalkylsilicon compounds provides an interesting method by which both the field of orientation in free radical addition reactions and the preparation and properties of fluoroalkyl-silicon compounds can be studied. The postulation of a free radical chain mechanism necessarily involves consideration of the other facets of free radical reactions.

DISCUSSION.

DISCUSSION SECTION.

The addition of silyl radicals to unsaturated compounds.

The reaction of silanes containing at least one silicon-hydrogen bond with olefins, under free radical conditions, has been shown to take place by a mechanism similar to that postulated by Kharasch[43] for the addition of polyhalomethanes to olefins.

$$SiHX_3 \xrightarrow{h\nu} \cdot SiX_3 + \cdot H, \quad \text{initiation}$$

$$\rangle C=C\langle + \cdot SiX_3 \longrightarrow \cdot C-C \cdot SiX_3, \quad \text{radical addition}$$

$$SiHX_3 + \cdot C-C \cdot SiX_3 \longrightarrow HC-C \cdot SiX_3 + \cdot SiX_3, \quad \text{radical displacement}$$
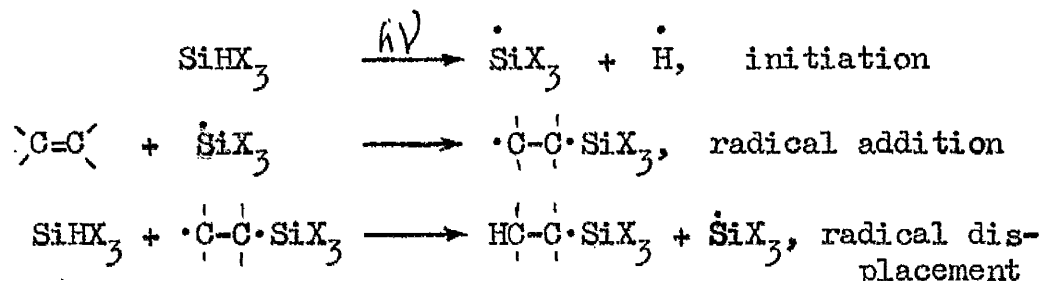
The direction of the addition reaction has been the subject of many publications[115] and it has been concluded that in many cases the polar and steric factors are of relatively minor importance in determining the direction of addition.[115] It has been shown that the reaction proceeds via the more stable intermediate radical $(\cdot C-C \cdot SiX_3)$. The direction of addition is therefore largely dependent on the relative stabilising effects of the groups attached to the carbon atom formally carrying the unpaired electron. The efficiency of various groups in increasing the radical stability can be assessed

by a simple comparison if the addition reaction is

unidirectional, (Table 4).[115]

TABLE 4

The direction of addition of CF_3 radical or of bromine atom to olefins.

Addition takes place exclusively at the position marked
by an asterisk.

$CH_3 \cdot \overset{*}{CH}:CH_2$	$Cl \cdot \overset{*}{CH}:CH_2$	$\overset{*}{CF_2}:CFCl$	$(CF_3)_2 \cdot C:\overset{*}{CH_2}$
$CF_3 \cdot CH:\overset{*}{CH_2}$	$F \cdot CH:\overset{*}{CH_2}$	$CH_3 \cdot \overset{*}{CH}:CF_2$	$CF_3(CF_2Cl) \cdot C:\overset{*}{CH_2}$
$MeO_2C \cdot CH:\overset{*}{CH_2}$	$CH \cdot \overset{*}{CH}:CH_2$	$CF_3 \cdot \overset{*}{CH}:CF_2$	
$CH_2Cl \cdot CH:\overset{*}{CH_2}$		$\overset{*}{CH_2}:CF_2$	

It appears that the order of stability for the radicals follows

the sequence tertiary > secondary > primary, where the terms

refer to groups other than hydrogen attached to the carbon atom

in question. This order is paralleled by the relative rates of

substitution at different carbon atoms in the free radical

halogenation of alkanes, (Table 5).[123]

TABLE 5

The selectivity of radicals for primary, secondary and tertiary atoms in the reaction $RH + \dot{X} \longrightarrow \dot{R} + XH$.

X	Relative rates of attack		
	CH_3	CH_2	CH
F	1	1.2	1.4
Cl	1	3.9	5.1
Br	1	82	1600

It has also been shown that the general order of stabilising

effect of different substituents is $Br > Cl > CF_3 > F > H$.[115]

With the refinements in analytical techniques now

available, e.g. gas-liquid chromatography, mass spectrography,

it has been found possible to detect cases of bidirectional

addition in which one adduct forms by far the greater

proportion of the product.   Bidirectional addition reactions

presumably take place when the stabilities of the two inter-

mediate radicals formed from the addition of a radical to a

polarised olefin are sufficiently close to allow similar rates

for the   reaction producing each adduct, i.e. $K_1 \simeq K_2$.

$$\begin{array}{c} \overset{A}{\underset{H}{|}}\overset{B}{\underset{H}{|}} \\ C=C \\ \end{array} + \overset{\bullet}{Si}X_3 \longrightarrow \begin{array}{c} \overset{A}{\underset{H}{|}}\overset{B}{\underset{H}{|}} \\ \bullet C-C \cdot SiX_3, \\ \end{array} \qquad K_1$$

$$\begin{array}{c} \overset{B}{\underset{H}{|}}\overset{A}{\underset{H}{|}} \\ C=C \\ \end{array} + \overset{\bullet}{Si}X_3 \longrightarrow \begin{array}{c} \overset{B}{\underset{H}{|}}\overset{A}{\underset{H}{|}} \\ \bullet C-C \cdot SiX_3, \\ \end{array} \qquad K_2$$
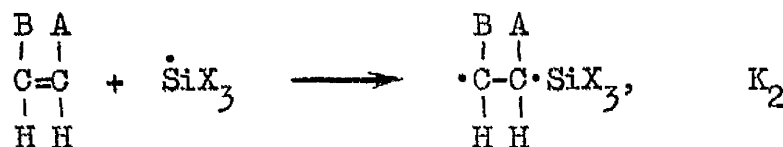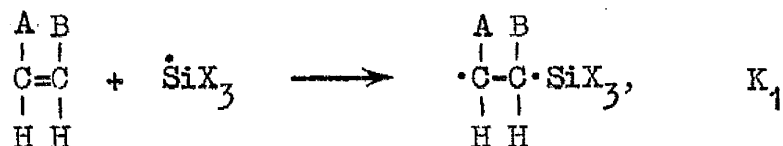
In such cases the minor effects of polarity and steric
requirement become apparent and in some cases these effects
may become the dominant factors which influence the direction
of the addition reaction.

When the present work was begun (1961), only one
report of a bidirectional addition reaction had appeared in
the literature.[131] In this case, both trifluoroiodomethane
and hydrogen bromide had been added across the double bond of
trifluoroethylene. Work carried out in this department had
also demonstrated the bidirectional addition of silanes to
hexafluoropropene.[132]

A re-examination[133] of an earlier investigation[134] of
the reaction of hydrogen bromide with hexafluoropropene
indicated that this also was a bidirectional addition reaction.
Considerable interest has been shown in the addition reaction
of thiyl radicals to fluoro-olefins, and the bidirectional

addition reactions of hydrogen sulphide[135] and various alkyl thiols[136] to trifluoroethylene have been reported. It has been claimed[137] that the addition of trifluoroiodomethane to vinyl fluoride is bidirectional. This last result is based on nuclear magnetic resonance spectra of a series of compounds obtained from the telomerisation of the olefin by benzoyl peroxide initiation. For a telomerisation involving trifluoroiodomethane it is possibly unwise to rule out radical recombinations which would lead to a pseudo-bidirectional reaction if evidence was based on $CF_3 \cdot CH_2-$ and $CF_3 \cdot CHF-$ resonances only, e.g.

$$\overset{\bullet}{C}F_3 + CH_2:CHF \longrightarrow CF_3 \cdot CH_2 \cdot \overset{\bullet}{C}HF$$

$$CF_3 \cdot CH_2 \cdot \overset{\bullet}{C}HF + nCH_2:CHF \longrightarrow CF_3 \cdot (CH_2 \cdot CHF)_n \cdot CH_2 \overset{\bullet}{C}HF$$

$$CF_3 \cdot (CH_2 \cdot CHF)_n \cdot CH_2 \cdot \overset{\bullet}{C}HF + \overset{\bullet}{C}F_3 \longrightarrow CF_3 \cdot CH_2 \cdot CHF \cdot (CH_2 CHF)_{n-1} \cdot CH_2 CHF \cdot CF_3$$
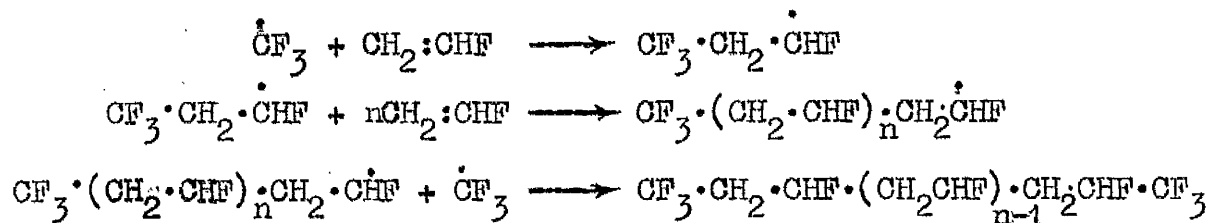
For an indication of a true bidirectional mechanism it would have been of greater value to observe resonances due to $-CHF \cdot CHF-$ and $-CHF \cdot CH_2 \cdot CHF-$ groupings in the telomers. It remains to be seen whether the two isomeric 1:1 adducts can be isolated and characterised or whether the apparent bidirectional character of the reaction is limited to telomer formation.

The early work on the addition of silyl radicals[132] and of thiyl radicals[136,138] to hexafluoropropene suggested that a correlation between the structure of the addend molecule and the orientation of the adducts might be possible.   In the event of a bidirectional addition reaction for a particular type of radical (e.g. thiyl, silyl, phosphinyl), it was thought that the relative rates of addition to each end of the double bond were dependent to a large extent on the electron density at the site at which the addition reaction takes place.   Thus, in those cases in which the carbon atom generally attacked by a radical (predicted on grounds of radical stability) is different from the more negatively polarised carbon atom (based on polarisation with respect to electrophilic attack by ethoxide ion), it is thought that strongly electrophilic radicals will have a distinct tendency to attack the latter type of carbon atom as well as the former.   From this argument one would predict that a variation in the electrophilicity of the radical would lead to a change in the isomer ratio of the adducts formed in a bidirectional addition reaction.

It was the purpose of this work to establish that the bidirectional addition reaction of silanes with fluoro-olefins under free radical conditions did occur, and to test the further

application of the correlation mentioned above.   The reactions
of various   silyl radicals with the olefins vinyl fluoride,
trifluoroethylene and 1-chloro-2-fluoroethylene were
investigated with this end in view.

For clarity, this section is divided into a
discussion of the experimental observations for the reactions
of each group of silyl radicals with a particular olefin and the
reactions of the adducts.   More involved theoretical
considerations relevant to all the reactions are discussed
together in the last section.

THE REACTIONS OF SILANES WITH FLUORO-OLEFINS AND THE DETERMINATION OF THE STRUCTURES OF THE PRODUCTS.

The reaction of silanes with vinyl fluoride.

The effect of the addend/olefin ratio upon free radical addition reactions has been the subject of an investigation of a number of addition reactions of halomethanes to olefins.[113] The results appear to be quite general. Qualitatively, the proportion of the addend must be sufficiently high to minimise telomerisation. In the present work initial experiments were carried out to determine the optimum silane/olefin ratio for the addition reaction of silyl radicals with fluoro-olefins.

In a typical experiment trichlorosilane and vinyl fluoride were condensed into a silica tube and irradiated with shaking in front of an ultra-violet lamp for 100 hr. Fractionation of the products in vacuo gave a good separation of the unreacted olefin, unreacted trichlorosilane, and a fraction consisting of the adduct contaminated with

trichlorosilane.   A small quantity of high
boiling material remained in the tube along with
an intractable brown compound on the side of the
tube nearest the lamp.   The 1:1 adduct was
obtained by distillation at atmospheric pressure
(usually of the products from two identical tube
reactions) and the pure adduct fraction was
collected in the boiling range 116-118°.   This
necessarily entailed some handling losses, but it was
found that these could be minimised by the addition
of a small volume of high boiling silicone oil near
the end of the distillation.   Traces of unreacted
trichlorosilane remaining in the adduct could be
detected by infra-red spectroscopy by means of the
characteristic silicon-hydrogen frequency at 4.6μ .
This impurity could be removed by further irradiation
of the adduct mixture with vinyl fluoride for a short
period (24 hr.).   The adducts were characterised
by elemental analysis for carbon, hydrogen, and
chlorine, and by their nuclear magnetic resonance
spectra and infra-red spectra.   Comparison of the
yield of pure 1:1 adduct with the percentage reaction
of the olefin gives some indication of the operation
of the telomerisation reaction (table _6_).

Silane.	Silane/ olefin ratio.	Time hr.	olefin consumed (%)	1:1 adduct, (% based on olefin consumed)	Foot- notes.
HSiCl$_3$	1:1	100	18	40	(a)
HSiCl$_3$	1:1	150	2	--	(a)(b)
HSiCl$_3$	2:1	70	21	80	
HSiCl$_3$	2:1	100	30	75	
HSiCl$_3$	2:1	150	95	73	(c)
HSiCl$_3$	2:1	200	22	95	(d)
HSiCl$_3$	5:1	100	54	88	
HSiCl$_3$	8:1	170	97	91	
MeSiHCl$_2$	5:1	100	56	95	
MeSiHCl$_2$	8:1	120	68	95	
Me$_3$SiH	2:1	100	18	11	
Me$_3$SiH	4:1	100	40	87	
Me$_3$SiH	6:1	300	80	90	(e)

TABLE 6. Photochemical reactions of silanes with vinyl fluoride (500 watt lamp)

(a) 250 watt ultra-violet lamp (b) Stationary reaction tube. (c) Shielding of the vapour phase (d) ca. 2% Hydrogen detected (e) mercury photosensitisation used, traces of ethylene were detected.

It is apparent that high silane/olefin ratios give a favourable conversion to the 1:1 adduct in the case of trichlorosilane and methyldichlorosilane, and that trimethylsilane adds less readily to vinyl fluoride than do trichlorosilane and methyldichlorosilane. The failure to observe hydrogen in most of the reactions indicates a high kinetic chain length. The hydrogen observed in the longer irradiations is throught to be formed by hydrogen abstraction:

$$H^{\bullet} + SiHX_3 \longrightarrow H_2 + \overset{\bullet}{Si}X_3$$

The ethylene observed in the reaction of trimethylsilane with vinyl fluoride is thought to arise by a fluorine abstraction reaction.

$$Me_3\overset{\bullet}{Si} + CH_2{:}CHF \longrightarrow Me_3SiF + CH_2{:}\overset{\bullet}{CH}$$

$$CH_2{:}\overset{\bullet}{CH} + Me_3SiH \longrightarrow CH_2{:}CH_2 + Me_3\overset{\bullet}{Si}$$
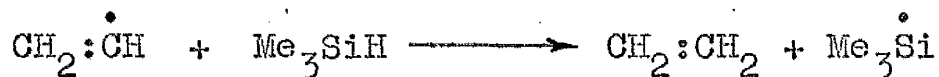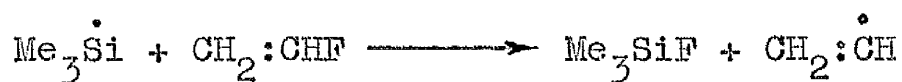
These points are more thoroughly discussed in conjunction with data from other reactions, pp 130.

A comparison of the results for the various silanes indicates that the percentage reaction of trimethylsilane with vinyl fluoride is lower than that for the other silanes used. The

very weak absorption of trimethylsilane in the
ultraviolet region suggests that this may be
related to a very inefficient initiation step.
Two methods of overcoming this were investigated.

i) Mercury was used as a photosensitising
agent. This method depends on the absorption of
resonance radiation by mercury atoms, followed
by transfer of this energy to the silane molecule
on collision. This high energy causes the silane
molecule to dissociate.

$$Hg^{O} \xrightarrow{\quad h\nu \quad} Hg^{*}$$

$$Hg^{*} + SiHX_{3} \longrightarrow \overset{\bullet}{Si}X_{3} + \overset{\bullet}{H} + Hg^{O}$$
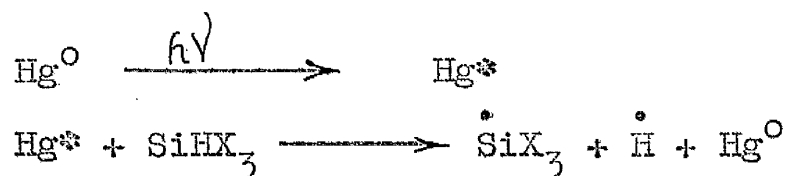
Irradiation of trimethylsilane alone and of
trimethylsilane with mercury gave hydrogen in yields
of 1% and 12% respectively after 4 days irradiation
which illustrates the effect of mercury atoms on the
photo-dissociation of trimethylsilane. It was found,
however, that explosions occurred when trimethylsilane
and vinyl fluoride were irradiated in the presence of
mercury at the temperature in the vicinity of the lamps
($\sim 35^{O}$). This difficulty was overcome by starting
the irradiation with the reactants completely frozen
down (-196°) and allowing the tube to warm up gradually.

It was found that this method was effective in promoting the addition of trimethylsilane to vinyl fluoride.

ii) An attempt was made to overcome the problem of initiation by using azobisisobutyronitrile which is known to act as a free radical initiator. It was established that no reaction occurred between trimethylsilane and vinyl fluoride in the presence of azobisisobutyronitrile at room temperature in the absence of light. Trimethylsilane and vinyl fluoride (silane/olefin ratio of 4:1) in the presence of azobisisobutyronitrile (0.5% of trimethylsilane) were heated to 80° with shaking for 24 hr. Complete decomposition of the initiator was observed (100% N_2), but only a small amount (ca.5%) of the 1:1 adduct of trimethylsilane with vinyl fluoride had been formed. No attempt was made to detect the initiator residue. A separate experiment showed that trimethylsilane and the initiator were immiscible at room temperature and this possibly explains the low yield of the 1:1 adduct in the reaction carried out with this initiator.

Investigation of the adducts of silanes with
vinyl fluoride and the determination of the
structure of the adducts,

It is conceivable that two structural
isomers might arise from the addition reaction
of a silane, $SiHX_3$, with vinyl fluoride:

$$SiHX_3 + CH_2:CHF \nearrow \begin{array}{l} CH_2F \cdot CH_2 \cdot SiX_3 \quad (1) \\ \\ CH_3 \cdot CHF \cdot SiX_3 \quad (2) \end{array}$$
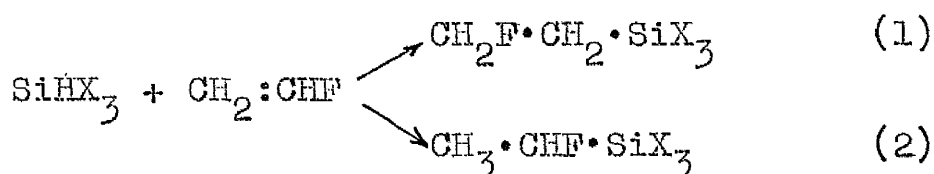
Current ideas on radical stabilities suggest that
the addition of silanes under free radical
conditions should give product (1) exclusively,
i.e. it is thought that the intermediate radical
$\overset{\bullet}{C}HF \cdot CH_2 \cdot SiX_3$ will be much more stable than the
intermediate radical $\overset{\bullet}{C}H_2 \cdot CHF \cdot SiX_3$. Theories of
heterolytic addition also require the addition of
electrophilic groups to the $=CH_2$ group.[139]

$$E^+ + CH_2:CHF \longrightarrow E \cdot CH_2 \cdot \overset{+}{C}HF.$$

It must be noted, however, that even though the
accepted polarisation of the silicon-hydrogen bond
is $\overset{+}{Si} - \overset{-}{H}$, the extent of the polarisation is low[140]
($\sim 2\%$ in SiH_4 as calculated from electronegativities)
and the direction of heterolysis can not be

unambiguously predicted.

It might be expected on these grounds that the greater proportion of the adduct will be a 2-fluoroethylsilane irrespective of the mechanism of the addition. The possibility of the inability of analytical techniques to detect small percentages of 1-fluoroethyl-silanes exists, and samples of the expected "minor" components (the 1-fluoroethyl-silanes) were prepared to verify this. It was found that 1-fluoroethyl-trichlorosilane was one of the products from the irradiation of 1-chloro-2-fluoroethylene with trichlorosilane, and that the percentage formation of this compound could be increased by working with a large excess of trichlorosilane.

$$\overset{\bullet}{S}iCl_3 + CHCl\!:\!CHF \longrightarrow \overset{\bullet}{C}HCl\cdot CHF\cdot SiCl_3$$

$$\overset{\bullet}{C}HCl\cdot CHF\cdot SiCl_3 + SiHCl_3 \longrightarrow CH_2Cl\cdot CHF\cdot SiCl_3 + \overset{\bullet}{S}iCl_3$$

$$\overset{\bullet}{S}iCl_3 + CH_2Cl\cdot CHF\cdot SiCl_3 \longrightarrow \overset{\bullet}{C}H_2\cdot CHF\cdot SiCl_3 + SiCl_4$$

$$\overset{\bullet}{C}H_2\cdot CHF\cdot SiCl_3 + SiHCl_3 \longrightarrow CH_3\cdot CHF\cdot SiCl_3 + \overset{\bullet}{S}iCl_3$$
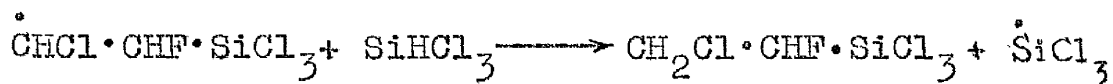
Pure 1-fluoroethyltrichlorosilane was obtained from the product mixture by fractional distillation, and the structure was verified by nuclear magnetic

resonance spectroscopy. 1-Fluoroethyltri-
methylsilane was prepared from this compound by
reaction with methylmagnesium iodide in di-n-butyl
ether.

The adducts from the photochemical
reactions were characterised by elemental analysis.
Investigation of the adduct by gas-liquid chromo-
tography using a "4m. silicone" column (M.S.550)
gave only pne peak for the adduct. Stationary
phases of squalane, squalane-silicone oil mixture,
and dinonyl phthalate were also used for the
investigation and only one peak was detected in each
case. Synthetic mixtures of the reaction products
(the adduct) and the prepared 1-fluoroethyl-silanes
were made up and investigated by gas-liquid
chromatography using the "4m. silicone" column described
above. It was found that the isomers were easily
separable. Typical retention times were
$CH_3 \cdot CHF \cdot SiMe_3$ 9.4 min., $CH_2F \cdot CH_2 \cdot SiMe_3$, 10.6 min.
(at 90°); and $CH_3 \cdot CHF \cdot SiCl_3$, 12.6 min.,
$CH_2F \cdot CH_2 \cdot SiCl_3$, 16.0 min. (at 150^OC). It is apparent
therefore, that only the 2-fluoroethylsilanes are
formed as the products of the reactions of vinyl
fluoride with silyl radicals.

It is, of course, not possible to assign the structure of complex compounds such as the 1-fluoroethyl- and 2-fluoroethyl-silanes merely on the basis of infra-red spectroscopy unless a large amount of other information is available. By a direct comparison of the spectra of the reaction products and the respective 1-fluoroethylsilanes it was possible to show that the latter compounds were not present in the reaction products to any detectable extent. This was done simply by noting the absence from the spectra of the reaction products of various unassigned bands which were present in the spectra of the 1-fluoroethylsilanes; e.g., bands at 10.88μ, 11.00μ, 11.30μ, all intense bands in the spectrum of 1-fluoroethyltrichlorosilane, are absent from the spectrum of 2-fluoroethyltrichloro-silane; and similarly the bands at 10.95μ, 11.05μ, and 11.55μ in the spectrum of 1-fluoroethyltrimethyl-silane are absent from that of 2-fluoroethyltrimethyl-silane.

The nuclear magnetic resonance spectra for both ^{1}H and ^{19}F were obtained. On the basis of these data the adducts were assigned the 2-fluoro-ethylsilane structures, i.e., $CH_2F \cdot CH_2 \cdot SiCl_3$,

$CH_2F \cdot CH_2 \cdot SiCl_2Me$, $CH_2F \cdot CH_2 \cdot SiMe_3$. The nuclear

magnetic resonance spectra of the fluoroalkyl-

silanes dealt with in this work are discussed on

page 294 and complete structural assignments are

presented for selected compounds. The limit of

detection with the spectrometer used (A.E.I model

RS-2) is 2% of a minor component. Therefore

nuclear magnetic resonance spectroscopy can only

be used to indicate the structure of the adduct

and not to detect low percentages of other isomers

present. Good evidence for exclusive addition

at the $:CH_2$ group of vinyl fluoride is available

from gas-liquid chromatography as discussed above,

confirmed by chemical evidence to be presented below.

Reactions of the adducts of silanes to vinyl
fluoride.

The hydrolyses and the pyrolyses of the
adducts of silanes to vinyl fluoride were
investigated to establish to what extent chemical
evidence is of value in determining the structure
of the adducts.

1) Hydrolyses.

Samples of the adducts from the
photochemical reaction of trichlorosilane,
methyldichlorosilane, and trimethylsilane with vinyl
fluoride were individually hydrolysed by the action
of 10% aqueous sodium hydroxide in vacuo at room
temperature.   The reaction gave ethylene
quantitatively as the only readily volatile product
in each case.

$$CH_2F \cdot CH_2 \cdot SiX_3 + OH^- \longrightarrow CH_2:CH_2 + (HOSiX_3) + F^-$$
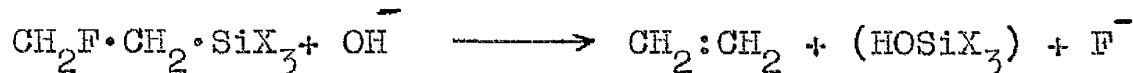
In each case fluoride ions were detected in the
aqueous residues after hydrolysis.   The sample of
the adduct of trimethylsilane with vinyl fluoride
contained a trace impurity (ca.,2%) of trimethyl-
silane which was present in the ethylene detected
after hydrolysis.   It was found that in both
2-fluoroethyltrichlorosilane and 2-fluoroethylmethyl-

dichlorosilane the silicon-chlorine bond could

be hydrolysed by distilled water without the formation

of ethylene:

e.g., $CH_2F \cdot CH_2SiCl_3 \xrightarrow{\quad H_2O \quad} (CH_2F \cdot CH_2 \cdot SiO_{1.5})_n$
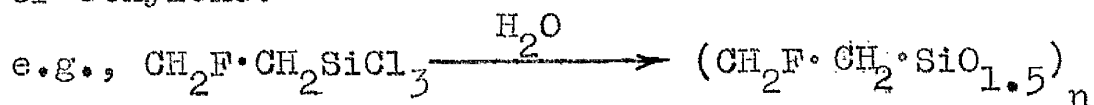
Similarly, fluoride ions could not be detected in

the aqueous residues after hydrolysis with distilled

water.   It is therefore apparent that the silicon-

carbon bond in this type of compound is susceptible

to attack by strongly nucleophilic reagents (OH^-) but

not by weak nucleophiles (H_2O).

The mechanism of the hydrolysis is thought

to involve a concerted β-elimination of fluoride

ion with olefin formation in the following manner.

$OH^- \quad X_3 \cdot Si \cdot CH_2 \cdot CH_2 \cdot Cl \longrightarrow X_3SiOH + CH_2:CH_2 + Cl^-$

$OH^- \quad X_3 \cdot Si \cdot CH_2 \cdot CH_2 \cdot F \longrightarrow X_3SiOH + CH_2:CH_2 + F^-$
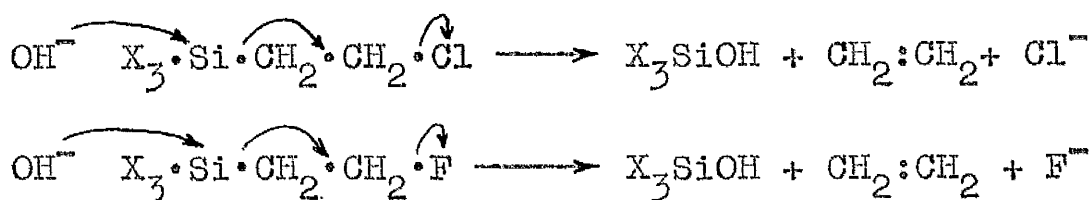
This is analogous to the mechanism which

has been postulated for the hydrolysis of similar

β- chloroethylsilanes.[141]

Hydrolysis of the analogous 1-chloroethyl-

trichlorosilane, $CH_3 \cdot CHCl \cdot SiCl_3$, has been shown not

to occur even in the presence of alcoholic potassium

hydroxide at room temperature[142] and an authentic sample

of 1-fluoroethyltrichlorosilane similarly did not eliminate ethylene in 10% aqueous sodium hydroxide at 100°:

$$CH_3 \cdot CHF \cdot SiCl_3 \xrightarrow{\;OH^-\;} \times \; CH_2 : CH_2 + SiO_2 + F^-.$$
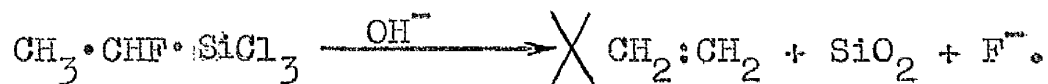
Polymers of the type $(CH_3 \cdot CHF \cdot SiO_{1.5})_n$ are presumed to have been formed by hydrolysis of the silicon-chlorine bonds. The quantitative evolution of ethylene from these hydrolyses supports the proposal that only 2-fluoroethylsilanes are formed in the reaction of silyl radicals with vinyl fluoride. The mechanism of the hydrolysis is discussed in conjunction with the hydrolysis data from other fluoroalkylsilicon compounds.

2.) Pyrolyses.

The adduct of trichlorosilane with vinyl fluoride was investigated by pyrolysis. Pyrolyses were carried out at 450°, and at 220° for 24 hr.

$$CH_2F \cdot CH_2 \cdot SiCl_3 \xrightarrow[24 \text{ hr.}]{450°} CH_2 : CH_2 + SiCl_3F$$
$$\phantom{CH_2F \cdot CH_2 \cdot SiCl_3 \xrightarrow[24 \text{ hr.}]{450°}} 78\% \qquad 95\%$$

$$CH_2F \cdot CH_2 \cdot SiCl_3 \xrightarrow[24 \text{ hr.}]{220°} CH_2 : CH_2 + SiCl_3F$$
$$\phantom{CH_2F \cdot CH_2 \cdot SiCl_3 \xrightarrow[24 \text{ hr.}]{220°} CH_2 : CH_2 +} 97\%$$
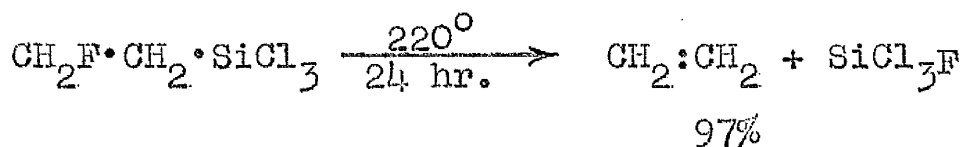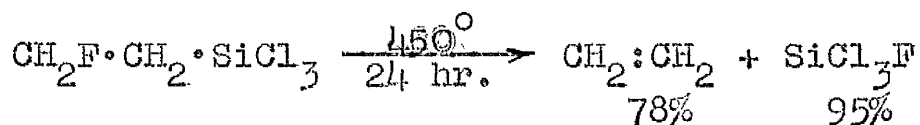
The reaction is thought to proceed with β-halogen elimination via a four-centred transition state,

similar to that proposed for the pyrolysis of
2,2-difluoroethyltrifluorosilane.[143,172]
i.e., by internal nucleophilic attack of fluorine
on silicon:

$$Cl_3Si - CH_2 \quad \longrightarrow \quad \left[\begin{array}{cc} Cl_3Si \cdots\cdots CH_2 \\ \\ F \cdots\cdots CH_2 \end{array} \right] \quad \longrightarrow \quad \begin{array}{c} Cl_3SiF \\ + \\ CH_2:CH_2. \end{array}$$
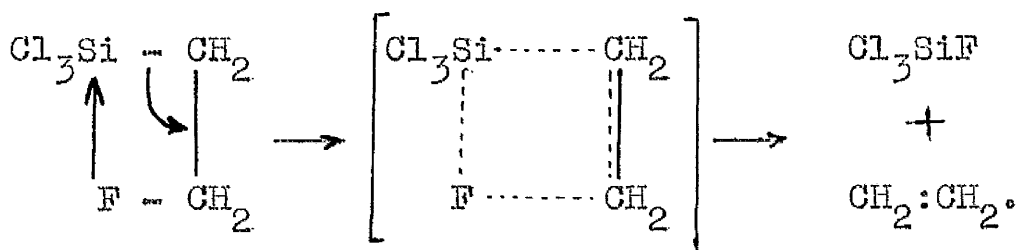
Work carried out in this department,[146] however,
suggests that the 1-fluoroethylsilanes would also
give ethylene as one of the pyrolysis products by
a process of α-elimination, followed by a carbene
rearrangement by hydrogen atom migration.

$$CH_3 \cdot \underset{\underset{F}{|}}{CH} \cdot SiCl_3 \quad \xrightarrow{\triangle} \quad CH_3 \cdot \ddot{C}H \quad + \quad SiCl_3F$$

$$CH_3 \cdot \ddot{C}H \quad \xrightarrow{\text{H-migration}} \quad CH_2:CH_2$$
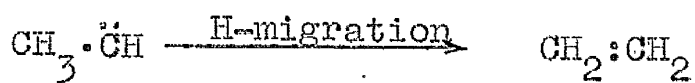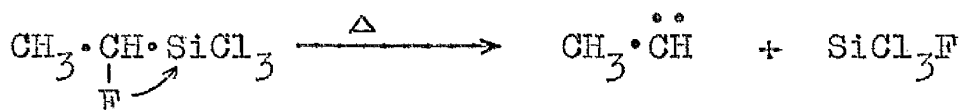
The formation of ethylene by a carbene rearrangement
has been observed in the photolysis of diazoethane.

$$CH_3 \cdot CH:N:N \quad \xrightarrow{h\nu} \quad CH_3 \cdot \ddot{C}H \quad \xrightarrow{\text{H-migration}} \quad CH_2:CH_2.$$
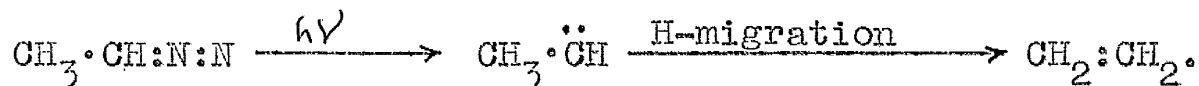
α-eliminations of this nature have been observed
along with reactions involving α-halogen exchange
with the halogen attached to the silicon atom,[146] e.g.,

$$CF_2H \cdot CF_2 \cdot SiCl_3 \xrightarrow{\text{α-elimination}} CHF:CF_2 + SiCl_3F \quad 29\%$$

Halogen exchange $\downarrow$

$$CF_2H \cdot CFCl \cdot SiFCl_2 \xrightarrow{\text{α-elimination}} CF_2:CHCl + SiCl_2F_2 \quad 21\%$$

Halogen exchange $\downarrow$

$$CF_2H \cdot CCl_2 \cdot SiF_2Cl \xrightarrow{\text{β-elimination}} CHF:CCl_2 + SiF_3Cl \quad 22\%$$
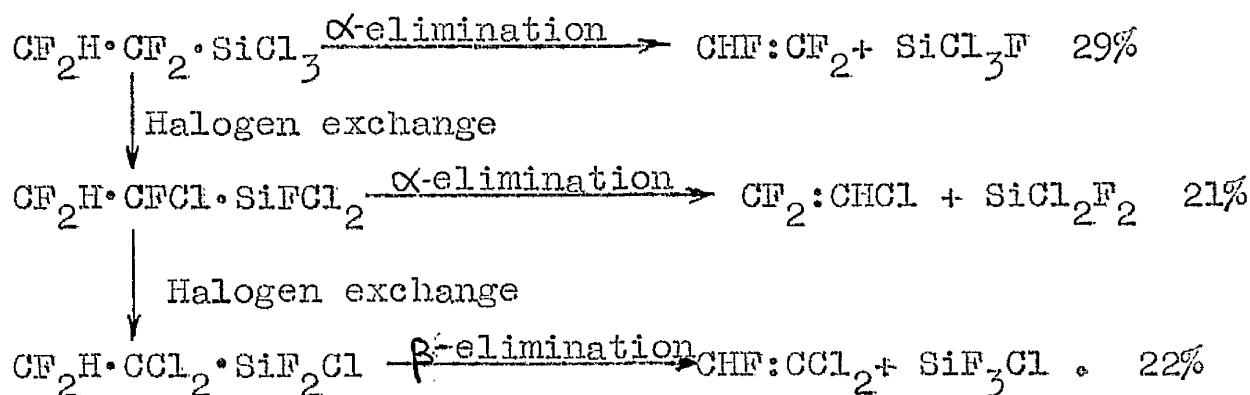
Pyrolysis of 1-fluoroethyltrichlorosilane at 250° for 24 hr. gave only 23% ethylene as the volatile product along with unidentified high boiling silicon compounds and a slight charring of the tube. Ethylene is presumably formed by α-elimination as above. The exchange reaction may however produce 1-chloroethyldichlorofluorosilane.

$$CH_3 \cdot \underset{\underset{F}{|}}{CH} \cdot SiCl_2 \xrightarrow{\hspace{2cm}} CH_3 \cdot CHCl \cdot SiFCl_2$$

The related compound 1-chloroethyltrichlorosilane is reported to be stable at 610°[147] and it is possible that the product of the exchange reaction of 1-fluoroethyltrichlorosilane would not break down at the pyrolysis temperature. No attempt was made to identify the silicon compounds formed in the reaction.

It is apparent that pyrolysis of the adducts of silyl radicals with vinyl fluoride is not a

satisfactory method for determining the structures of the isomers present, nor for detecting the possible presence of two isomers. The formation of high yields (97%) of ethylene however indicates the presence of a high proportion of the β-fluoroethyl-isomer in the product, but does not exclude low percentages of the α-fluoroethyl-isomer. The mechanism of the pyrolysis is discussed in conjunction with data from the pyrolysis of other fluoroalkylsilicon compounds.

3) Fluorination

An attempt was made to replace the silicon-chlorine bonds by silicon-fluorine bonds by fluorination with antimony trifluoride. This should have provided the compound 2-fluoroethyltrifluorosilane ($CH_2F \cdot CH_2 \cdot SiF_3$) which was of interest for pyrolysis studies. It was found that conventional fluorination by passing the silicon compound through a tube packed with antimony trifluoride which had previously been moistened with a few drops of antimony pentachloride resulted in the formation of only break-down products

$$CH_2F \cdot CH_2 \cdot SiCl_3 \xrightarrow[\text{SbCl}_5]{\text{SbF}_3} SiF_4 + CH_2{:}CH_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad 90\% \qquad 90\%$$
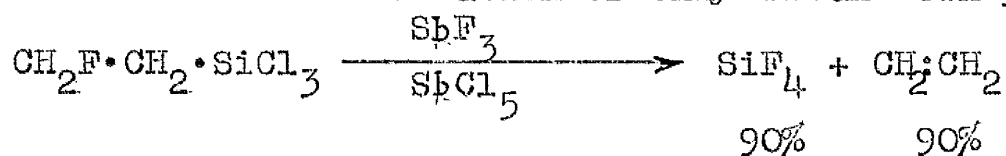
The method was modified by activating the antimony

trifluoride with chlorine gas and excluding the
addition of antimony pentachloride.   This was
done by passing a stream of chlorine through the
tube for a few minutes before the reaction.
It was found that the fluoroalkylfluorosilane could
be prepared in this way, but the product slowly
decomposed on standing to ethylene and silicon
tetrafluoride.

$$CH_2F \cdot CH_2 \cdot SiCl_3 \xrightarrow[\text{reaction}]{70\%} \begin{cases} CH_2F \cdot CH_2 \cdot SiF_3 & 60\% \\ CH_2:CH_2 \\ SiF_4 \end{cases} \Big\} \; 40\%$$

$$CH_2F \cdot CH_2 SiF_3 \longrightarrow CH_2:CH_2 + SiF_4$$
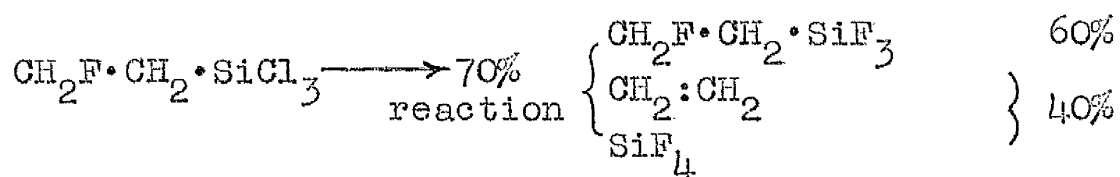
This is possibly because of the high silicon-fluorine
bond energy and the gain in stability in forming
silicon tetrafluoride, (e.g., D(Si-C), 76; D(Si-Cl),
91; D(Si-F), 135 Kcal/mole;)[148]

There is, therefore, excellent evidence that
the addition reactions of silanes with vinyl fluoride
under homolytic conditions are unidirectional.   The
products are 2-fluoroethylsilanes.   Hydrolysis with
aqueous alkali provides a good method for determining
the structure of these compounds, but pyrolysis data
are unambiguous only when the yield of ethylene is
quantitative.

The reaction of silanes and trifluoroethylene.

   The silane and trifluoroethylene were irradiated
in silica tubes with silane/olefin ratios of between
5:1 and 6:1; with shaking for about four days (see
table 7). Two slightly different techniques were
adopted for handling the products from the reaction.
For the chlorosilanes, trichlorosilane and methyl-
dichlorosilane, the reaction products were fractionated
in vacuo through a series of cold traps and each
fraction was separately examined by infra-red spectroscopy,
gas-liquid chromatography, and, where applicable, molecular
weight determination. This allowed crude separation of
the adduct from the unreacted starting materials and an
estimate of the percentage reaction from the recovery of
the starting materials. The adduct fraction, usually
from two identical reactions, was then fractionally
distilled to remove traces of unreacted silane and to
obtain a pure sample of the 1:1 adduct. The purity of
the sample was then checked by infra-red spectroscopy
and elemental analysis. The yield of the 1:1 adduct
obtained in this manner will be lower than the true
yield because of the column hold-up. Pot-residues
were generally found to have similar infra-red absorption
spectra to the 1:1 adduct, but the chlorine analysis
indicated an average chain length of ca.2 olefin units

possibly arising from a distribution of telomers with 1,2,3 and more olefin units.

For irradiations with trimethylsilane the products were fractionated in vacuo through a series of cold traps, repeated vacuum fractionation of the adduct fraction being sufficient to remove all but a trace of unreacted trimethylsilane. The purity and identity of the adduct were checked by infra-red spectroscopy, gas-liquid chromatography, and elemental analysis. The percentage reactions was determined by gas-liquid chromatography and infra-red spectroscopy as before.

The reactions of trichlorosilane and methyldichlorosilane with trifluoroethylene were found to take place smoothly to give good percentage yields (93% and 80% respectively) after 100 hr. irradiation. Only the 1:1 adduct and small amounts of telomeric material were found along with unreacted starting materials. No side reaction was detectable. Similarly, the photochemical reaction of trimethylsilane with trifluoroethylene gave 20% reaction to the adduct after 12 hr. It was found however that a reaction carried out for 140 hr. in the presence of atomic mercury gave a trace of a compound identified by gas-liquid chromatography, as 1,1,2-trifluoroethane (less than 0.5%) and that for a reaction

carried out for 250 hr. in the absence of mercury low percentages of hydrogen (ca. 1.5%), trimethylfluorosilane (ca.10%), and an unidentified compound, assumed to be a difluoroethyltrimethylsilane (ca.6%) were detected. Trichlorosilane and trifluoroethylene were sealed in a silica tube in the mole ratio 2:1 and warmed to 85° for 100 hr. in the absence of light.   No reaction was observed which indicated that ultraviolet light was necessary for reaction, i.e., the addition reaction was probably a free radical process.   Factors which support this assumption and the possible mechanism for the production of these compounds are discussed later (pp.130)

TABLE 7	Photochemical reactions of silanes with trifluoroethylene.			
Silane	Ratio ^{s}/o	time hr.	% reaction (olefin)	Yield of 1:1 adduct (%)
$SiHCl_3$	5:1	100	93	77
$MeSiHCl_2$	5:1	100	80	85
Me_3SiH	5.5:1	140	100	90 (a)
Me_3SiH	5.5:1	250	100	88 (b)
Me_3SiH	5:1	12	20	100

(a) Mercury photosensitisation used, trace of $CF_2H \cdot CH_2F$ produced.

(b) $H_2(1.5\%)$, $Me_3SiF(10\%)$, + other compounds.

Investigation of the adducts of silanes with
trifluoroethylene and the determination of the
structuresof the adducts.

The adducts were investigated by use of
gas-liquid chromatography in an attempt to determine
the position of the silyl group relative to the
difluoromethylene group.   Theories of both homolytic
and heterolytic addition reactions would suggest that
either a silyl radical or an incipient siliconium ion
would become attached to the $=CHF$ group in preference
to the $=CF_2$ group of trifluoroethylene.   Free radical
addition mechanisms predict the preferred formation of
the most stable free radical intermediate:

i.e., $\overset{\bullet}{C}F_2 \cdot CHF \cdot SiX_3$ is more stable than $CHF \cdot \overset{\bullet}{C}F_2 \cdot SiX_3$.

The electrophilic addition of ethoxide ion[138] indicates
the polarisation of the electron density towards the
$=CHF$ group:

i.e.. $EtO^- + CHF{:}CF_2 \longrightarrow \overset{-}{CHF} \cdot CF_2 \cdot OEt$
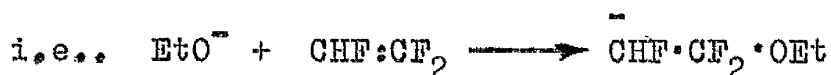
It may be noted, however, that even though the accepted
polarisation of the silicon-hydrogen bond is in the
direction $Si^+ \!-\! H^-$, the extent of the polarisation is low[148]
(estimated at $\sim 2\%$ in silane (SiH_4) from electronegativities)
and consequently the presence of electronegative groups

could facilitate heterolysis in the reverse direction

during the addition reactions of chlorosilanes, i.e.,

$$Cl_3 \xleftarrow{\quad} \overset{\delta-}{Si} \overset{\delta+}{\underline{\quad}} H .$$
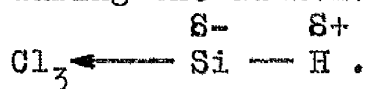
From these arguments it might be suggested that the

major component of the adduct, if in fact there are

two components, would be a 1,2,2-trifluoroethylsilane,

$CHF_2 \cdot CHF \cdot SiX_3$.

The gas-liquid chromatograms for the adducts

with trichlorosilane, methyldichlorosilane, and

trimethylsilane consisted of one peak, a main peak with

a small shoulder, and two distinct peaks respectively.

The nuclear magnetic resonance spectra (^{1}H and ^{19}F) of

the adduct with trichlorosilane indicated the presence

of only a 1,2,2-trifluoroethyl group (i.e., within the

limits of detection of the spectrometer). The possibility

that a low percentage ($\sim$ 5%) of the other isomer,

1,1,2-trifluoroethyltrichlorosilane, was present, and was

not separated by gas-liquid chromatography was investigated.

A pure sample of 1,1,2-trifluoroethyltrichlorosilane

had been prepared by the addition reaction of trichlorosilane

with chlorotrifluoroethylene followed by dechlorination in

situ, and its structure was verified by nuclear magnetic

spectroscopy.[146]

$$SiHCl_3 + CF_2{:}CFCl \xrightarrow{h\nu} CHClF{\cdot}CF_2{\cdot}SiCl_3$$

$$CHClF{\cdot}CF_2{\cdot}SiCl_3 + SiHCl_3 \xrightarrow{h\nu} CH_2F{\cdot}CF_2{\cdot}SiCl_3 + SiCl_4$$
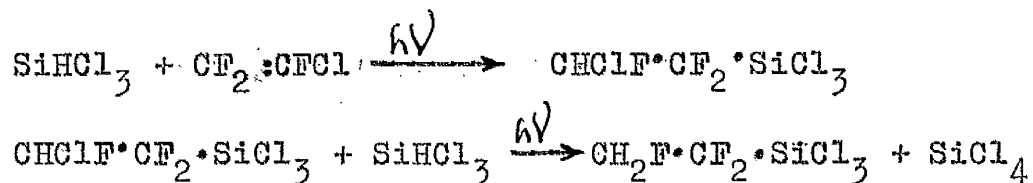
A comparison of retention times between this compound
and the adduct of trichlorosilane with trifluoroethylene
and an examination of a synthetic mixture of the two,
showed that even small amounts (ca. 5%) of 1,1,2-trifluoro-
ethyltrichlorosilane were well separated from the adduct
during gas-liquid chromatography. In this way it was
shown that the adduct was exclusively 1,2,2-trifluoroethyl-
trichlorosilane.

Examination of the adduct of methyldichlorosilane
with trifluoroethylene by nuclear magnetic resonance
spectroscopy indicated the present of a compound containing
1,2,2,-trifluoroethyl group as the main component, with
a trace ($\sim$5%) of a compound containing a 1,1,2-trifluoro-
ethyl group. As gas-liquid chromatography also indicates
the presence of a major and a minor component it is
concluded that addition of methyldichlorosilane to
trifluoroethylene takes place to an extent of ca. 95% at
the =CHF group and that some addition, ca. 5% takes place
at the =CF$_2$ group. Hydrolysis data discussed below is in
agreement with this. Authentic samples of the two isomers
were not synthesised.

The adduct of trimethylsilane with trifluoroethylene
was found to consist of two compounds by examination

using gas-liquid chromatography.   As the components
were in the ratios 36:64 and 41:59 from different
reactions, the nuclear magnetic resonance spectra would
be expected to be too complex to allow valuable
interpretation.   To overcome this difficulty samples
of the two expected adducts were synthesised.
1,2,2-Trifluoroethyltrimethylsilane was prepared by
the Grignard reaction of methyl magnesium iodide with
1,2,2-trifluoroethyltrichlorosilane (the structure of
which had been determined as described above).
1,1,2-Trifluoroethyltrimethylsilane was prepared by the
addition reaction of trimethylsilane followed by
dechlorination in situ in a similar manner to the
preparation of 1,1,2-trifluoroethyltrichlorosilane
previously described.   The structure was verified by
nuclear magnetic resonance spectroscopy.

Comparison of the retention times for the adduct
of trimethylsilane with trifluoroethylene with those for
the synthesised compounds indicated that the major
component was 1,2,2-trifluoroethyltrimethylsilane, and
that the minor component was 1,1,2-trifluoroethyltrimethyl-
silane.

Silane	addition at CHF(%)	addition at CF_2 (%)	time of irradiation (hr.).
Cl_3SiH	greater than 98	-	100
Cl_2MeSiH	95	5	100
Me_3SiH	64	36	140
Me_3SiH	59	41	250

TABLE 8 — Isomer distribution by gas-liquid chromatography.

It is notable that the isomer ratio for the addition of trimethylsilane to trifluoroethylene is not constant. It was found, however, that a low conversion reaction which was designed to obtain an isomer ratio with the minimum of interference from side reactions or telomerisations, gave after 12 hours irradiation 20% reaction to a mixture of the adducts in the ratio 65:35 for =CHF and =CF_2 addition respectively. The ratio obtained for the 250 hr. reaction (Table 8), coupled with the observation of different products in low percentages (trimethylfluorosilane and an unidentified compound), indicated that further reaction of the adducts is taking place on extended irradiation, and that the rate of this reaction is not the same for the two adducts. A

possible mechanism for this reaction is discussed in conjunction with similar data from other addition reactions, pp 145.

For the peak areas obtained by gas-liquid chromatrography to be truly indicative of the actual percentage of each isomer present, it must be ascertained that differences in thermal conductivity (for measurement by thermistor detectors) are negligible. The adduct of trimethylsilane with trifluoroethylene gives the highest degree of bidirection addition, and a calibration of the fractometer for these two isomers was carried out. A pure sample of 1,2,2-trifluoroethyl-trimethylsilane was prepared by the Grignard reaction from 1,2,2-trifluoroethyltrichlorosilane.

$$CF_2H \cdot CHF \cdot SiCl_3 + 3CH_3MgI \xrightarrow[\substack{\text{di-n-butyl} \\ \text{ether}}]{0^{\circ}C} CF_2H \cdot CHF \cdot Si(CH_3)_3 + 3MgICl \quad 25\%$$
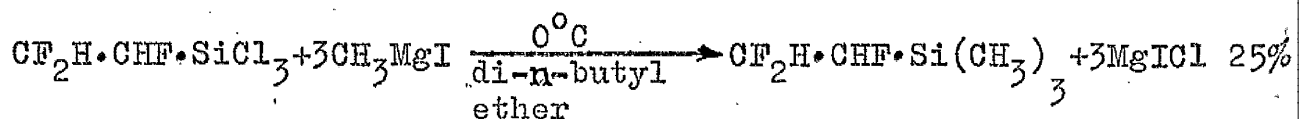
Mixtures of the two isomers, $CF_2H \cdot CHF \cdot Si(CH_3)_3$ and $CH_2F \cdot CF_2 \cdot Si(CH_3)_3$, of known composition were made up and investigated by gas-liquid chromatography. It was found that the very slight difference in thermistor response (0.2%) was of the same order as the reproducability of the fractometer and that percentages quoted by gas-liquid chromatography must be allowed a possible error of $\pm$ 0.5%.

Reactions of the adducts of silanes with trifluoroethylene.

The hydrolyses and the pyrolyses of the
adducts of silanes with trifluoroethylene were
investigated to establish to what extent chemical evidence
was of value in deciding the isomer ratios of the adducts.

(i) Hydrolyses.

The adducts obtained from the photochemical
addition reactions were hydrolysed in vacuo with 10%
aqueous sodium hydroxide. The products consisted of
1,1,2-trifluoroethane and either one or two difluoroethylenes
which were identified by infra-red spectroscopy and gas-
liquid chromatography. It was found that decreasing the
strength of the sodium hydroxide solution led to an increase
in the percentage of fluoroalkane $(CF_2H \cdot CFH_2)$ formation,
but that attempted hydrolysis with water led to the
hydrolysis of the silicon-chlorine bonds only. Examination
of the volatile products from the hydrolysis indicated the
presence of both 1,2-difluoroethylene and 1,1-difluoroethylene
in the case of the adducts of dichloromethylsilane and
trimethylsilane to trifluoroethylene. The olefin
1,1-difluoroethylene could not be detected in the case of
the adduct with trichlorosilane, (see table 9).

Silane	hydrolysis (aqueous solution)	% reaction	$\%CF_2H \cdot CH_2F$	$\%CFH:CFH$	$\%CH_2:CF_2$
Cl_3SiH	NaOH 10%	100	80	20	–
Cl_3SiH	NaOH 1%	100	87	13	–
Cl_2MeSiH	NaOH 10%	100	57	41	2
Cl_2MeSiH	NaOH 1%	99	84	15.5	0.5
*Me_3SiH	NaOH 10%	98.5	43	41	16

TABLE 9   HYDROLYSIS OF THE ADDUCTS OF SILANES WITH TRIFLUOROETHYLENE.

* - from the 140 hr. reaction.

Since it has been shown that 1,1,2-trifluoroethane is not attacked by aqueous alkali it may be concluded that the fluoroalkane and the fluoroolefins arise from the competing processes which operate during the hydrolysis. These may be:

(i) displacement of a carbanion,
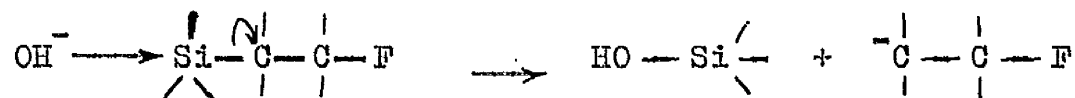
followed by either attack on a water molecule or loss of a fluoride ion,

or (ii) a concerted β-halogen elimination,

$$OH^- \cap Si - C - C - F \longrightarrow HO - Si\langle \; + \rangle C = C\langle \; + F^- \;.$$
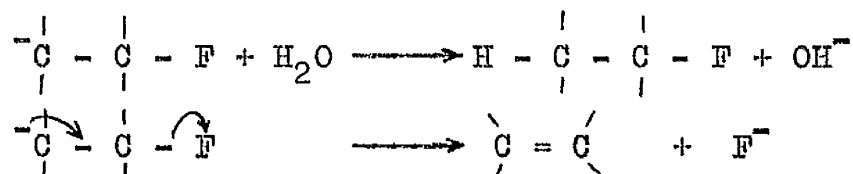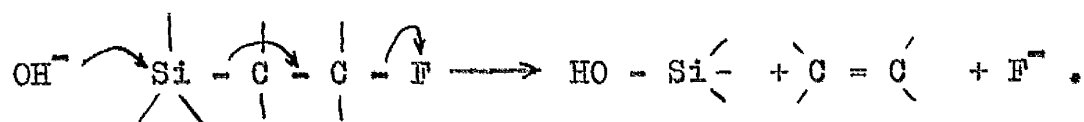
It appears that with 1% sodium hydroxide solution the
carbanion displacement followed by alkane formation
predominates. If β-fluorine elimination takes place,
1,2-difluoroethylene arises from the hydrolysis of
1,2,2-trifluoroethylsilanes, and 1,1-difluoroethylene
arises from hydrolysis of 1,1,2-trifluoroethylsilanes.
The percentage of β-elimination for two isomers need not
be the same and as the percentage of alkane formation is
high it is clear that isomer ratios can not be obtained in
this way. This is illustrated by a comparison of the
isomer ratios for the addition reaction of trimethylsilane
with trifluoroethylene obtained from gas-liquid chromatography
(g.l.c.) and from hydrolysis data, (table 10).

TABLE 10	Isomer ratios by gas-liquid chromatography (g.l.c.) and by alkaline hydrolysis $H(CHF \cdot CF_2)SiMe_3$.	
Method	Addition at $= CHF$ group	Addition at $= CF_2$ group.
g.l.c.	64%	36%
hydrolysis	72%	28%

It must be pointed out at this stage of the
argument that the reaction schemes presented above are only
proposed mechanisms which fit the known facts. It is clear

that this approach, though useful for indicating the
presence of both isomers, is of no value for determining
isomer ratios unless quantitative formation of olefin is
observed.   The relative merits of the proposed mechanisms
of hydrolysis are discussed in conjunction with data from
other hydrolyses, (pp. 173).   The final conclusion is
that β-elimination is the most probable mechanism.

It is interesting to note in this context that
the percentage of olefin formation on hydrolysis with 10%
aqueous sodium hydroxide increases with increasing number
of methyl groups attached to the silicon atom.   This
probably results from a facilitation of an electron shift
of the β-elimination type.
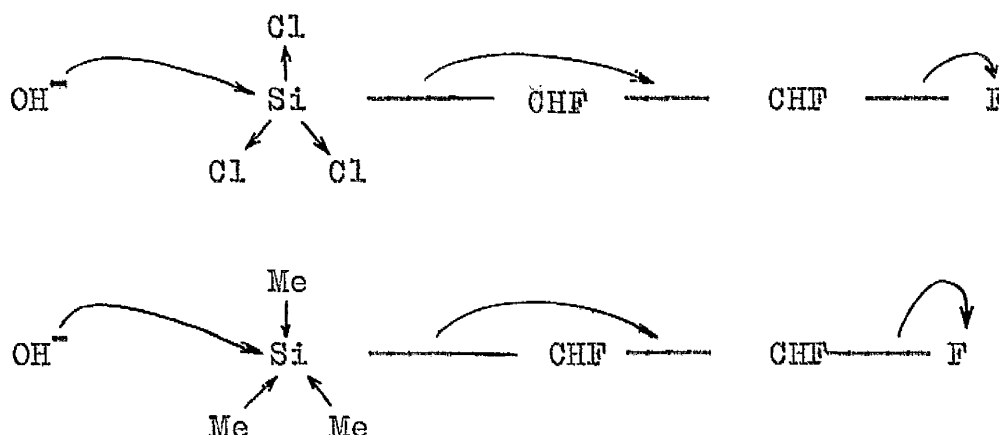
The effect of the substituents attached to silicon may be
conflicting, i.e., electron withdrawal from silicon assists

nucleophilic attack but hinders β-elimination, and vice-versa for electron release.   The experimental evidence available indicates that polarisation before the attack of the nucleophile might be the more important effect, but more experimental data is needed before such substituent effects are fully understood.

(ii) Pyrolyses

The adducts obtained from the photochemical reactions of silanes with trifluoroethylene were pyrolysed in vacuo at 280° for 18 hr., and the products were identified by infra-red spectroscopy and molecular weight determination as a mixture of fluoro-olefins with a silicon halide.   The products were shaken with water in a hydrolysis bulb to remove the silicon compound (by hydrolysis of the silicon-chlorine bonds) and the remaining volatile component(s) was then re-examined by infra-red spectroscopy, molecular weight determination, and the composition determined by means of gas-liquid chromatography.   The adduct with trimethylsilane was not pyrolysed.   Results are given below (table 11) along with the result from the pyrolysis of 1,1,2-trifluoroethyltrichlorosilane which was prepared independently.

TABLE 11	The Pyrolysis of the adducts of silanes with trifluoroethylene	
Compound	Reaction conditions.	% organic product.
$CF_2H \cdot CHF \cdot SiCl_3$	280°, 18 hr.	49% CHF:CHF + tar
$CF_2H \cdot CHF \cdot SiCl_3$	225°, 16 hr.	47% CHF:CHF + tar
$CH_2F \cdot CF_2 \cdot SiCl_3$	225°, 16 hr.	60% CH_2:CH_2; 19% CHF:CHF; 7% CHF:CH .
$H-(CF_2 \cdot CHF) \cdot SiCl_2Me$	280° 18 hr.	95% CHF:CHF; 5% CH_2:CF_2 .

The pyrolysis of 1,2,2-trifluoroethyltrichlorosilane was repeated at 225° for 16 hr. for comparison with the results from the pyrolysis of 1,1,2-trifluoroethyltrichlorosilane.

The formation of 1,2-difluoroethylene in the pyrolysis of 1,2,2-trifluoroethyltrichlorosilane can be explained by nucleophilic attack of a β-fluorine atom on the silicon atom with a synchronous electron rearrangement (similar to that in β-elimination).

$$Cl_3Si \cdot CHF \cdot CF_2H \xrightarrow{\Delta} \left[\begin{array}{c} Si - CHF \\ F - CHF \end{array} \right] \longrightarrow \begin{array}{c} Cl_3SiF \\ + \ CHF:CHF \end{array}$$
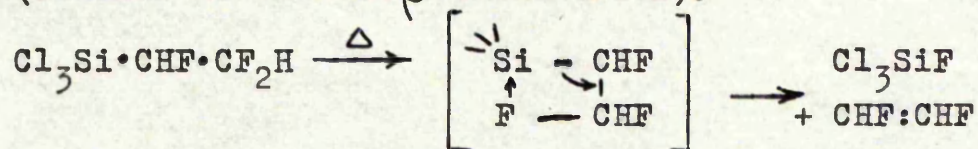
The products observed in the pyrolysis of the compound isomeric with this, i.e. 1,1,2-trifluoroethyltrichlorosilane as part of an extensive investigation carried out by Bevan,[146]

necessitated the postulation of a complex cycle of

α-silicon-carbon halogen exchanges and α- halogen

elimination with carbene rearrangement.[146]

$$CH_2F \cdot CF_2 \cdot SiCl_3 \xrightarrow{\alpha\text{-elimination}} CH_2F \cdot \overset{\cdot\cdot}{C}F \longrightarrow CHF:CHF \quad (19\%)$$
$$+ SiCl_3F$$

$\downarrow \alpha\text{-exchange}$

$$CH_2F \cdot CFCl \cdot SiCl_2F \xrightarrow{\alpha\text{-elimination}} CH_2F\overset{\cdot\cdot}{C}Cl \longrightarrow CHF:CHCl \quad (7\%)$$
$$+ SiCl_2F_2$$

$\downarrow \alpha\text{-exchange}$

$$CH_2F \cdot CCl_2 \cdot SiClF_2 \xrightarrow{\beta\text{-elimination}} CH_2:CCl_2 + SiF_3Cl \quad (60\%)$$
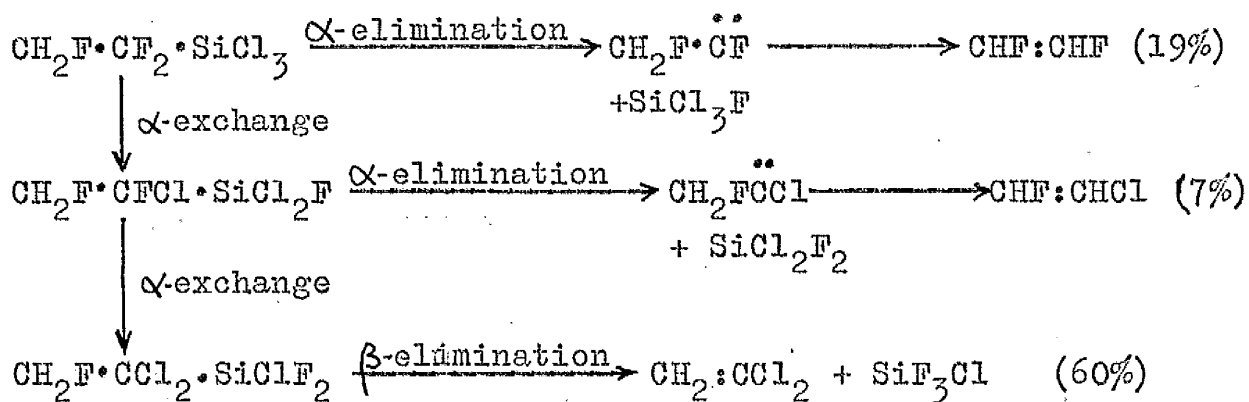
Although the major proportion of the product from

the above pyrolysis is formed from a β- elimination

mechanism it is clear in view of the complexity of the

reaction in one case and the low olefin yield in the

other, that the method is of no diagnostic value for

mixtures of these isomers.   The apparent coincidence of

the percentages of the olefins formed during hydrolysis

and pyrolysis of the adduct of dichloromethylsilane and

trifluoethylene must be regarded as fortuitous until it

is independently established that each isomer breaks down

exclusively by the same mechanism.   The mechanism is

is discussed more fully in conjunction with data from other

pyrolyses.

The reaction of silane (SiH_4) with trifluoroethylene

A preliminary reaction of silane with trifluoroethylene was carried out with a silane/olefin ratio of 1:1 for 150 hr. Complete reaction of the olefin and ca. 50% reaction of the silane were observed. The products were found to consist of five unidentified components and fluorosilane (H_3SiF). It is apparent that the reaction is unsuitable for the purpose of this investigation.

THE REACTION OF SILANES WITH 1-CHLORO-2-FLUOROETHYLENE.

The olefin was irradiated in the presence of a large excess of the silane in a silica tube in vacuo as previously described. It was found that the reaction was greatly complicated by a side reaction. The reactions of trichlorosilane and trimethylsilane with 1-chloro-2-fluoroethylene are, therefore, discussed separately.

The reaction of trichlorosilane with 1-chloro-2-fluoroethylene.

The reaction was carried out with silane/olefin ratios of 2.5:1, 5:1 and 10:1. The same procedure was used for the investigation of the products of the reactions for each ratio. Fractionation in vacuo gave a crude product which was fractionally distilled to give a compound recognised by elemental analysis as the 1:1 adduct of trichlorosilane with 1-chloro-2-fluoroethylene. The 1:1 adduct was collected over the boiling range of 140-146° which appeared to be rather wide for a pure compound.

The 1:1 adducts from the reactions with different ratios were investigated by gas-liquid chromatography and were shown to consist of two distinct components. Investigation of the product from the reaction with a silane/olefin ratio of 5:1 by

nuclear magnetic resonance spectroscopy indicated the possible presence of both -CHF- and -CH$_2$F groups, but the spectra were too complex to allow any definite interpretation.

It is important to note that the ratios of the two components and also the percentage of the 1:1 adduct isolated were quite different for the reactions with different silane/olefin ratios, (table 12). These differences are better understood when the other products of the reaction are considered.

In the reaction with a silane/olefin ratio of 2.5:1, 73% of the olefin was consumed of which only 41% was accounted for by the organosilicon compounds isolated. A high boiling polymeric material was found and this is presumed to account for the deficit. Fractional distillation of the crude product gave a forerun to the 140-146° fraction which was shown by gas-liquid chromatography to consist of silicon tetrachloride and 1-fluoroethyltrichlorosilane (3% of the olefin consumed), in addition to a trace of the compounds constituting the 140-146° fraction. The two components of the 140-146° fraction (38% of the olefin consumed) were in the ratio 18:82 in order of elution.

In the reaction with a silane/olefin ratio of 5:1, 67% of the olefin was consumed of which 89% was accounted for by the organosilicon compounds isolated. Telomer formation had occurred to a lesser extent than in the 2.5:1 reaction, presumably because of the higher silane/olefin ratio. Fractional distillation of the product gave a forerun as above, shown by gas-liquid chromatography to consist of silicon tetrachloride and 1-fluoroethyltrichlorosilane (10% of the olefin consumed) in addition to a trace of the compounds constituting the 140-146° fraction. The two components of the 140-146° fraction (79% of the olefin consumed) were in the ratio 25:75 in order of elution.

In the reaction with a silane/olefin ratio of 10:1, 98% of the olefin was consumed of which 91% was accounted for by the organosilicon compounds isolated. Telomer formation had occurred, again to a lesser degree than in the 2.5:1 reaction. Fractional distillation of the product gave silicon tetrachloride, 1-fluoroethyltrichlorosilane (61%), 2-fluoroethyltrichlorosilane (12%) and the 140-146° fraction (8%). (Percentages quoted are percentages of the olefin consumed). The two components of the 140-146° fraction were in the ratio 42:58 in order of elution.

The two isomeric fluoroethylsilanes from the

10:1 reaction were well separated by fractional distillation

($CH_2F.CH_2.SiCl_3$, b.p. 116-118°/760; $CH_3.CHF.SiCl_3$,

b.p. 102-104°/760) and identification was by elemental

analysis for carbon, hydrogen and chlorine, and by nuclear

magnetic resonance spectroscopy.   The 2-fluoroethyltrichloro-

silane prepared in this way was identical with a sample

prepared by the addition reaction of trichlorosilane with

vinyl fluoride.   The 1-fluoroethyltrichlorosilane from this

reaction was used as a gas-liquid chromatographic standard for

identifying the 1-fluoroethyltrichlorosilane produced in other

reactions.

Considered together (table 12), these results

suggest that a bidirectional addition reaction is taking place

to give a mixture of the two possible 1:1 adducts.   The

140-146° fraction was suggested to be the adduct mixture

because: (i) the elemental analysis was correct for the adduct,

(ii) the fraction contained two components of higher boiling

point than the fluoroethyltrichlorosilanes, and

(iii) hydrolysis of a sample of this fraction (discussed

later) gave the two olefins vinyl fluoride and vinyl chloride.

The nuclear magnetic resonance spectra of the mixture were too

complex to allow worthwhile interpretation, but the possible presence of both -CHF- and -CH$_2$F groups was indicated.

At low silane/olefin ratios extensive telomer formation occurred. Although this was reduced at higher silane/olefin ratios, the reaction was further complicated by a side reaction which produced the fluoroethylsilanes. As this side reaction became more important as the silane/olefin ratio was increased, it is thought that the reaction involved the interaction of either a silane molecule or a silyl radical with the 1:1 adduct, rather than a light induced unimolecular decomposition of the 1:1 adduct. The detection of silicon tetrachloride, 1-fluoroethyltrichlorosilane, and 2-fluoroethyltrichlorosilane in increasing yields as the yield of the 1:1 adduct decreases (table 12) is in agreement with this.

The observation that the photochemical addition reaction of trichlorosilane with vinyl fluoride takes place to give exclusively 2-fluoroethyltrichlorosilane also suggests, in this context, that 1-fluoroethyltrichlorosilane was formed by a reaction of the excess silane, or a silyl radical, with the 1:1 adduct.

TABLE 12

The reaction of trichlorosilane with 1-chloro-2-fluoroethylene.

Ratio silane: olefin	Time of Reaction (hr.)	Reaction of olefin (%)	1:1 adduct H(CHCl:CHF)SiCl₃ (A)			1:1 dehalogenated adduct H(CH₂CHF)SiCl₃ (B)			% dehalogenation $\frac{B}{A+B} \times 100$
			% based on olefin consumed	% addition at		% based on olefin consumed	% addition to give		
				$=CHF$	$=CHCl$		$-CHFCH_3$	$-CH_2CH_2F$	
2.5:1	116	73	38	82	18	3	95	-	7
5:1	100	67	79	75	25	10	95	-	12
10:1	100	98	8	58	42	73	83	17	91

At this stage of the argument the reaction may be represented thus:

$$SiHCl_3 + CHCl:CHF \xrightarrow{h\nu} H(CHCl \cdot CHF)SiCl_3 \xrightarrow[h\nu]{HSiCl_3} \begin{array}{l} SiCl_4 \\ + \\ CH_3 \cdot CHF \cdot SiCl_3 \\ + \\ CH_2F \cdot CH_2 \cdot SiCl_3 \end{array}$$
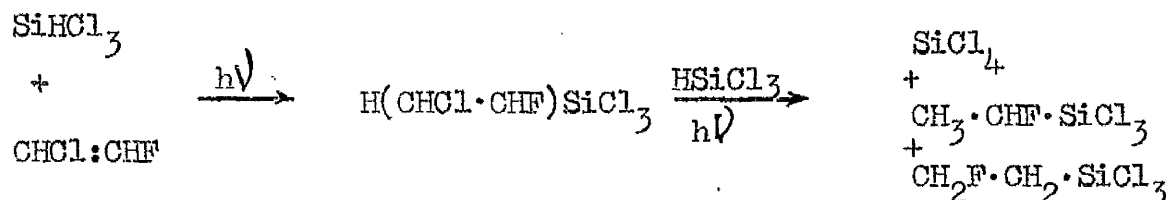
i.e., an addition reaction followed by a halogen abstraction reaction.

During this work it was not found possible to achieve complete preparative separation of the two components of the 140-146° fraction by gas-liquid chromatography, and the expected isomers of the 1:1 adduct were not independently synthesised. Consequently, the use of this further reaction of the 1:1 adduct is a valuable guide to the course of the addition reaction. The appearance of two separable and identifiable fluoroethyltrichlorosilanes is evidence for the operation of a bidirectional addition reaction, and is also useful for suggesting the structures of the 1:1 adducts originally formed.

As the structures proposed for the 1:1 adduct depend to a large extent on the observation of the two fluoroethyltrichlorosilanes, it is important to consider in detail the mechanisms by which they could be formed.

A sample of the 1:1 adduct, of which the ratio of the two components was known, was sealed _in vacuo_ in a silica tube with a 10:1 molar excess of trichlorosilane and allowed to remain at room temperature for 336 hr. in the absence of light. No reaction was found to have occurred and the ratio of the components of the 1:1 adduct was identical with the original ratio. This indicates that the abstraction reaction may be a light induced free radical process in which the trichlorosilyl radical abstracts a chlorine atom from the adduct to produce silicon tetrachloride.

$$RCl + \overset{\bullet}{SiCl_3} \longrightarrow \overset{\bullet}{R} + SiCl_4$$

The fact that 1-fluoroethyl- and 2-fluoroethyl-trichlorosilane were isolated allows the suggestion that these compounds were formed by abstraction from two chlorofluoroethyltrichlorosilanes, i.e. the 1:1 adducts. The reaction scheme can now be elaborated.

$$SiHCl_3 + CHCl{:}CHF$$

$$CH_2Cl{\cdot}CHF{\cdot}SiCl_3 \qquad\qquad CH_2F{\cdot}CHCl{\cdot}SiCl_3$$
$$(I) \qquad\qquad\qquad\qquad (II)$$

$$CH_3{\cdot}CHF{\cdot}SiCl_3 \qquad\qquad CH_2F{\cdot}CH_2{\cdot}SiCl_3$$
$$(III) \qquad\qquad\qquad\qquad (IV)$$
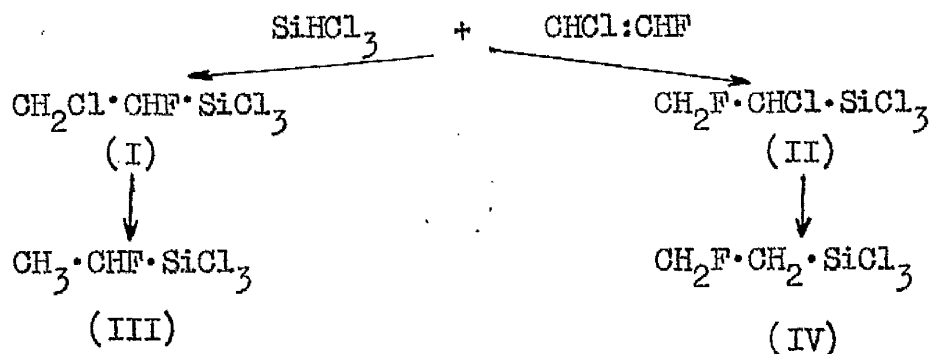
This mechanism is consistent with the observation that the percentage of the compounds assumed to be the 1:1 adducts was reduced as the percentage of the fluoroethyltrichlorosilanes was increased. The observation that the ratio of the isomers present in the 1:1 adduct was not constant indicated that the halogen abstraction was taking place more readily with one isomer of the 1:1 adduct. The isomer which was more readily reduced was the second component of the 140-146° fraction to be eluted.

As the reduced adduct consisted mainly of 1-fluoroethyltrichlorosilane (III), it is suggested that the compound more readily reduced was 2-chloro-1-fluoroethyltrichlorosilane (I) and that this corresponded to the second compound to be eluted, (i.e., the major product in the 2.5:1 and 5:1 reactions).

It is not sufficient, however, to carry the argument further on these grounds and conclude that the isolation and identification of 2-fluoroethyltrichlorosilane (IV) indicates the presence of 1-chloro-2-fluoroethyltrichlorosilane (II) in the 1:1 adduct. This is clear if the mechanism of the halogen abstraction from 2-chloro-1-fluoroethyltrichlorosilane is considered.

The reaction is thought to proceed via an intermediate alkyl radical thus:

$$CH_2Cl \cdot CHF \cdot SiCl_3 + \dot{S}iCl_3 \longrightarrow \dot{C}H_2 \cdot CHF \cdot SiCl_3 + SiCl_4$$

$$\dot{C}H_2 \cdot CHF \cdot SiCl_3 + SiHCl_3 \longrightarrow CH_3 \cdot CHF \cdot SiCl_3 + \dot{S}iCl_3$$
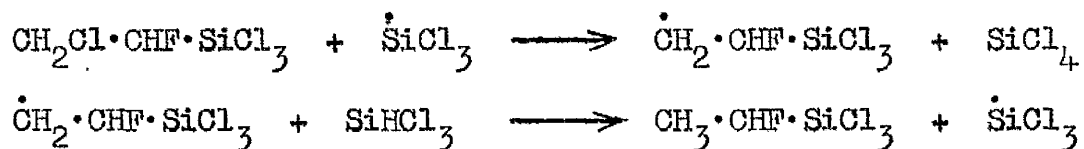
and similarly, via the intermediate radical $\dot{C}HF \cdot CH_2 \cdot SiCl_3$, for the other isomer, leading to the formation of 2-fluoroethyltrichlorosilane.   Three other possible routes to the latter compound exist, none of which involve prior formation of the expected adduct 1-chloro-2-fluoroethylsilane. These are considered below.

(i) Free radical elimination from the intermediate. This is equivalent to the reverse of an addition process.   The addition reaction of trichlorosilane with vinyl fluoride indicates that the intermediate radical $\dot{C}HF \cdot CH_2 \cdot SiCl_3$ is more stable than the radical $\dot{C}H_2 \cdot CHF \cdot SiCl_3$.   It can be seen that the intermediate radicals from the addition reaction and the abstraction reaction are identical.   Reversibility of the addition reaction would therefore lead to breakdown of the intermediate radicals formed by chlorine abstraction:

e.g., $\dot{C}H_2 \cdot CHF \cdot SiCl_3 \overset{?}{\rightleftharpoons} CH_2 : CHF + \dot{S}iCl_3$
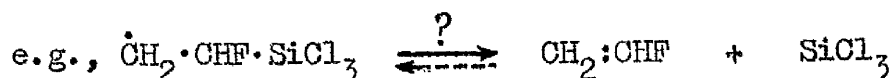
This could then be followed by an addition reaction of the type previously described to give 2-fluoroethyltrichlorosilane.

$$\dot{S}iCl_3 + CH_2:CHF \underset{?}{\overset{}{\rightleftharpoons}} \dot{C}HF \cdot CH_2 \cdot SiCl_3$$

$$\dot{C}HF \cdot CH_2 \cdot SiCl_3 + SiHCl_3 \longrightarrow CH_2F \cdot CH_2 \cdot SiCl_3$$
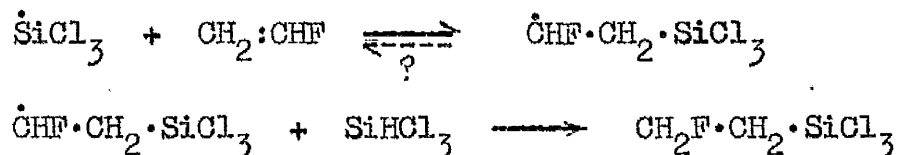
In other words, both dehalogenated adducts could be formed from only one isomer $(CH_2Cl \cdot CHF \cdot SiCl_3)$ of the 1:1 adduct of trichlorosilane to 1-chloro-2-fluoroethylene.

(ii) <u>Preliminary abstraction from the olefin.</u> The reaction of trimethylsilane with 1-chloro-2-fluoroethylene in the presence of mercury produced mainly vinyl fluoride (96%) and trimethylchlorosilane. As trimethylsilane undergoes addition to vinyl fluoride very slowly, only a trace of the 1:1 adduct of trimethylsilane to vinyl fluoride was detected. If, however, a similar mechanism was in operation in the reaction with trichlorosilane, the vinyl fluoride produced would react with excess trichlorosilane to give 2-fluoroethyltrichlorosilane as shown by the first series of reactions described in this dissertation. Again, 2-fluoroethyltrichlorosilane would have been produced without the formation of 1-chloro-2-fluoroethyltrichlorosilane.

$$CHCl{:}CHF + \dot{S}iCl_3 \longrightarrow \dot{C}H{:}CHF + SiCl_4$$

$$\dot{C}H{:}CHF + SiHCl_3 \longrightarrow CH_2{:}CHF + \dot{S}iCl_3$$

$$CH_2{:}CHF + \dot{S}iCl_3 \longrightarrow \dot{C}HF{\cdot}CH_2{\cdot}SiCl_3$$

$$\dot{C}HF{\cdot}CH_2{\cdot}SiCl_3 + SiHCl_3 \longrightarrow CH_2F{\cdot}CH_2{\cdot}SiCl_3 + \dot{S}iCl_3$$
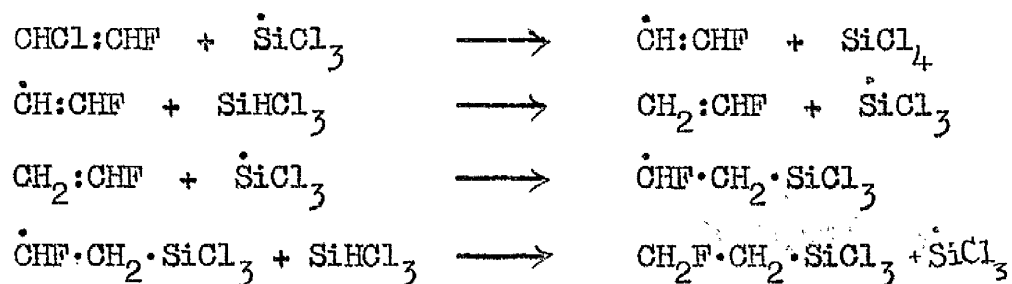
(iii) <u>Rearrangement via a bridged intermediate.</u>   A free radical rearrangement via a bridged intermediate would also lead to the production of both fluoroethyltrichlorosilanes from one chlorofluoroethyltrichlorosilane.

$$CH_2Cl{\cdot}CHF{\cdot}SiCl_3 + \dot{S}iCl_3 \longrightarrow \dot{C}H_2{\cdot}CHF{\cdot}SiCl_3 + SiCl_4$$
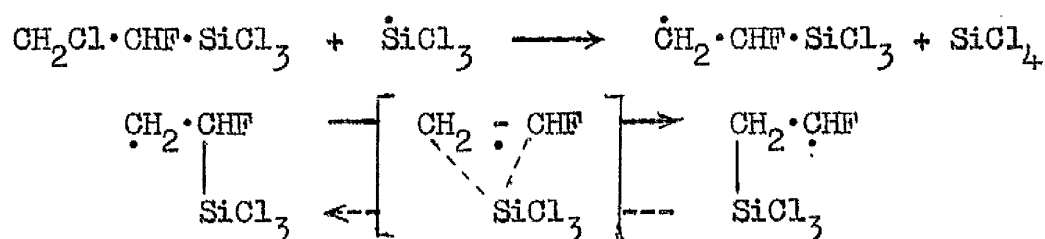
Experiments were carried out to verify the operation of these mechanisms.   Simply stated it is argued that for (i) it should be possible to detect either free vinyl fluoride or an adduct of a different silane to vinyl fluoride if the reduction is carried out by a large excess of a silane other than trichlorosilane.

Reaction of a sample of the 1:1 adduct with methyldichlorosilane in a 10:1 molar excess produced no vinyl fluoride and no 2-fluoroethylmethyldichlorosilane.   The reduced adducts, unreacted 1:1 adducts, and methyltrichlorosilane

were the only compounds detected. Similarly, reaction of
the 1:1 adduct with a 10:1 molar excess of trimethylsilane
gave no vinyl fluoride and no 2-fluoroethyltrimethylsilane.
The reduced adducts and trimethylchlorosilane were the only
compounds detected (along with excess of the reducing silane),
table **13** . This suggests that (i) does not apply.

$$CH_2Cl \cdot CHF \cdot SiCl_3 \xrightarrow{\overset{o}{SiCl_3}} \overset{\bullet}{CH_2} \cdot CHF \cdot SiCl_3 \xrightarrow{SiHCl_3} CH_3 \cdot CHF \cdot SiCl_3$$

$$(i) \Big\downarrow \hspace{-0.5em}\times$$

$$CH_2:CHF + SiCl_3 \xrightarrow{SiHMeCl_2} CH_2F \cdot CH_2 \cdot SiCl_2Me$$

<div align="right">not detected.</div>

The second mechanism, (ii) cannot be discounted
completely. As it would occur before adduct formation, the
operation of this mechanism cannot be directly tested. It may
be argued that the reaction is unlikely on the following grounds.

Trimethylsilane is a more reactive abstraction reagent
than is trichlorosilane.[149] Preliminary abstraction from the
olefin does not take place to any significant extent during the
addition reaction of trimethylsilane with 1-chloro-2-fluoro-
ethylene in the absence of mercury. This is indicated by the
formation of 1-fluoroethyltrimethylsilane as the only
fluoroalkylsilicon compound in the reaction of trimethylsilane

with 1-chloro-2-fluoroethylene with a silane/olefin ratio of
10:1.   It is possible that in the case of the addition reaction
of trichlorosilane the abstraction similarly does not occur.

The third mechanism, (iii), is more difficult to
exclude on experimental grounds in an investigation of this
nature, but it is argued that if this mechanism takes place
then a change in the total ratio of α-fluoro:β-fluoro should
occur on reduction of the adduct.   It is known that the
radical $\overset{\bullet}{C}HF \cdot CH_2 \cdot SiCl_3$ does not rearrange in this manner,
therefore if the rearrangement occurs for the radical
$\overset{\bullet}{C}H_2 \cdot CHF \cdot SiCl_3$ it will be non-reversible, and hence lead to a
reduction in the total proportion of α-fluoro compound present.
Reduction of samples with an adduct ratio of 4.4:1 and 0.9:1
$CH_2Cl \cdot CHF \cdot SiCl_3$ to $CH_2F \cdot CHCl \cdot SiCl_3$ to an extent of 70% and 100%
reaction respectively gave no alteration in the total ratio of
α-fluoro- to β-fluoro- compounds, (table 13).   This indicates
that mechanism (iii) does not take place.

TABLE 13

Photochemical reactions of silanes with the adduct H(CHCl·CHF)SiCl₃

Silane	Ratio silane: olefin	Time hr.	Ratio of adducts (in) $\frac{CH_2Cl \cdot CHF \cdot SiCl_3}{CH_2F \cdot CHCl \cdot SiCl_3}$	Percent reaction	Ratio of adducts (out) $\frac{CH_2Cl \cdot CHF \cdot SiCl_3}{CH_2F \cdot CHCl \cdot SiCl_3}$	Ratio reduced adducts $\frac{CH_3 \cdot CHF \cdot SiCl_3}{CH_2F \cdot CH_2 \cdot SiCl_3}$	Notes
MeSiHCl₂	10:1	100	4.4	70	2.0	15.3	No CH₂:CHF or CH₂F·CH₂·SiCl₂Me
Me₃SiH	10:1	50	0.93	100	-0-	0.93	No CH₂:CHF or CH₂F·CH₂·SiMe₃
Cl₃SiH	10:1	14 days	In the absence of light at 20°C.	0	-0-	-0-	-0-

The mechanism of the abstraction reaction is discussed at greater length in conjunction with data from other reactions. The results indicate that the formation and identification of both 1-fluoroethyltrichlorosilane and 2-fluoroethyltrichlorosilane is good evidence for the suggested structures of the 1:1 adducts and for the operation of a bidirectional addition reaction.

The hydrolysis of the adduct of trichlorosilane with 1-chloro-2-fluoroethylene.

A sample of the adduct from the addition reaction of trichlorosilane with 1-chloro-2-fluoroethylene with a silane/olefin ratio of 5:1 was shown by gas-liquid chromatography to consist of two components in the ratio 1:3 in order of elution. The nuclear magnetic resonance spectra of the mixture were complex but the possible presence of -CHF- and CH_2F- groups was indicated. Further interpretation was not possible.

Hydrolysis of a sample of this adduct in vacuo with 10% aqueous sodium hydroxide gave vinyl chloride (24%) and vinyl fluoride (76%). The total evolution of gas was equivalent to 98% reaction assuming the sample hydrolysed to be the 1:1 adduct. Fluoride and chloride ions were detected in the aqueous residue. Hydrolysis of a similar sample with distilled water gave vinyl fluoride as the only volatile product (equivalent

to 75% reaction assuming the composition of the sample hydrolysed). Fluoride ions were not detected in the aqueous residue.

On the basis of the currently accepted theory of hydrolysis, it is suggested that the two olefins were formed by a process of β- elimination.

$$OH^- \quad Si - CHF - CH_2 - Cl \longrightarrow CHF{:}CH_2 + Cl^- + SiO_2$$

$$OH^- \quad Si - CHCl - CH_2 - F \longrightarrow CHCl{:}CH_2 + F^- + SiO_2$$
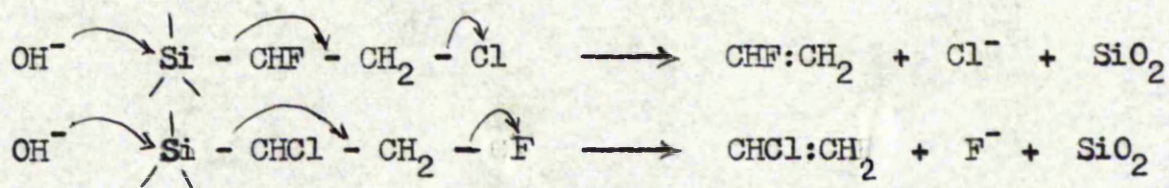
Other possible mechanisms of hydrolysis exist and these are considered in relation to all the hydrolysis data on the compounds dealt with in this work (pp. 173). Whilst β - elimination is not the only possible mechanism of olefin formation it may reasonably be regarded as the probable mechanism.

It is notable that the alkaline hydrolysis proceeds to give good yields of the olefins (98%) and that the corresponding haloalkane, 1-chloro-2-fluoroethane, is not produced. This is in contrast to the alkaline hydrolysis of trifluoroethyl-trichlorosilanes in which high yields of the fluoroalkane were observed. The formation of vinyl fluoride by preliminary formation of the haloalkane followed by elimination from it was excluded as a sample of 1-chloro-2-fluoroethane was not hydrolysed under the reaction conditions.

$$Cl_3Si \cdot CHCl \cdot CH_2F \xrightarrow{OH^-} \bar{C}HCl \cdot CH_2F \xrightarrow{H_2O} \diagup\!\!\!\!\diagdown CH_2Cl \cdot CH_2F$$

$$OH^- \frown H - CHF \frown CH_2 - \overset{\frown}{Cl} \xrightarrow[NaOH]{10\% \text{ aqueous}} \diagup\!\!\!\!\diagdown CH_2:CHF + Cl^- + H_2O$$
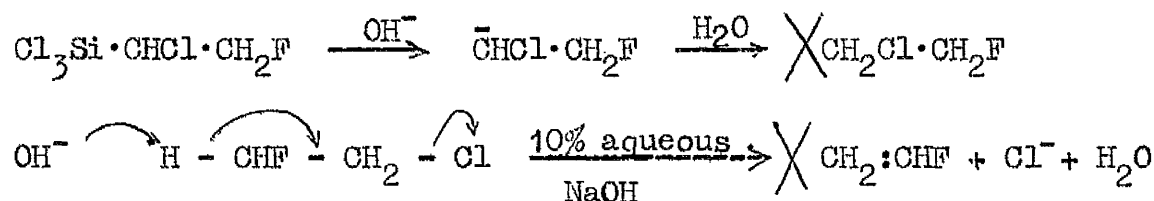
This observation suggests that the close correspondence of the isomer ratio obtained by gas-liquid chromatography with the ratio of the olefins obtained upon hydrolysis is not fortuitous. Mixtures of the 1:1 adduct containing the isomers in different ratios gave the olefins in the same ratios as the original adducts on hydrolysis. This suggests that in those cases in which olefin formation exceeds 98%, the hydrolysis results serve as a good indication of the isomer ratio.

The observation that hydrolysis with water gave vinyl fluoride only (75%) and that fluoride ions were not detected in the aqueous residue indicates that Si-C bond fission had occurred only in the isomer with a β-chlorine atom and that a polysiloxane had been formed from the other isomer. This is in agreement with the observed stability of the Si-C bond in 2-fluoroethyltrichlorosilane towards water as compared to the ready aqueous hydrolysis of 2-chloroethyltrichlorosilane. The effect of the α-halogen atom is questionable. Whereas an α-substituent which is electron withdrawing renders the silicon atom more

susceptible to nucleophilic attack, it should also hinder the electron shift which leads to elimination of the β- atom:

e.g.,

$$\text{OH}^- \longrightarrow \text{Si} - \overset{\underset{\displaystyle F}{H}}{C} - \overset{\underset{\displaystyle H}{H}}{C} - Cl$$
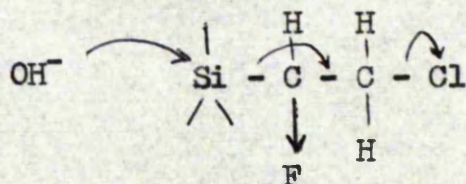
In cases in which fluoroalkane formation occurs on alkaline hydrolysis, e.g. the trifluoroethylsilanes dealt with in this work, it appears that α- substituents which are electron-withdrawing hinder β- elimination. It appears, therefore, that in the alkaline hydrolyses described above, the elimination is sufficiently facile for these effects to be negligible.

The reaction of trimethylsilane with 1-chloro-2-fluoroethylene.

The reactions of trimethylsilane were carried out in sealed silica tubes _in vacuo_ as previously described, but it was found most convenient to limit fractionation _in vacuo_ to the separation of the components which were liquids at room temperature, (the reactants are both gases at room temperature) from the more volatile components. The products were then investigated by infra-red spectroscopy and gas-liquid chromatography.

It has been found that the reaction of trimethylsilane with vinyl fluoride proceeds with difficulty, and that the addition of mercury appears to facilitate the addition. It was thought that this was due to a difficulty of initiation and that the presence of mercury atoms, which readily absorb energy from mercury resonance lamps, would provide a means of transfer of energy to the silane molecule.

$$Hg \xrightarrow{h\nu} Hg^*$$

$$Hg^* + Me_3SiH \longrightarrow Hg + Me_3\overset{\bullet}{Si} + \overset{\bullet}{H}$$
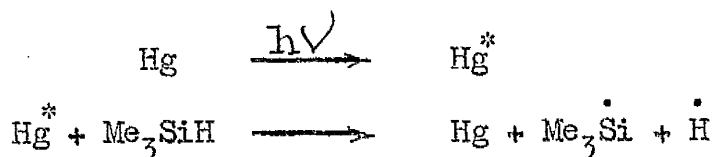
Consequently, an initial experiment was carried out with trimethylsilane and 1-chloro-2-fluoroethylene in the presence of mercury with a silane/olefin ratio of 9:1. The products

were, however, found to be vinyl fluoride (89%), a trace of ethylene (less than 1%), trimethylchlorosilane (96%), and a compound with the same retention time as a fluoroethyl-trimethylsilane (ca. 4%). The reaction was repeated and gave identical results within the limits of experimental error. 1-chloro-2-fluoroethylene gave 1-fluoroethyltrichlorosilane and 2-fluoroethyltrichlorosilane in addition to the expected 1:1 adducts in reactions with silane/olefin ratios of 2.5:1, 5:1, and 10:1:

e.g.,

$$SiHCl_3 + CHCl{:}CHF \xrightarrow{h\nu} CH_2Cl{\cdot}CHF{\cdot}SiCl_3$$

$$CH_2Cl{\cdot}CHF{\cdot}SiCl_3 + SiHCl_3 \xrightarrow{h\nu} CH_3{\cdot}CHF{\cdot}SiCl_3 + SiCl_4$$
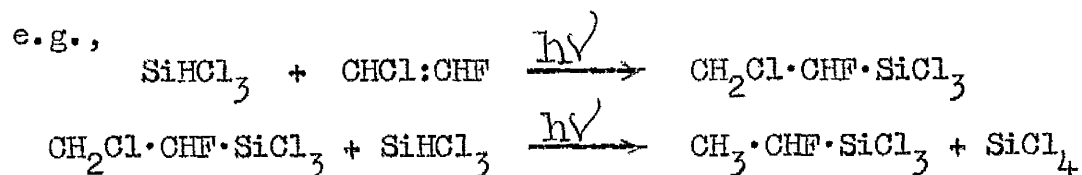
The percentage halogen abstraction was higher with the higher silane/olefin ratios. The formation of 1-fluoroethyltrimethyl-silane in the reaction of trimethylsilane with 1-chloro-2-fluoro-ethylene can be similarly visualised especially with a silane/olefin ratio of 9:1.

$$Me_3SiH + CHCl{:}CHF \xrightarrow{h\nu} CH_2Cl{\cdot}CHF{\cdot}SiMe_3$$

$$CH_2Cl{\cdot}CHF{\cdot}SiMe_3 + Me_3SiH \xrightarrow{h\nu} CH_3{}CHF{\cdot}SiMe_3 + Me_3SiCl$$
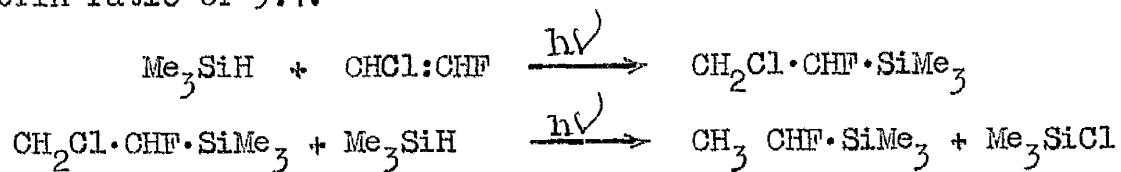
It can be seen that reaction paths to both 1-fluoroethyl- and 2-fluoroethyl- trimethylsilanes are possible, and that the

structure of the unidentified fluoroethyltrimethylsilane cannot be predicted.

As the photochemical reactions of other silanes with fluoro-olefins gave mainly the adduct of the silane to the olefin, or the product of a further reaction of the adduct it was thought that the reaction of trimethylsilane with 1-chloro-2-fluoroethylene might be anomalous. The reaction was, therefore, carried out in the absence of mercury with silane/olefin ratios of 1:1 and 5:1. The possibility of condensation of minute traces of mercury along with the reactants cannot be excluded as pressures were measured by means of mercury manometers. Reactions carried out "in the absence of mercury" were, therefore, in the absence of purposely introduced mercury as no special precautions were taken to exclude the fortuitous introduction of mercury.

Trimethylsilane and 1-chloro-2-fluoroethylene with a silane/olefin ratio of 1:1 were irradiated, in the absence of mercury, in vacuo for 90 hr. Complete reaction of the 1-chloro-2-fluoroethylene was observed, but only 62% reaction of the trimethylsilane. The products were vinyl fluoride ($\sim$ 4%), trimethylchlorosilane ($\sim$ 19% of the trimethylsilane reacted) and a viscous high-boiling liquid. Of the

trimethylsilane which had reacted, 19% of it is accounted for by the trimethylchlorosilane (presumably formed by an abstraction reaction), therefore the high-boiling liquid must account for ca. 50% of the trimethylsilane originally present and ca. 96% of the 1-chloro-2-fluoroethylene originally present.

As the liquid could not be investigated by gas-liquid chromatography a sample was hydrolysed in vacuo with 10% aqueous sodium hydroxide as an attempt to understand the composition of the liquid. Hydrolysis gave vinyl fluoride (equivalent to 5% of the olefin consumed as the only volatile component. If it is assumed that silanes containing substituted ethyl groups break down by β - elimination on hydrolysis (if there is a β - group to eliminate), then the formation of vinyl fluoride gives an indication of the 1:1 adduct

$$OH^- \quad Me_3Si - CHF - CH_2 - Cl \longrightarrow CH_2:CHF + Cl^- + Me_3SiOH$$
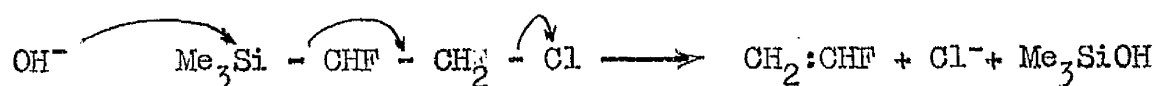
As the percentage of vinyl fluoride was low ($\sim$ 5%) it was assumed that telomer formation was occurring in preference to the formation of the 1:1 adduct.

Although extensive telomerisation of this nature has not been a general feature of this work it is relevant here that the reaction of trichlorosilane with 1-chloro-2-fluoroethylene

with a silane/olefin ratio of 2.5:1 gave considerable telomer
formation.   It is also of note that other radical initiators,
e.g. phosphine, neither add to 1-chloro-2-fluoroethylene nor
facilitate   telomer formation.[150]

It is also important that neither vinyl chloride nor
ethylene were detected upon alkaline hydrolysis of the high-
boiling liquid.   If the same assumption about β- elimination
is made as above, the absence of vinyl chloride and ethylene
indicates the absence of 1-chloro-2-haloethyl- and 2-haloethyl-
trimethylsilanes.

$$OH^- \quad Me_3Si - CHCl - CH_2 - X \longrightarrow CHCl{:}CH_2 + X^- + Me_3SiOH$$

$$OH^- + Me_3Si - CH_2 - CH_2 - X \longrightarrow CH_2{:}CH_2 + X^- + Me_3SiOH$$
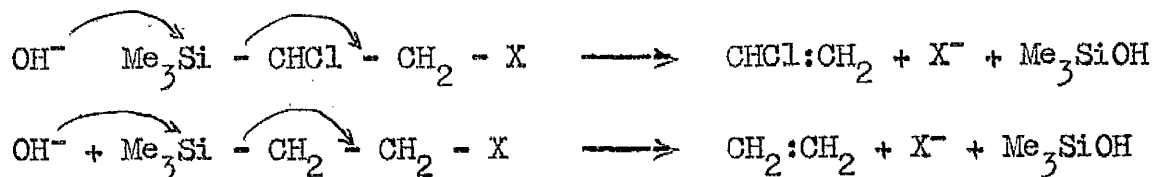
In the case under discussion the compounds expected would be
those in which X is fluorine (in the compounds above).

$$CHCl{:}CHF \qquad\qquad CH_2Cl\cdot CHF\cdot SiMe_3 \qquad\qquad CH_3\cdot CHF\cdot SiMe_3$$
$$+ \qquad\longrightarrow\qquad + \qquad\longrightarrow$$
$$Me_3SiH \qquad\qquad CH_2F\cdot CH_2Cl\cdot SiMe_3 \qquad\qquad CH_2F\cdot CH_2\cdot SiMe_3$$
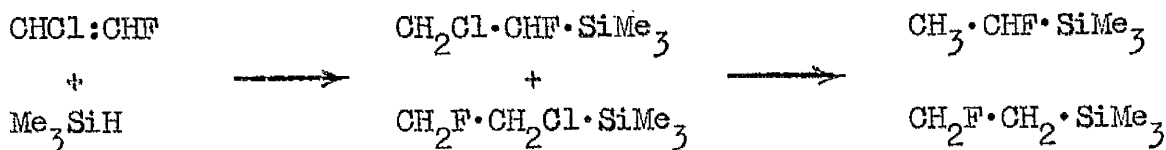
The following would be predicted on the basis of β- elimination.

$$CH_2Cl \cdot CHF \cdot SiMe_2 \xrightarrow{OH^-} CH_2:CHF$$

$$CH_2F \cdot CHCl \cdot SiMe_3 \xrightarrow{OH^-} CH_2:CHCl$$

$$CH_2F \cdot CH_2 \cdot SiMe_3 \xrightarrow{OH^-} CH_2:CH_2$$

$$CH_3 \cdot CHF \cdot SiMe_3 \xrightarrow{OH^-} \text{No reaction.}$$
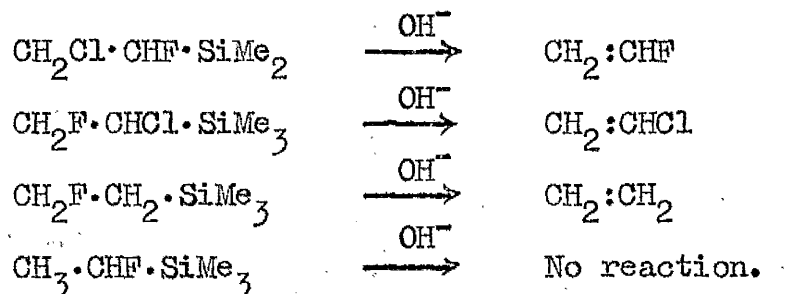
The detection of vinyl fluoride only suggests that either a) the reaction is unidirectional, or b) the intermediate radical for the isomer not detected, $\dot{C}HF \cdot CHCl \cdot SiMe_3$, preferentially initiates telomerisation. As an attempt to understand this point, the reaction was carried out with silane/olefin ratios of 5:1 and 10:1.

Trimethylsilane and 1-chloro-2-fluoroethylene with a silane/olefin ratio of 5:1 were irradiated, in the absence of mercury, in vacuo for 100 hr. Fractionation in vacuo gave unreacted 1-chloro-2-fluoroethylene (50%), unreacted trimethyl-silane (40% + the 4 molar excess) and vinyl fluoride (equivalent to 4% of the olefin reacted), along with a liquid remaining in the tube at room temperature. Investigation of the liquid products by gas-liquid chromatography gave two peaks in the ratio 4:1. The retention time of the first corresponded to that of trimethylchlorosilane. The identification of trimethylchlorosilane (confirmed by infra-red spectroscopy)

suggested the formation of the fluoroethyltrimethylsilanes,
but this should be to the same extent as the formation of the
trimethylchlorosilane.   Calibration runs with ethyltrimethyl-
silane, 1-fluoroethyltrimethylsilane, and trimethylchlorosilane
indicated that these compounds were not separated under the
range of conditions used.   An attempt to probe the nature and
composition of the liquid was made by hydrolysing a sample in vacuo
with 10% aqueous sodium hydroxide.   Products from hydrolysis
were a trace of trimethylsilane (present in the liquid before
hydrolysis), vinyl fluoride, and 1-fluoroethyltrimethylsilane
in the ratio of about 1:1 respectively, but these products only
accounted for ca. 60% of the sample hydrolysed.   If it is
assumed that the vinyl fluoride was formed from the adduct
1-fluoro-2-chloroethyltrimethylsilane as previously described,
then the percentage of trimethylchlorosilane can be calculated
as the difference between the weight of sample hydrolysed and
the quantity of products observed on hydrolysis.

$$Me_3SiH + CHCl{:}CHF \longrightarrow CH_2Cl{\cdot}CHF{\cdot}SiMe_3 \longrightarrow CH_3CHF{\cdot}SiMe_3 + Me_3SiCl$$

$$\downarrow OH^- \qquad\qquad no\ reaction \qquad\qquad \downarrow OH^-$$

$$CH_2{:}CHF \qquad\qquad CH_3{\cdot}CHF{\cdot}SiMe_3 \qquad\qquad \downarrow$$

$$Me_3SiOSiMe_3$$
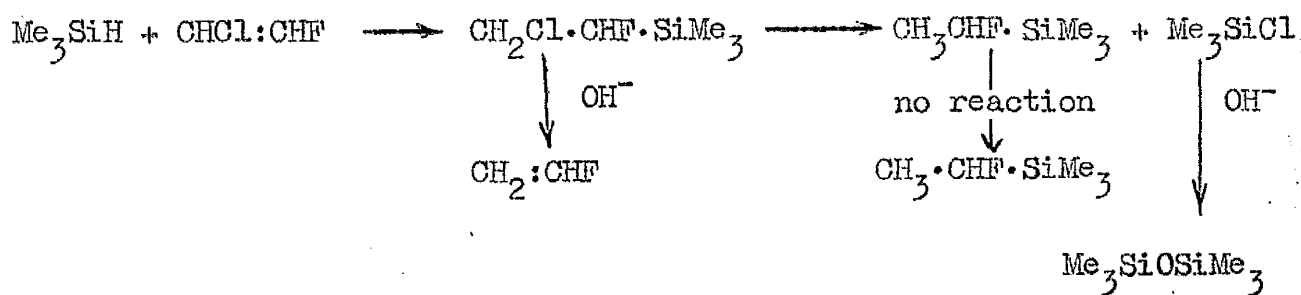
The compound 2-chloro-1-fluoroethyltrimethylsilane was not
separately identified, but the absence of both vinyl chloride
and ethylene on hydrolysis suggests that no addition to give
1-chloro-2-fluoroethyltrimethylsilane had taken place.

$$Me_3SiH + CHCl:CHF \xrightarrow{\quad\quad} \xcancel{CH_2F \cdot CHCl \cdot SiMe_3} \xrightarrow{\quad\quad} CH_2F \cdot CH_2 \cdot SiMe_3$$

$$\downarrow OH^- \qquad\qquad\qquad\qquad \downarrow$$

$$CH_2:CHCl \qquad\qquad\qquad\qquad CH_2:CH_2$$
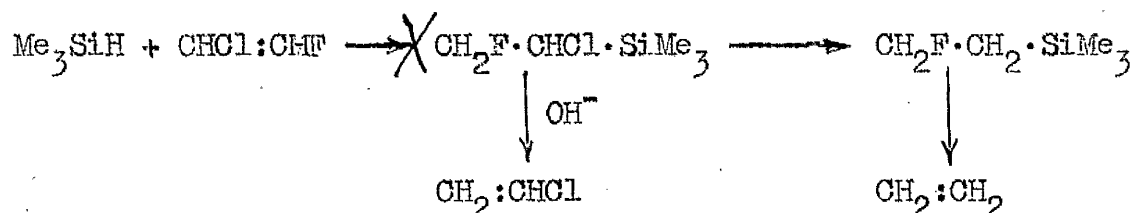
It is clear from the two addition reactions described
above that the formation of the 1:1 adduct will always be in
low yield because of either telomerisation or halogen abstraction.
The hydrolysis data suggest that the reaction is unidirectional
within the working error of the quantity used and the method
adopted. A reaction was carried out with a silane/olefin
ratio of 10:1 to complete the halogen abstraction on a larger
scale and to detect any trace of either 2-fluoroethyltrimethyl-
silane or of ethylene (on hydrolysis). After 200 hr.
irradiation of trimethylsilane with 1-chloro-2-fluoroethylene
at a mole ratio of 10:1, complete consumption of the olefin
was observed. Investigation of the products by gas-liquid
chromatography gave only one peak in addition to unreacted
trimethylsilane (79%). Hydrolysis of the liquid with 10%
aqueous sodium hydroxide gave 1-fluoroethyltrimethylsilane

(ca. 98%) and hexamethyldisiloxane (equivalent to ca. 98% based on formation from trimethylchlorosilane). No ethylene, no vinyl fluoride and no vinyl chloride were detected in the hydrolysis products. Vinyl fluoride was not detected in the irradiation products.

In an attempt to show that both the addition and the abstraction reactions were radical reactions initiated by ultraviolet light, the reaction of trimethylsilane with 1-chloro-2-fluoroethylene at 85° in the absence of light was carried out for 100 hr. Fractionation in vacuo gave 98% recovery of the reactants and no other product was detectable.

DISCUSSION OF THE MECHANISM OF THE ADDITION REACTION AND RELATED REACTIONS.

The results obtained in this work indicate that the silanes containing one silicon-hydrogen bond react with olefins to form adducts with the overall stoichiometry of the equation below.

$$\equiv Si-H + \; \underset{/}{\overset{\backslash}{C}} = \underset{\backslash}{\overset{/}{C}} \longrightarrow \equiv Si-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-H$$
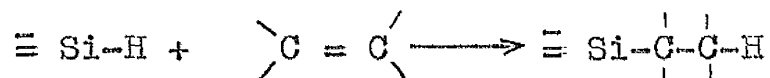
This is in agreement with a large body of published work.[34] Three reaction schemes explaining these results can be visualised. It is necessary to examine the reaction conditions and some of the results in the wider context of previous work of a similar character to decide which reaction scheme most closely approaches the true mechanism.

a) The ionic mechanism

The polarisation of the silicon hydrogen bond is low ($\sim 2\%$ in SiH_4),[140] and it is consequently unwise to predict the direction of heterolysis of various substituted silanes in the absence of catalysts. Determination of the structure of the product for information on the direction of addition

is therefore an insufficient indication of the possible mechanism. In cases where structural determination indicates a rearrangement of the substrate an ionic mechanism is strongly suggested, e.g.,

$$X_3SiH + CH_3 \cdot CH_2 \cdot CH:CH \cdot CH_3 \longrightarrow nCH_3 \cdot (CH_2)_4 \cdot SiX_3$$

The formation of 1:1 adducts with olefins which are known to polymerise rapidly under free radical conditions may also indicate the operation of an ionic mechanism. Thus 1:1 adducts with styrene may be formed in the presence of free radical inhibitors. Telomer formation may occur during ionic addition reactions with olefins which are susceptible to carbanion attack, e.g., fluoro-olefins. Initiation by hydride ion could give telomers as below.

$$SiHX_3 \xrightarrow{\text{catalyst}} H^- + S\overset{+}{i}X_3$$

$$H^- + \text{C} = \text{C} \longrightarrow H \cdot \text{C} \cdot \text{C}^-$$

$$H \cdot C \cdot C^- + \text{C} = \text{C} \longrightarrow H \cdot C \cdot C \cdot C \cdot C^-$$

$$H \cdot C \cdot C \cdot C^- + SiHX_3 \longrightarrow H \cdot C \cdot C \cdot C \cdot C \cdot SiX_3$$
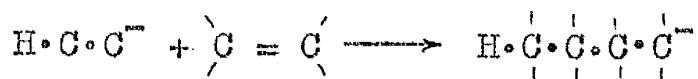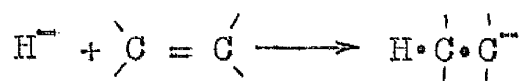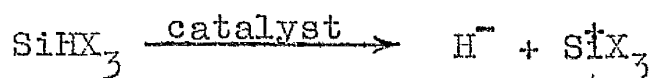
Catalysts are usually required to facilitate the abnormal silicon-hydrogen heterolysis.

Previous work has shown that it is possible to draw the distinction between the conditions for the ionic addition reaction and for the free radical addition reaction (see introduction pp. 15). Reactions were carried out to test the operation of an ionic addition reaction in the work described in this thesis by attempting to observe any acceleration of the reaction with an increase in temperature in the absence of light. Reactions of selected pairs of silanes and olefins were carried out at room temperature and at 85°in the absence of light. In each case no reaction was observed; this indicates that the reaction is not ionic.

(b) The 4-centre mechanism

The 4-centre mechanism involves the formation of a transition state of a type which cannot explain the production of telomers in the reaction, i.e., the products are formed by one bimolecular reaction.

$$
\text{SiHX}_3 + \begin{matrix} \text{A} & \text{B} \\ | & | \\ \text{C} : \text{C} \\ | & | \\ \text{H} & \text{H} \end{matrix} \longrightarrow \begin{bmatrix} \text{A} & \text{B} \\ | & | \\ \text{H-C-C-H} \\ \vdots \\ \text{X}_3\text{Si-H} \end{bmatrix} \longrightarrow \text{CH}_2\text{B} \cdot \text{CHA} \cdot \text{SiX}_3
$$

$$
\text{or} \longrightarrow \begin{bmatrix} \text{A} & \text{B} \\ | & | \\ \text{C - C} \\ \vdots \\ \text{H---SiX}_3 \end{bmatrix} \longrightarrow \text{CH}_2\text{A} \cdot \text{CHB} \cdot \text{SiX}_3
$$
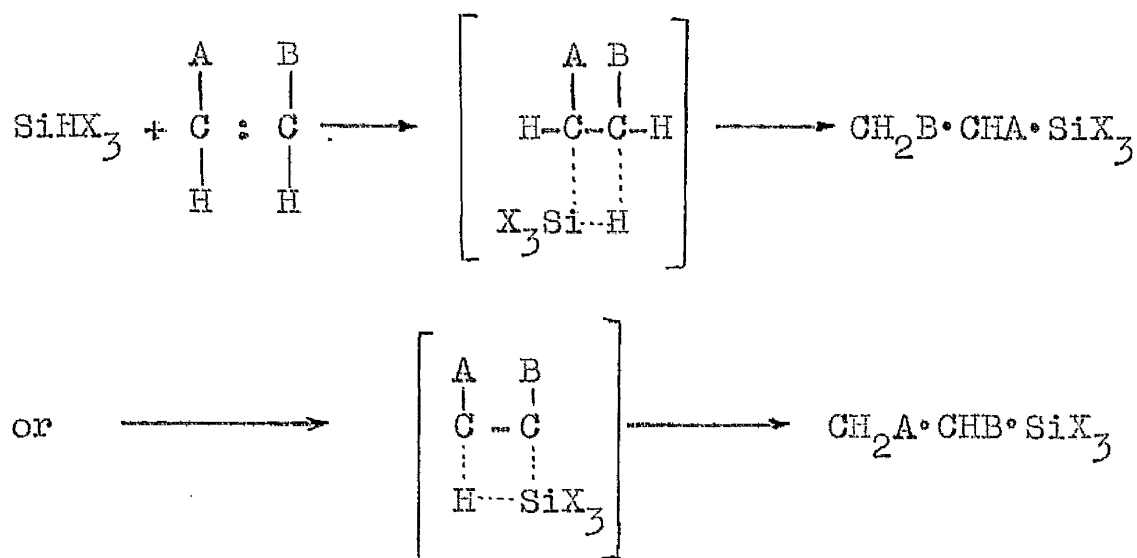
The necessity of ultraviolet light for the reaction to proceed similarly suggests that a 4-centre mechanism is not involved in the reaction.

(c)   The free radical mechanism

The necessity of ultraviolet light, and the formation of telomers suggests that the reactions dealt with in this work proceed by a free radical mechanism.   Viewed in relation to the large body of previous work carried out under similar conditions, and with known free radical initiators this suggestion seems reasonable.   Chain transfer constants have been obtained for certain silanes but detailed kinetic work on the addition reaction has not been carried out.   Comparison of reported approximate bond energies for homolysis and

heterolysis   in the gas phase indicate that
homolysis is more feasibly energetically;
(D(Si-H)= 76 kcal/mole, ionic bond energy (Si-H)=
250 kcal/mole).

Consideration of the various mechanisms
suggests that the free radical mechanism is the
most probable and it is necessary to examine to
what extent the observed side reactions are
consistent with a free radical mechanism.   The
following may generally be noted for the photo-
chemical reactions of silanes with fluoro-olefins.

a)   An increase in the time of irradiation
increases the percentage reaction of the olefin, and
the yield of the adduct.

b)   An increase in the silane/olefin ratio
increases the percentage reaction of the olefin and
decreases the degree of telomer formation.

c) The percentage reaction for any silane-
olefin pair is slightly variable for any specific set
of conditions.

d) Non-condensable gases are detected only
in the longer irradiations.

e) Reduction of both olefin and adduct may

occur, particularly when chlorine atoms are present
in the original olefin. If the mechanism is a
free radical addition reaction as has been suggested,
the following reaction scheme may represent the
sequence of the addition reaction.

$$X_3Si-H \xrightarrow{h\nu} X_3\overset{\bullet}{Si} + \overset{\bullet}{H} \qquad \text{initiation} \quad (1)$$

$$X_3\overset{\bullet}{Si} + \overset{}{\underset{}{C}}=\overset{}{\underset{}{C}} \longrightarrow -\overset{}{\underset{}{C}}-\overset{}{\underset{}{C}}-SiX_3 \qquad \text{addition} \quad (2)$$

$$-\overset{\bullet}{\underset{}{C}}-\overset{}{\underset{}{C}}-SiX_3 + X_3SiH \longrightarrow H\cdot\overset{}{\underset{}{C}}-\overset{}{\underset{}{C}}-SiX_3 \qquad \text{displacement} \quad (3)$$
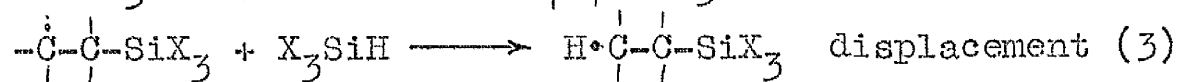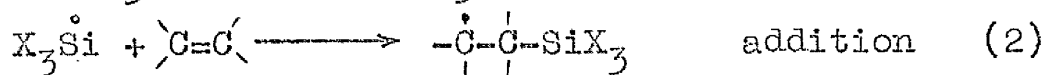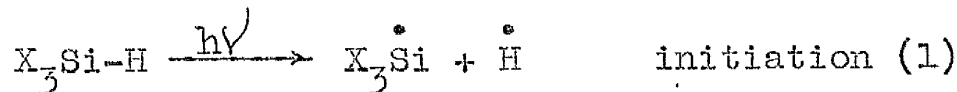
The formation of telomers is the result of the
successful competition of the intermediate radical
$-\overset{\bullet}{\underset{}{C}}-\overset{}{\underset{}{C}}-SiX_3$ with silyl radicals for the olefin molecules.

$$-\overset{\bullet}{\underset{}{C}}-\overset{}{\underset{}{C}}-SiX_3 + \overset{}{\underset{}{C}}=\overset{}{\underset{}{C}} \longrightarrow -\overset{\bullet}{\underset{}{C}}(C)_3 SiX_3 \qquad (4)$$

$$-\overset{\bullet}{C}(C)_3 SiX_3 + n\overset{}{\underset{}{C}}=\overset{}{\underset{}{C}} \longrightarrow -\overset{\bullet}{\underset{}{C}}-\overset{}{\underset{}{C}}-(\overset{}{\underset{}{C}}-\overset{}{\underset{}{C}})_{n+1} SiX_3 \qquad (5)$$

$$-\overset{\bullet}{\underset{}{C}}-\overset{}{\underset{}{C}}(\overset{}{\underset{}{C}}-\overset{}{\underset{}{C}})_{n+1} SiX_3 + X_3SiH \longrightarrow H(\overset{}{\underset{}{C}}-\overset{}{\underset{}{C}})_{n+2} SiX_3 \qquad (6)$$
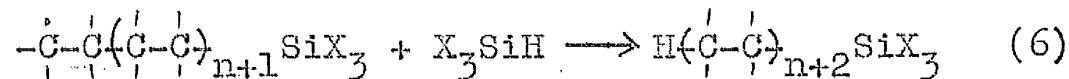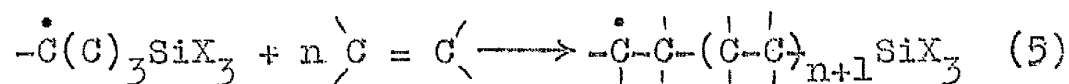
It is clear that the first two observations
a) and b) which relate to the yield of the 1:1 adduct,
are consistent with this mechanism. The times of
irradiation involved in these reactions are long
compared to those of many photochemical reactions,
but such times are not unusual in photochemical

reactions with silanes. This may be related to an inefficient initiation step which results from poor absorption by the reaction mixture, rather than to a low kinetic chain length. This is indicated by the absence of hydrogen in all but the long term irradiations ($\geqslant$ 300 hr.). The absence of hydrogen is not however conclusive.

The formation of telomers suggests a free radical chain mechanism as described above, but it is necessary to reduce the formation of the telomers to a minimum without sacrificing the percentage conversion of the olefin if meaningful comparisons of the ratios of the 1:1 adducts are to be obtained.

In accordance with previous work it has been found that increasing the ratio of the silane to the olefin affords a method of controlling telomerisation. In effect this is an attempt to make the addition step (equation 2,) rate-determining, and so avoid any accumulation of intermediate radicals which would result if the displacement step (equation 3) was rate-determining. Experimentally, this was done in two ways. One method was by shielding the gas phase

andirradiating the liquid phase only (in which the
silane/olefin ratio for dissolved olefin will be
higher than the silane/olefin ratio of original
reactants), and the second method was simply by
charging more silane into the reaction vessel and
vigorously shaking it.   The first method does not,
of course, apply in cases where the olefin is liquified
under the reaction conditions.

Preliminary reactions of trichlorosilane
with vinyl fluoride illustrate this, table 14 .

TABLE 14   The addition reaction of trichlorosilane
with vinyl fluoride.

Irradiation time hr.	S/O ratio	% reaction of olefin	product $H(CH_2CHF)_n SiCl_3$
100	1:1	20	$n > 1$
150*	1:1	1.5	—
100	2:1	30	$n > 1$
200+	2:1	22	$n = 1$
100	5:1	52	$n = 1$
176	8:1	96	$n = 1$

* tube stationary   + shielded vapour phase.

The second method was found to be most convenient
as the separation of liquid phase from gas phase

reactions is not included in the purpose of this work.

The observation (c) that the percentages of reaction of the olefins experimentally determined were slightly variable for any specific set of conditions, is probably related to extraneous factors such as deterioration of the ultraviolet lamps, in addition to the small variations expected due to manipulative technique.

The formation of compounds such as hydrogen, and reduced adducts or olefins due to reactions other than the addition reaction, gives an interesting insight into the nature of the reaction and of the reacting species, but for the purpose of this discussion it is necessary to consider separately products formed in reactions related to the principal mechanism (i.e., the addition reaction), and products formed by further reaction of the adducts (i.e., the reduction or abstraction mechanism).

The formation of hydrogen and the formation of the fluoroalkane.

The failure to observe the formation of hydrogen in most reactions suggests the existence of a high kinetic chain length, but the necessity of long irradiation times is contrary to this suggestion. If all hydrogen atoms produced in the system are assumed to react to give hydrogen as discussed below, then the amount of hydrogen formed should correspond approximately to half the number of chains initiated. This statement is however of doubtful validity in view of the other possible reactions of the hydrogen atom.

Hydrogen gas is assumed to be formed mainly by H-abstraction by hydrogen atoms, equations (7) and (8) .

$$SiHX_3 \xrightarrow{\text{h}\nu} \overset{\bullet}{SiX_3} + \overset{\bullet}{H} \tag{7}$$

$$SiHX_3 + \overset{\bullet}{H} \longrightarrow \overset{\bullet}{SiX_3} + H_2 \tag{8}$$
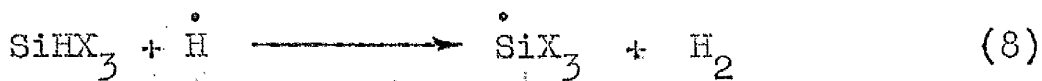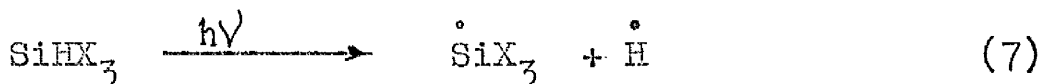
The formation of hydrogen by hydrogen atom recombination, which is extremely energetic, is most likely to occur in the presence of a third body such as the wall of the reaction vessel

$$\overset{\bullet}{H} + \overset{\bullet}{H} + M \longrightarrow H_2 + \overset{\bullet}{M} \qquad (9)$$
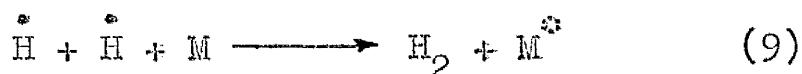
In view of the excess of the silane used, it is thought that hydrogen formation by reaction (9) is fairly improbable, and that termination will occur through other radical recombinations e.g., 1,4-disilylbutane has been detected in the reaction of silane, SiH_4, with ethylene:[41]

$$\overset{\bullet}{SiH_3} + CH_2{:}CH_2 \longrightarrow CH_2{\cdot}CH_2{\cdot}SiH_3 \qquad (10)$$

$$\overset{\bullet}{CH_2}{\cdot}CH_2{\cdot}SiH_3 + SiH_4 \longrightarrow CH_3{\cdot}CH_2{\cdot}SiH_3 + \overset{\bullet}{SiH_3} \qquad (11)$$

$$2\ CH_2{\cdot}CH_2{\cdot}SiH_3 \longrightarrow H_3Si{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SiH_3 \qquad (12)$$
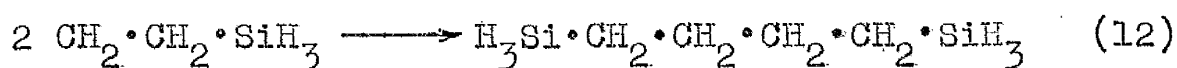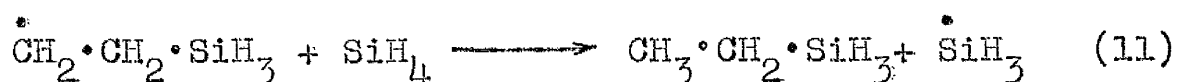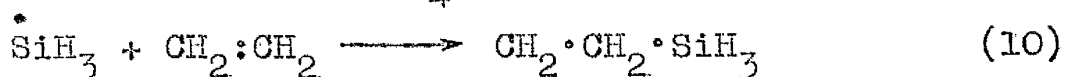
Reaction of the hydrogen atom with the olefin would give a fluoroalkyl radical which might be expected to react further with a molecule of a silane to give a fluoroalkane (equations (13) and (14). This would be even more difficult to detect in low percentages than hydrogen.

$$\overset{\bullet}{H} + C{=}C \longrightarrow {\cdot}C - C{\cdot}H \qquad (13)$$

$$SiHX_3 + {\cdot}C{\cdot}C{\cdot}H \longrightarrow H{-}C{-}C{-}H + \overset{\bullet}{SiX_3} \qquad (14)$$
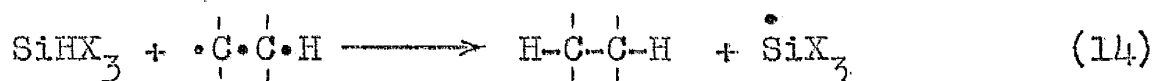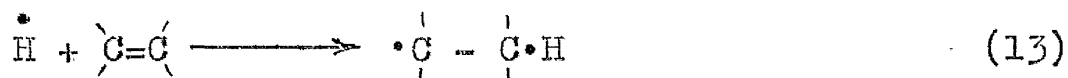
Evidence for the formation of 1,1,2-trifluoroethane in the reaction of trimethylsilane with trifluoroethylene for 250 hr. was obtained by gas-liquid chromatography. The 1,1,2-trifluoroethane was

present in extremely small amounts (less than 0.5%).
No evidence for this type of reaction was obtained
from other irradiations.

The detection of hydrogen (ca. 2%) in
the reactions which were carried out for much
longer periods than most of the irradiations
(150 - 300 hr.) indicates the plausibility of
reactions (7) and (8). Experiments in which
the silanes were irradiated alone gave low
percentages of products which can be accounted for
by a hydrogen abstraction reaction. For example,
the irradiation of trichlorosilane for 90 hr.
gave hydrogen chloride (ca. 2%) and hydrogen (ca. 0.7%),
and the irradiation of trimethylsilane for 100 hr.
gave hydrogen (ca. 1%). These results indicate that
hydrogen atoms generated in this way are sufficiently
energetic to be indiscriminate in their position of
attack (equations (15) (16) (17) and (18).

$$SiHCl_3 + \overset{\bullet}{H} \longrightarrow \overset{\bullet}{Si}HCl_2 + HCl \qquad (15)$$

$$SiHCl_3 + \overset{\bullet}{H} \longrightarrow \overset{\bullet}{Si}Cl_3 + H_2 \qquad (16)$$

$$CH_3 \cdot Si(CH_3)_2 H + \overset{\bullet}{H} \longrightarrow \overset{\bullet}{C}H_2 \cdot Si(CH_3)_2 H + H_2 \qquad (17)$$

$$(CH_3)_3 SiH + \overset{\bullet}{H} \longrightarrow (CH_3)_3 \overset{\bullet}{Si} + H_2 \qquad (18)$$
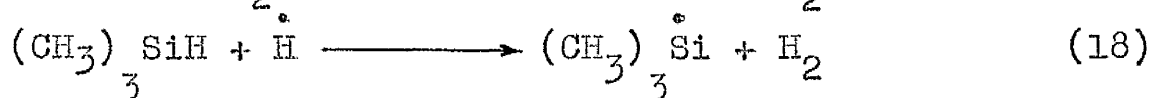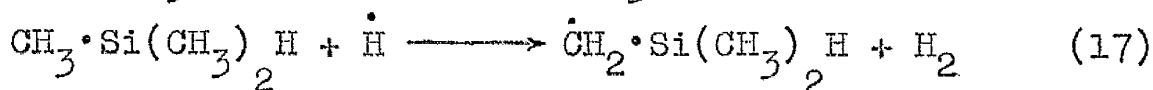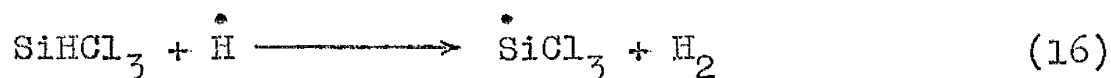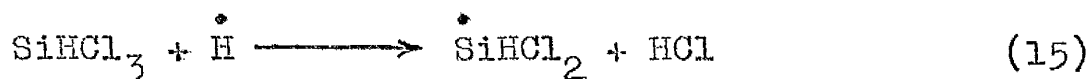
It is evident that the formation of hydrogen
and hydrogen chloride may continue irrespective
of the presence of the olefin.

The fact that termination products
were not detected for most of the reactions
dealt with in this thesis suggests the existence
of a long kinetic chain length.   The long
periods of irradiation necessary for the reactions
to proceed to give the adducts in good yields,
however, are not in agreement with this.
It is possible that this is due to an inefficient
initiation step.   The initiation step is discussed
later in more detail, (pp.166).

The formation of reduced olefins.

The formation of olefins carrying fewer halogen atoms than the parent olefin in some of the photochemical reactions was not expected. In cases where the yield of the new olefin was high, a silicon compound in which the original silicon-hydrogen bond had been replaced by a silicon-halogen bond was detected. The reaction appeared to have the stoichiometry of the following equation.

$$SiHX_3 + \ \ \diagup\!\!\!\!\diagdown C:C \diagup^{\diagdown}_{Y} \longrightarrow SiX_3Y + \ \ \diagdown\!\!\!\!\diagup C:C \diagdown^{\diagup}_{H}$$

The results (summarised in table 15) show that reduced olefins were only detected in the reactions of trimethylsilane and of dimethylsilane with fluoro-olefins. The formation of reduced olefins is also associated with the introduction of mercury into the reaction tubes. The presence of small traces of mercury cannot, however, be excluded from the reactions in which mercury was not purposely introduced as all pressure measurements were made with mercury manometers

TABLE 15	The photochemical reaction of silanes with fluoro-olefins. The formation of reduced olefins.			
Silane	Olefin	Silane/ olefin ratio	time (hr.)	Reduced olefin
Me_3SiH/Hg	$CH_2:CHF$	6:1	300	$CH_2:CH_2$ ($\sim$1%)
Me_2SiH_2	$CH_2:CHF$	4:1	200	$CH_2:CH_2$ (18%)
Me_3SiH/Hg	$CHF:CHCl$	9:1	96	$CH_2:CHF$ (90%) $CH_2:CH_2$ ($\sim$1%)

The reaction of trimethylsilane with vinyl fluoride in the presence of mercury with a silane/olefin ratio of 6:1 for 300 hr. gave the 1:1 adduct (80%), ethylene ($\sim$1%), and presumably trimethylfluorosilane, although this was not detected.

$$Me_3SiH + CH_2:CHF \xrightarrow[Hg]{h\nu} CH_2F{\cdot}CH_2{\cdot}SiMe_3, \quad CH_2:CH_2, \quad (Me_3SiF)$$
$$(80\%) \qquad (\sim1\%) \quad \text{not detected}$$
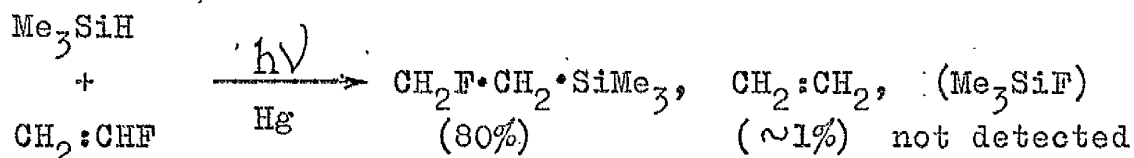
A similar reaction of trimethylsilane with 1-chloro-2-fluoroethylene in the presence of mercury with a silane/olefin ratio of 9:1 for 96 hr. gave vinyl fluoride (90%), ethylene ($\sim$1%), trimethylchlorosilane (96%), and a fluoroethyltrimethylsilane ($\sim$4%).

$$Me_3SiH$$

$$+ \xrightarrow[\text{Hg}]{h\nu} CH_2:CHF, CH_2:CH_2, Me_3SiCl,$$
$$\quad\quad\quad\quad\quad (90\%) \quad (\sim1\%) \quad (96\%)$$

$$CHCl:CHF \quad\quad\quad\quad\quad\quad +$$

$$H(CH_2 \cdot CHF)SiMe_3$$
$$(\sim4\%)$$
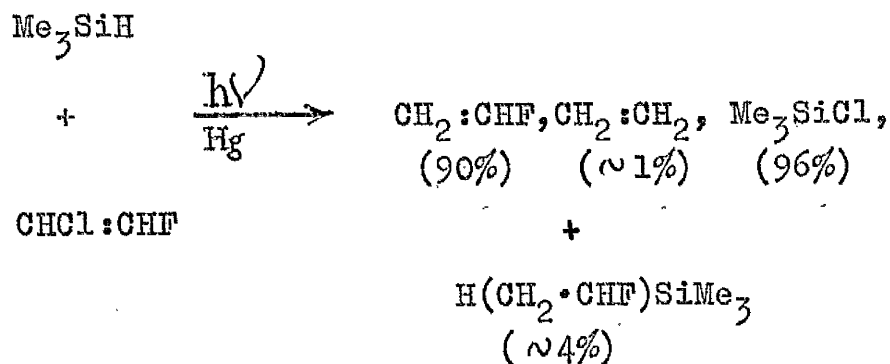
The ethylene was probably formed by a reaction similar to the previous reaction, but the absence of more of the adduct of trimethylsilane with vinyl fluoride is surprising.

Chlorine abstraction from the olefins is evidently easier than fluorine abstraction. This is in agreement with the observation that both α-chlorine and β-chlorine atoms are abstracted from 1-chloro-2-fluoroethyl-trichlorosilane, $CH_2F \cdot CHCl \cdot SiCl_3$, and 2-chloro-1-fluoroethyl-trichlorosilane, $CH_2Cl \cdot CHF \cdot SiCl_3$, in preference to abstraction of either α-fluorine or β-fluorine atoms, (pp.145).

$$CH_2F \cdot CHCl \cdot SiCl_3 + Me_3SiH \xrightarrow{h\nu} CH_2F \cdot CH_2 \cdot SiCl_3 + Me_3SiCl$$

$$CH_2Cl \cdot CHF \cdot SiCl_3 + Me_3SiH \xrightarrow{h\nu} CH_3 \cdot CHF \cdot SiCl_3 + Me_3SiCl$$
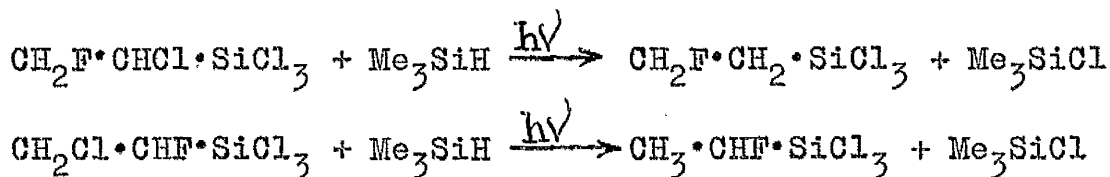
Ethylene was not detected in any of the reactions of trimethylsilane with vinyl fluoride in the absence of mercury. The reaction of trimethylsilane with 1-chloro-2-fluoroethylene with silane/olefin ratios

of 1:1 and 5:1 in the absence of mercury for ca.100 hr.

gave vinyl fluoride (4%) along with the 1:1 adduct, the

reduced adduct, and a compound assumed to be a telomer of

trimethylsilane with 1-chloro-2-fluoroethylene, e.g., with

a silane/olefin ratio of 5:1,

$$Me_3SiH + CHCl:CHF \longrightarrow CH_2:CHF, CH_3 \cdot CHF \cdot SiMe_3, Me_3SiCl, CH_2Cl \cdot CHF \cdot SiMe_3,$$
$$(4\%) \quad (42\%) \quad (45\%) \quad (20\%)$$
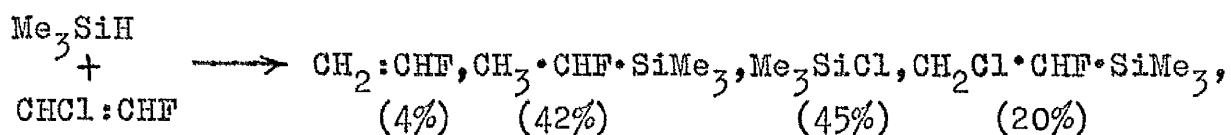
A controlled irradiation of 1-chloro-2-fluoroethylene

in the absence of mercury also gave vinyl fluoride ($\sim$2%)

after 90 hr., together with a polymer of 1-chloro-2-fluoro-

ethylene ($\sim$82%)

These results indicate the importance of

the added mercury in the reaction but the presence of

small quantities of mercury condensed into the reaction

vessel cannot be excluded as mentioned above. The following

reactions of trimethylsilane in the absence of olefin were

carried out in an attempt to understand the function of

the mercury.

Trimethylsilane was irradiated alone for

100 hr. and gave hydrogen ($\sim$1%) and unreacted trimethyl-

silane (98%). The reaction was repeated in the presence

of mercury and gave after 100 hr. hydrogen (12%), a trace

of an unidentified yellow oil, and unreacted trimethylsilane

(82%). These results suggest that the function of the

mercury is to assist Si - H homolysis. It is assumed
that the hydrogen is formed as shown below:

$$(CH_3)_3SiH \xrightarrow{h\nu} (CH_3)_3\overset{\bullet}{Si} + \overset{\bullet}{H}$$

$$(CH_3)_3SiH + \overset{\bullet}{H} \longrightarrow (CH_3)_3\overset{\bullet}{Si} + H_2$$

$$(CH_3)_3SiH + \overset{\bullet}{H} \longrightarrow \overset{\bullet}{CH_2}SiH(CH_3)_2 + H_2$$
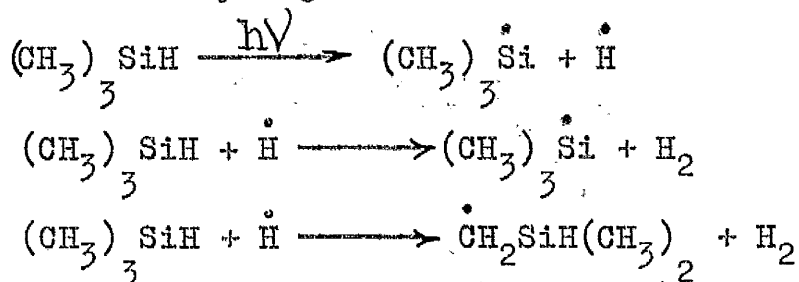
If this were the case, however, the
difference between the results from the reaction of
trimethylsilane with 1-chloro-2-fluoroethylene with
and without mercury should be a difference in degree and
not a difference in kind. It is possible that the
trimethylsilyl radicals produced by mercury photo-
sensitisation behave differently from those produced
by non-sensitised photolysis i.e. the two might differ in
electronic states, but it is certainly unwise to carry
such speculation further in the absence of more experimental
results.

It was found that when trimethylsilane was
irradiated with vinyl fluoride in the presence of mercury
an explosion occurred when the irradiation was started at
room temperature (two occasions). When the irradiation
was started with the reactants frozen down (-196°) the
addition proceeded without explosion. Similarly no

explosion occurred when the irradiation was started at room temperature if bulk mercury was not present in the tube.

Whilst it is evident that the presence of mercury is important it appears that its function is complex and beyond the scope of the present investigation.

As the reaction which produces the reduced olefins takes place under conditions usually associated with free radical reactions, further reaction of the reduced olefin with the excess of the reducing silane is possible. This would lead to the formation of a compound identical to a reduced adduct.

$$SiHX_3 + \begin{array}{c} \diagdown \\ \diagup \end{array} C = C \begin{array}{c} \diagup \\ \diagdown Y \end{array} \longrightarrow \begin{array}{c} \diagdown \\ \diagup \end{array} C = C \begin{array}{c} \diagup \\ \diagdown H \end{array} + SiX_3Y$$

$$SiHX_3 + \begin{array}{c} \diagdown \\ \diagup \end{array} C = C \begin{array}{c} \diagup \\ \diagdown H \end{array} \longrightarrow H \cdot \overset{|}{C} \cdot \overset{|}{C} \cdot SiX_3$$
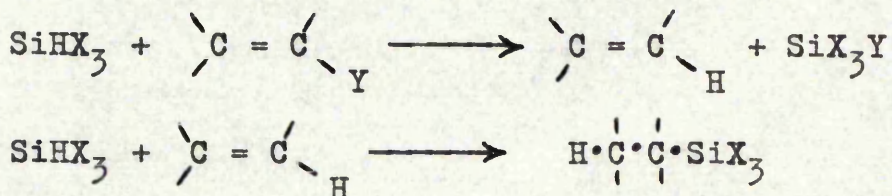
In the case of silanes which readily react with fluoro-olefins a reduced olefin may be formed and then completely consumed during the reaction. In such cases the reaction would be indistinguishable from a normal addition reaction followed by a halogen abstraction from the 1:1 adduct.

$$SiHX_3 + \begin{array}{c} \diagdown \\ \diagup \end{array} C = C \begin{array}{c} \diagup \\ \diagdown Y \end{array} \longrightarrow Y \cdot \overset{|}{C} \cdot \overset{|}{C} \cdot SiX_3$$

$$SiHX_3 + Y \cdot \overset{|}{C} \cdot \overset{|}{C} \cdot SiX_3 \longrightarrow H \cdot C \cdot C \cdot SiX_3 + SiX_3Y$$
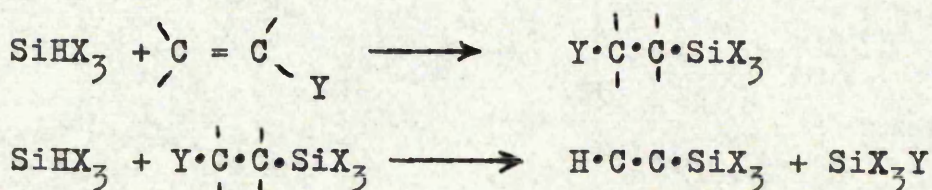
For example the reactions of trimethylsilane and trifluoro-ethylene gave trimethylfluorosilane and a difluoroalkylsilane.

This clearly indicated that fluorine abstraction had
occurred at some stage of the reaction.   It would be
possible to account for these observations either
(1) by fluorine abstraction from the olefin followed
by addition of trimethylsilane to the reduced olefin or
(2) by addition of trimethylsilane to the original olefin
followed by fluorine abstraction from the 1:1 adduct.
In most cases it is not possible to distinguish between
these alternatives.

In view of this it is necessary to
examine the possible mechanisms for the olefin formation.
It has been suggested that the addition reaction involves
a free radical mechanism (pp.121), and it is similarly
suggested that the abstraction reaction involves a free
radical mechanism, since as the reaction does not take
place in the absence of light.   Three mechanisms are
possible

(a) <u>Halogen abstraction from the 1:1 adduct followed
by a free radical elimination.</u>   This is similar to the
reverse of an addition reaction.

$$Y \cdot \overset{|}{\underset{|}{C}} \cdot \overset{\cdot}{\underset{|}{C}} \cdot SiX_3 + \overset{\cdot}{SiX_3} \longrightarrow \cdot \overset{|}{\underset{|}{C}} \cdot \overset{|}{\underset{|}{C}} \cdot SiX_3 + SiX_3Y$$

$$\cdot \overset{|}{\underset{|}{C}} \cdot \overset{|}{\underset{|}{C}} \cdot SiX_3 \rightleftharpoons \overset{\cdot}{C} = C + \overset{\cdot}{SiX_3}$$
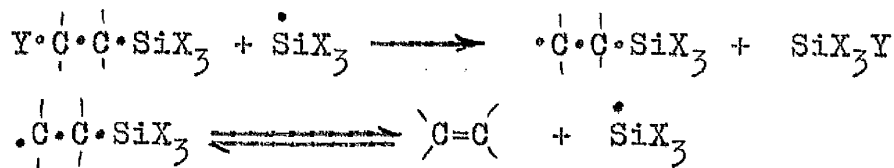
This mechanism has been shown not to apply for the intermediate

radicals $CH_2F \cdot \overset{\bullet}{C}H \cdot SiCl_3$ and $\overset{\bullet}{C}H_2 \cdot CHF \cdot SiCl_3$ produced by

halogen abstraction from the respective chlorofluoroethyl-

trichlorosilanes. This is discussed in detail in the

next section. The results of the addition reactions of

the addition reactions of both trichlorosilane and

trimethylsilane with chlorotrifluoroethylene also indicate

that this mechanism does not apply. This is discussed below.

The addition reaction of silyl radicals

with chlorotrifluoroethylene is unidirectional.

$$CF_2{:}CFCl + \overset{\bullet}{S}iX_3 \longrightarrow \overset{\bullet}{C}FCl \cdot CF_2 \cdot SiX_3$$

$$\overset{\bullet}{C}FCl \cdot CF_2 \cdot SiX_3 + SiHX_3 \longrightarrow CHFCl \cdot CF_2 \cdot SiX_3 + \overset{\bullet}{S}iX_3$$
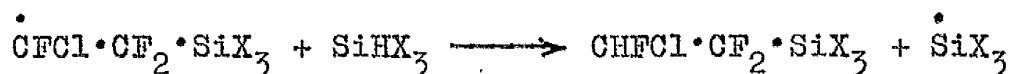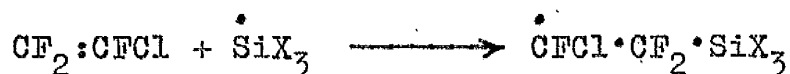
Abstraction of the chlorine atom from the adduct produces a

1,1,2-trifluoroethyl-silane if hydrogen abstraction by the

intermediate radical takes place

$$CHFCl \cdot CF_2 \cdot SiX_3 + \overset{\bullet}{S}iX_3 \longrightarrow \overset{\bullet}{C}HF \cdot CF_2 \cdot SiX_3 + SiX_3Cl$$

$$SiHX_3 + \overset{\bullet}{C}HF \cdot CF_2 \cdot SiX_3 \longrightarrow CH_2F \cdot CF_2 \cdot SiX_3 + \overset{\bullet}{S}iX_3$$

If, however, the intermediate radical dissociates by

mechanism (a) then trifluoroethylene will be produced.

$$\overset{\bullet}{C}HF \cdot CF_2 \cdot SiX_3 \longrightarrow CHF{:}CF_2 + \overset{\bullet}{S}iX_3$$
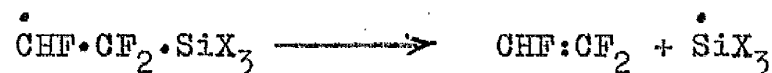
Subsequent addition of a silyl radical to trifluoroethylene

would produce a 1,2,2-trifluoroethyl-silane as shown by the

reactions of silyl radicals with trifluoroethylene described

in this work (pp. 77).

$$SiHCl_3 + CF_2:CHF \longrightarrow CHF_2 \cdot CHF \cdot SiCl_3 \quad (> 98\%).$$

$$Me_3SiH + CF_2:CHF \longrightarrow CHF_2 \cdot CHF \cdot SiMe_3 \quad (64\%)$$
$$+$$
$$CH_2F \cdot CF_2 \cdot SiMe_3 \quad (36\%)$$
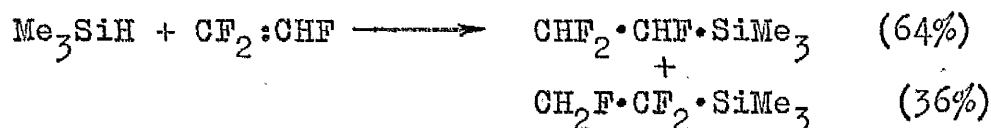
In fact only the 1,1,2-trifluoroethyl-compounds were detected among the reduced adducts from the reactions of silyl radicals with chlorotrifluoroethylene. This result, and the work on the reaction of trichlorosilane with 1-chloro-2-fluoroethylene discussed below (pp.93), suggest that the reduced olefins were not formed by mechanism (a).

(b) **Light induced decomposition of the olefin.**

It is possible that the reduced olefins were formed by irradiation of the parent olefin and that the silane was only used as a hydrogen source for the initial reaction.

$$\ce{>C = C<^Y} \xrightarrow{h\nu} \ce{>C = \overset{\bullet}{C}<}$$

$$\ce{>C = \overset{\bullet}{C}<} + SiHX_3 \longrightarrow \ce{>C = C<^H} + \overset{\bullet}{Si}X_3$$
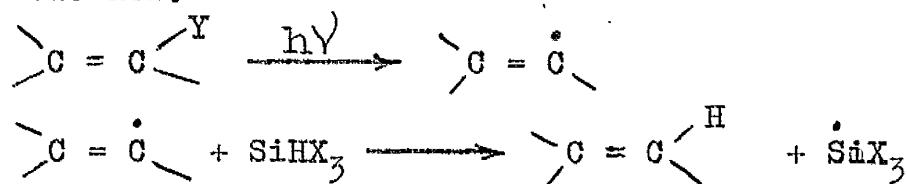
The olefins were irradiated alone to examine their behaviour in the absence of a silane. The results presented below (table 16) show that the olefins all reacted differently.

Olefin	Time (hr.)	olefin consumed (%)	Products
TABLE 16		The irradiation of the olefins.	
$CH_2:CHF$	113	8	$CH:CH(\sim 8\%)$
$CHF:CHCl$	90	84	$CH_2:CHF(2\%)+$ polymer
$CHF:CF_2$	113	17	unidentified brown tar. *

* possibly polymeric trifluoroethylene.

The reasons for the different behaviour of the various olefins, and the detailed aspects of the mechanism have not been studied, but the results suggest that photolytic decomposition of the olefins is not likely.

(c) <u>Halogen abstraction from the olefin.</u>   A chain reaction involving halogen abstraction from the olefin by a silyl radical is the most probable mechanism.

$$SiHX_3 \xrightarrow[]{h\nu} \dot{S}iX_3 + \dot{H}$$

$$\underset{/}{\overset{\backslash}{C}} = C \overset{Y}{\underset{\backslash}{}} + \dot{S}iX_3 \longrightarrow \underset{/}{\overset{\backslash}{C}} = \dot{C} \overset{\backslash}{} + SiX_3Y$$

$$\underset{/}{\overset{\backslash}{C}} = \dot{C} \overset{\backslash}{} + SiHX_3 \longrightarrow \underset{/}{\overset{\backslash}{C}} = C \overset{H}{\underset{\backslash}{}} + \dot{S}iX_3$$
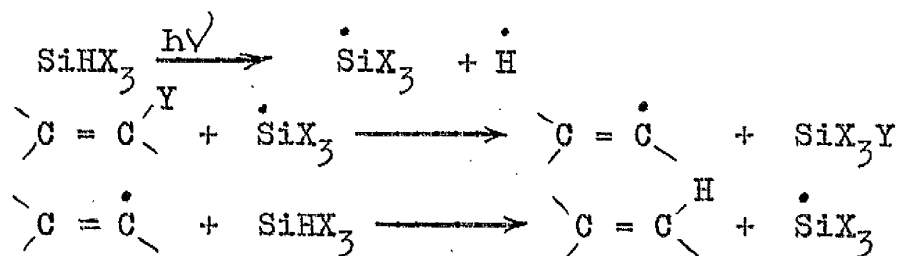
As this reaction involves a vinylic radical identical with that suggested in the previous mechanism (b), the two mechanisms will be indistinguishable after the initiation step. It is possible that mercury would assist initiation by this mechanism, but since the effect of mercury on the photolysis

of the olefins has not been studied, a true comparison can
not be made.

It is possible that the reduced olefins
are produced by mechanisms (b) and (c),but the nature of
the reaction is such that more experimental data are
necessary before any definite conclusions can be drawn.

The formation of reduced adducts.

The appearance of reduced adducts in the irradiations discussed in this work provided one of the most interesting aspects of the behaviour of silyl radicals.

A brief report of the detection of a compound corresponding to a reduced adduct from the addition reaction of trichlorosilane with chlorotrifluoroethylene was published in 1960,[65] and a possible reaction scheme was presented.

$$\overset{\bullet}{S}iCl_3 + CF_2:CFCl \longrightarrow \overset{\bullet}{C}FCl \cdot CF_2 \cdot SiCl_3$$

$$\overset{\bullet}{C}FCl \cdot CF_2 \cdot SiCl_3 + SiHCl_3 \longrightarrow CHFCl \cdot CF_2 \cdot SiCl_3 + \overset{\bullet}{S}iCl_3$$

$$CHFCl \cdot CF_2 \cdot SiCl_3 + \overset{\bullet}{S}iCl_3 \longrightarrow \overset{\bullet}{C}FH \cdot CF_2 \cdot SiCl_3 + SiCl_4$$

$$\overset{\bullet}{C}HF \cdot CF_2 \cdot SiCl_3 + SiHCl_3 \longrightarrow CH_2F \cdot CF_2 \cdot SiCl_3$$
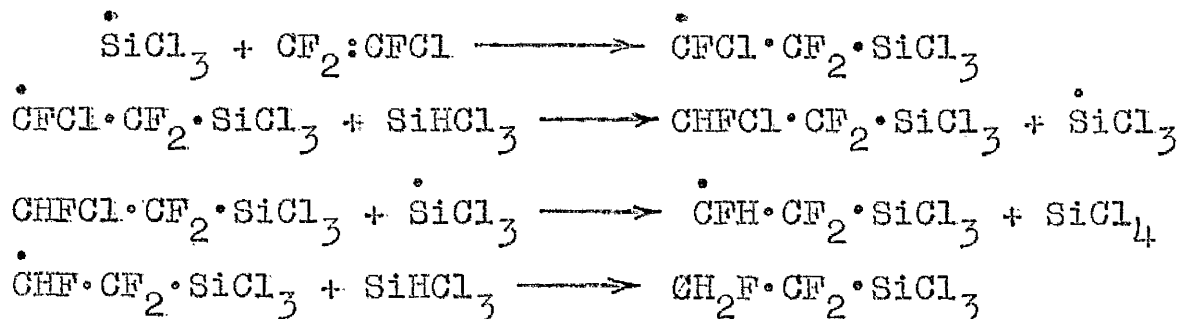
The reaction is often referred to as a halogen abstraction reaction, but when written in general terms it may be seen that it is analogous to the displacement step of the addition reaction.

$$\overset{\bullet}{R} + X - S \longrightarrow RX + \overset{\bullet}{S}$$

Many reactions of this type where R is alkyl have been reported.[123] In such cases the alkyl radical abstracts hydrogen (X = H). In cases where R is a silyl radical, e.g., the photochemical reaction

of trichlorosilane with chlorotrifluoroethylene
discussed above, the atom abstracted is chlorine
(X = Cl). This difference in behaviour of the
alkyl and silyl radicals is probably related to
the different strengths of the bonds formed
and of the bonds broken, (table 17).

TABLE 17	Bond energies (Kcal/mole)[140]		
Silicon bond	Bond energy	Carbon bond	Bond energy
Si - H	76	C - H	98.7
Si - Cl	91	C - Cl	81
Si - F	135	C - F	116

It is this difference in behaviour which allows the
possibility of a rapid chain process for halogen
abstraction by a silyl radical.

$$RX + \overset{\bullet}{S}iCl_3 \longrightarrow \overset{\bullet}{R} + SiCl_3X$$
$$\overset{\bullet}{R} + SiHCl_3 \longrightarrow RH + \overset{\circ}{S}iCl_3$$

For the reaction:

$$\equiv C - Cl + \equiv Si \cdot H \longrightarrow \equiv C - H + \equiv Si \cdot Cl,$$
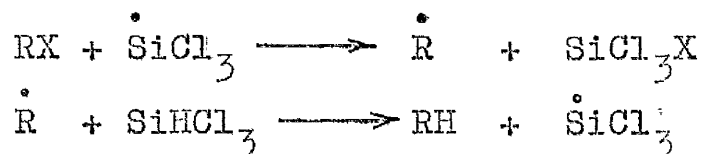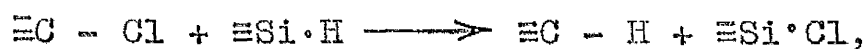
the change in bond energy is equal to
ca. 33 kcal/mole.

The strength of the bond broken is also

important.   Although the silicon-fluorine bond
energy is higher than that of the silicon-chlorine
bond, the carbon-fluorine bond energy is also
sufficiently high to preclude a simple fluorine
abstraction, e.g.,

$$CH_2F \cdot CHCl \cdot SiCl_3 + Me_3SiH \xrightarrow{h\nu} CH_2F \cdot CH_2 \cdot SiCl_3 +$$
$$Me_3SiCl$$

$$CH_2Cl \cdot CHF \cdot SiCl_3 + Me_3SiH \xrightarrow{h\nu} CH_3 \cdot CHF \cdot SiCl_3 +$$
$$Me_3SiCl$$
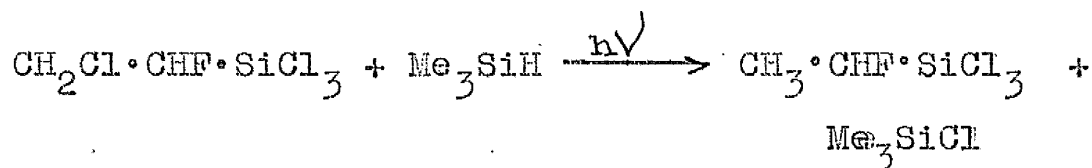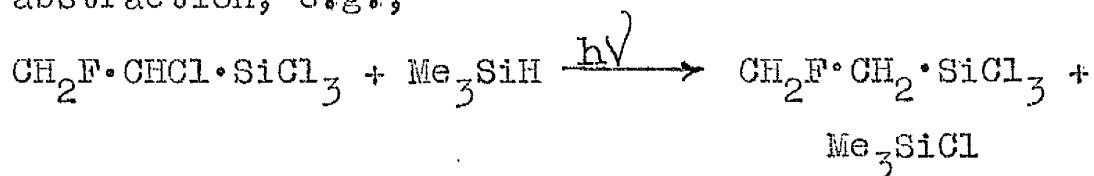
This work, and other work carried out
in this department,   has shown that the
abstraction reaction observed by Haszeldine and
Young[65] can be extended to general chlorine
abstraction by silyl radicals.   In a study of
the orientation of free radical addition reactions
it is, therefore, necessary to consider the
mechanism of the abstraction reaction in detail.

The experimental results from the
reaction of silanes with 1-chloro-2-fluoroethylene
indicate that a process similar to that postulated
by Haszeldine and Young may be taking place.   The
results (table 18)   indicate that the extent of
chlorine abstraction depends on the concentration of

the silane.   This is consistent with an abstraction
by the silane, or a silyl radical, as opposed to
light induced decomposition of the adduct:

$$CH_2Cl \cdot CHF \cdot SiCl_3 \xrightarrow{\quad\times\quad} \overset{\bullet}{C}H_2 \cdot CHF \cdot SiCl_3 + \overset{\bullet}{C}l.$$
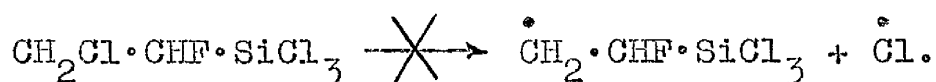
The observation that the reaction does not take place
in the absence of light indicates that a radical
reaction is probably involved.

TABLE 18	The photochemical reaction of silanes with 1-chloro-2-fluoroethylene.				
Silane	Silane/ olefin ratio	time (hr.)	Consumption of olefin (%)	Yield of 1:1 adduct (%)	Yield of dehalog- enated adduct (%)
$SiHCl_3$	2.5:1	116	73	38	3
$SiHCl_3$	5:1	100	67	79	10
$SiHCl_3$	10:1	100	98	8	73
$SiHCl_3$	10:1	14 days	--	--	-- ※
Me_3SiH	1:1	90	100	5+	--
Me_3SiH	5:1	100	50	20+	42
Me_3SiH	10:1	100	100	--	98
Me_3SiH	10:1	100	--	--	-- ※※

※   In the absence of light at 20°,
※※ In the absence of light at 85°,
+   Estimated from olefin produced on alkaline
        hydrolysis.

The estimation of the percentage of attack at either end of the olefins dealt with in this work was obtained by measurement of isomer ratios, i.e., by product analysis. This method depends upon a knowledge of the fate of all the intermediate radicals produced by the addition reaction.

e.g., $\overset{\bullet}{C}HCl \cdot CHF \cdot SiCl_3$, $\overset{\bullet}{C}HCl \cdot CHF \cdot SiMe_3$,

$\overset{\bullet}{C}HF \cdot CHCl \cdot SiCl_3$
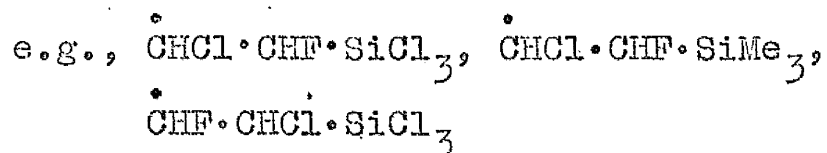
For a bidirectional addition reaction, telomerisation may take place faster with one intermediate radical than with the other. The telomers were too complex to allow structural determination. The measurement of 1:1 adduct ratios alone would give a false ratio of the actual percentages of the original addition reaction if telomer formation had occurred at different rates from the intermediate radicals. Telomer formation must be minimised, therefore, if a comparison of isomer ratios is to be made.

The method most frequently used to reduce telomer formation is to work in the presence of a large excess of the addend (in this case the silane). In reactions with fluoro-olefins containing chlorine

(e.g., CHF:CHCl,CF_2:CFCl) this leads to abstraction of the chlorine atom from the 1:1 adducts. An estimation of the ratio of addition at either end of the olefin must, therefore, take the ratio of the reduced adducts into account in addition to the ratio of the 1:1 adducts. For this approach to be successful the mechanism of the formation of the reduced adducts must be known, i.e., one must establish that one isomer of the adduct does not give rise to the formation of both isomers of the reduced adduct.

The abstraction reaction is possibly a free radical reaction as discussed above.

$$CH_2Cl \cdot CHF \cdot SiCl_3 + \overset{\circ}{S}iX_3 \longrightarrow \overset{\circ}{C}H_2 \cdot CHF \cdot SiCl_3 + SiX_3Cl$$

$$CH_2F \cdot CHCl \cdot SiCl_3 + \overset{\circ}{S}iX_3 \longrightarrow CH_2F \cdot \overset{\bullet}{C}H \cdot SiCl_3 + SiX_3Cl$$
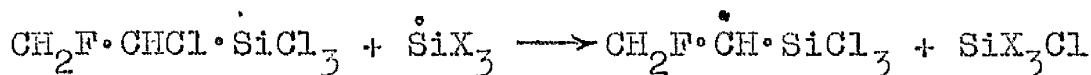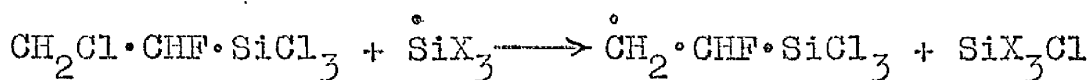
The intermediate radical may however react in three different ways. These are discussed below.

a) <u>Hydrogen abstraction.</u> This is the reaction path proposed for the formation of 1,1,2-trifluoroethyltrichlorosilane in the reaction of trichlorosilane with chlorotrifluoroethylene. The reaction is uncomplicated and should lead to the formation of the reduced adducts without any alteration of the isomer ratios.

$$\overset{\bullet}{C}H_2 \cdot CHF \cdot SiCl_3 + SiHX_3 \longrightarrow CH_3 \cdot CHF \cdot SiCl_3 +$$
$$\overset{\bullet\bullet}{S}iX_3$$

$$CH_2F \cdot \overset{\bullet}{C}H \cdot SiCl_3 + SiHX_3 \longrightarrow CH_2F \cdot CH_2 \cdot SiCl_3 +$$
$$\overset{\bullet}{S}iX_3$$
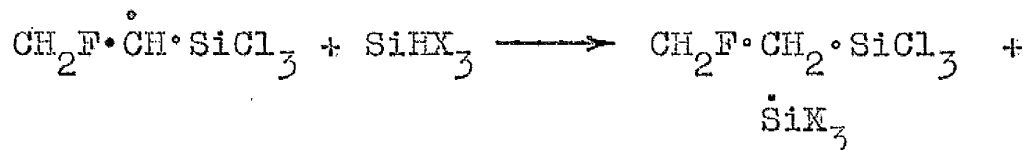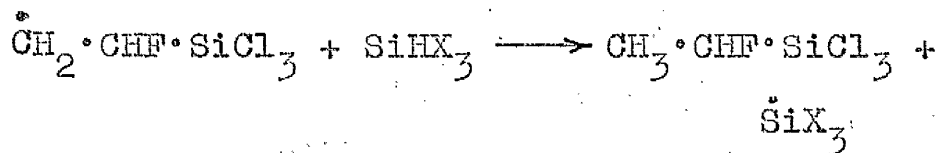
The addition reaction of trichloro-silane to vinyl fluoride gave 2-fluoroethyltrichloro-silane, $CH_2F \cdot CH_2 \cdot SiCl_3$, exclusively. This indicates that the intermediate radical $\overset{\bullet}{C}HF \cdot CH_2 \cdot SiCl_3$ is more stable than the intermediate radical $\overset{\bullet}{C}H_2 \cdot CHF \cdot SiCl_3$. This also suggests that there is no tendency for the radical $\overset{\bullet}{C}HF \cdot CH_2 \cdot Si \cdot Cl_3$ to produce the other isomer $CH_3 \cdot CHF \cdot SiCl_3$. As the radical $\overset{\bullet}{C}H_2 \cdot CHF \cdot SiCl_3$ would be less stable than $\overset{\bullet}{C}HF \cdot CH_2 \cdot SiCl_3$, the second and third mechanisms discussed may be visualised as possible routes from the less stable radical to the more stable one.

b) <u>Free radical elimination</u>. This is equivalent to the reverse of an addition reaction, i.e., elimination of an atom or group as a radical from the position $\beta-$ to the radical centre.

$$\overset{\bullet}{C} \cdot \overset{|}{\underset{|}{C}} \cdot SiX_3 \rightleftharpoons \overset{\diagdown}{\diagup}C = C\overset{\diagup}{\diagdown} + \overset{\bullet}{S}iX_3$$
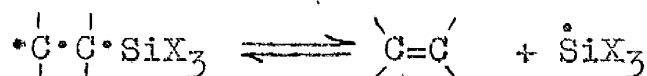
This type of reaction has been shown to occur in other systems. The reaction appears

to take place because of relatively low strengths of the bonds between the radical eliminated and the carbon atom to which it is attached. For example, Sivertz[151] has demonstrated the reversibility of the addition reactions of thiols to cis- and trans- butenes by the accelerated isomerisation of the olefins:
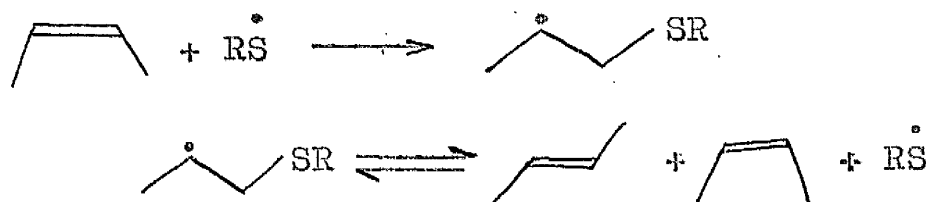
The formation of isobutene from the reaction phenyl radicals with di-t-butanethiol is also thought to be a radical elimination reaction.[152]

$$C_6H_5{\cdot} \ + \ (CH_3)_3 C{\cdot}S{\cdot}C(CH_3)_3 \longrightarrow \overset{\bullet}{C}H_2{-}\overset{\underset{|}{CH_3}}{\underset{|}{C}}{-}S{-}C(CH_3)_3 + C_6H_6$$

$$\overset{\bullet}{C}H_2{-}\overset{\underset{|}{CH_3}}{\underset{|}{C}}{-}S{-}C(CH_3)_3 \longrightarrow CH_2{:}C(CH_3)_2 \ + \ (CH_3)_3\overset{\circ}{C}S$$
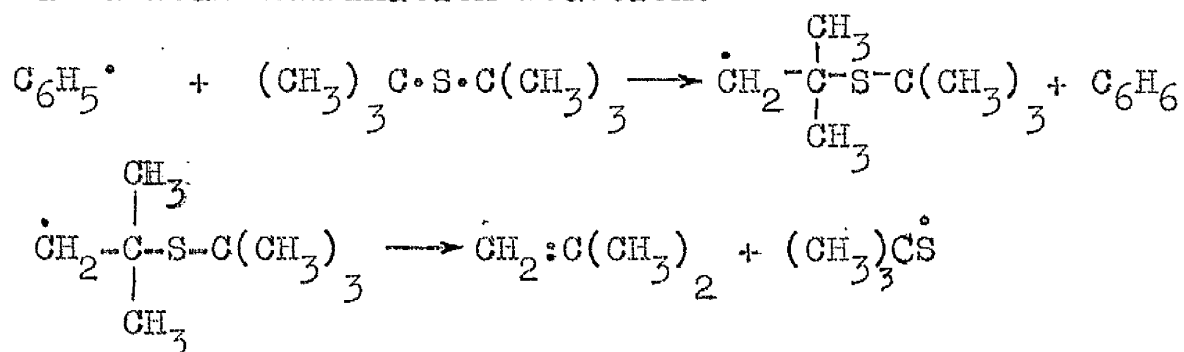
A series of addition reactions of silanes to cis- and trans- butenes has been reported, but no data on the relative rates of isomerisation were given.[153]

In some of the abstraction reactions dealt with in this thesis the operation of this mechanism would lead to the formation of two isomers of the reduced adduct from only one isomer of the 1:1 adduct.

e.g., $CH_2Cl \cdot CHF \cdot SiCl_3 + \overset{\bullet}{Si}X_3 \longrightarrow \overset{\bullet}{CH_2} \cdot CHF \cdot SiCl_3 +$

SiX_3Cl

$\overset{\bullet}{CH_2} \cdot CHF \cdot SiCl_3 \longrightarrow CH_2{:}CHF + \overset{\bullet}{Si}Cl_3 \longrightarrow$

$\overset{\bullet}{CHF} \cdot CH_2 \cdot SiCl_3$

and

$CHClF \cdot CF_2 \cdot SiMe_3 + \overset{\bullet}{Si}Me_3 \longrightarrow \overset{\bullet}{CHF} \cdot CF_2 \cdot SiMe_3 +$

$MeSiCl_3.$

$\overset{\bullet}{CHF} \cdot CF_2 \cdot SiMe_3 \longrightarrow CHF{:}CF_2 + \overset{\bullet}{Si}Me_3 \longrightarrow$

$\overset{\bullet}{CF_2} \cdot CHF \cdot SiMe_3 \qquad (65\%)$
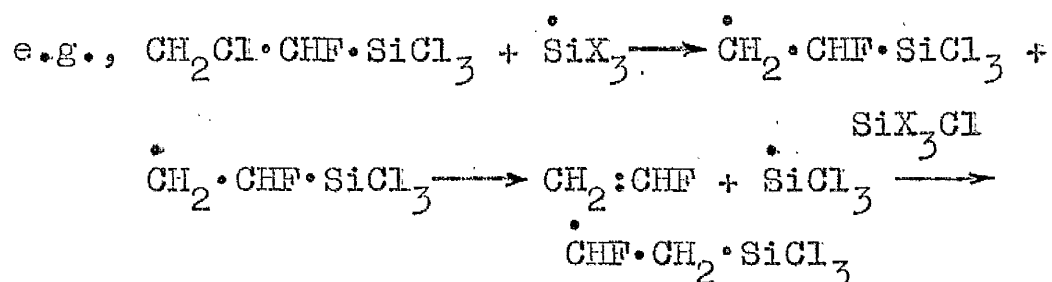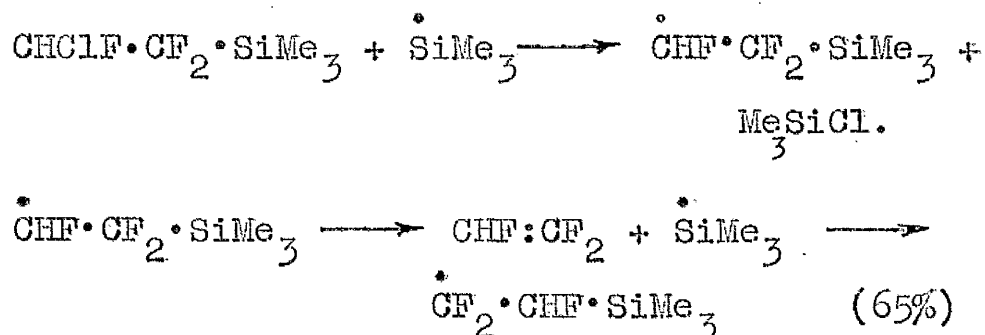
The fact that 1,2,2-trifluoroethylsilanes were not detected in the addition reaction of trichlorosilane and of trimethylsilane with chlorotrifluoroethylene when the reaction was allowed to proceed to give the reduced adduct, a 1,1,2-trifluoroethylsilane, indicates that the radical elimination reaction is not operating in these cases.   For the case of the abstraction from the chlorofluoroethyltrichlorosilanes, however, the

position is complicated by the presence of both
isomers of the 1:1 adduct.   As it was not found
possible to achieve complete preparative separation
of the two isomers of the 1:1 adduct a separate
experiment was carried out to test the operation
of an elimination reaction.

The halogen abstraction reaction from a
mixture of the isomers 1-chloro-2-fluoroethyltri-
chlorosilane and 2-chloro-1-fluoroethyltrichlorosilane
was carried out with a large excess of methyldichloro-
silane or trimethylsilane.   If the radical elimination
occurs, then either (1) the adduct of the reducing
silane with vinyl fluoride will be detected (for
silanes which react readily with vinyl fluoride
e.g., methyldichlorosilane, or (ii) vinyl fluoride
will be detected (for silanes which do not react
readily with vinyl fluoride, e.g. trimethylsilane)

$$CH_2Cl \cdot CHF \cdot SiCl_3 \longrightarrow \overset{\bullet}{C}H_2 \cdot CHF \cdot SiCl_3 \longrightarrow CH_3 \cdot CHF \cdot SiCl_3$$

$$\downarrow CH_3SiHCl_2$$

$$\overset{\bullet}{SiCl_3} + CH_2:CHF \longrightarrow CH_2F \cdot CH_2 \cdot SiCl_2CH_3$$

$$CH_2F \cdot CHCl \cdot SiCl_3 \longrightarrow CH_2F \cdot \overset{\bullet}{C}H \cdot SiCl_3 \longrightarrow CH_2F \cdot CH_2 \cdot SiCl_3$$
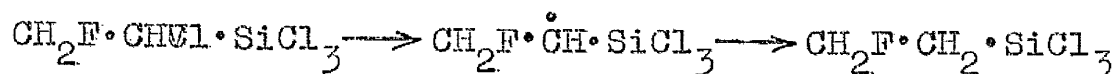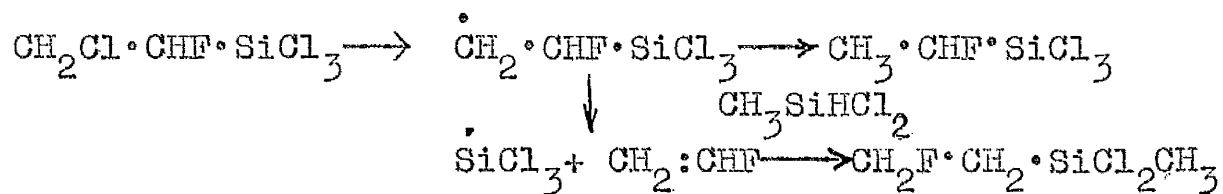
The reduction of the adduct was carried
out for 100 hr. with methyldichlorosilane and with
trimethylsilane, both with silane/olefin ratios of
10:1, (table 19).

The adducts of trimethylsilane and of
methyldichlorosilane to vinyl fluoride were not
detected in the reaction products.   Similarly vinyl
fluoride was not detected in the reaction products.
This suggests that the elimination mechanism does
not occur in these addition and abstraction reactions.

c) Free radical rearrangement.   A free radical
rearrangement of the intermediate free radical may
occur via a bridged intermediate of the type discussed
by Skell.[130]

$$\overset{\bullet}{C}H_2 \cdot CHF \quad \underset{SiCl_3}{|} \quad \longrightarrow \quad CH_2 \overset{\diagdown \diagup}{\underset{SiCl_3}{\diagup}} CHF \quad \longrightarrow \quad CH_2 \cdot \overset{\circ}{C}HF \quad \underset{SiCl_3}{|}$$
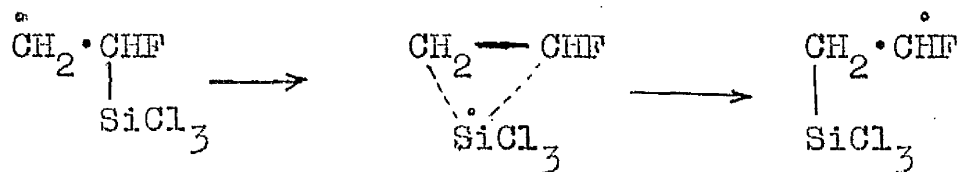
As the 1:1 adducts could not be separated in
sufficient quantity for separate halogen abstraction
from each isomer to be carried out this mechanism could
only be tested by establishing that the ratios of
fluoroethyl-compounds were the same before and
after the reaction

The arguments against this mechanism are not as sound as those against the previous reaction path, but it is suggested that if a bridged, non-classical free radical intermediate is formed, it should collapse to an equilibrium mixture of the two isomers. If, therefore, the isomer ratio stays the same before and after the dehalogenation it may be possible to say that either (i) the bridged structure is not involved, or (ii) the ratio of isomers in question fortuitously coincides with the percentages of each isomer obtained from the collapse of the bridge to equilibrium.

The observation that the total ratios of $\alpha:\beta$ fluoroethyl - compounds before and after irradiation remains the same, even after starting from ratios as different as 4.4:1 and 0.93:1, indicates that the bridged intermediate is improbable. The nature of this investigation precluded further investigation of the mechanism of this interesting reaction. It is realised that the arguments given above against the bridged intermediate are not conclusive.

TABLE 19

Photochemical reactions of silanes with the adduct H(CHCl CHF)SiCl₃

Silane	Ratio silane: olefin	Time hr.	Ratio of adducts (in) $\frac{CH_2Cl \cdot CHF \cdot SiCl_3}{CH_2F \cdot CHCl \cdot SiCl_3}$	Percent reaction	Ratio of adducts (out) $\frac{CH_2Cl \cdot CHF \cdot SiCl_3}{CH_2F \cdot CHCl \cdot SiCl_3}$	Ratio reduced adducts $\frac{CH_3 \cdot CHF \cdot SiCl_3}{CH_2F \cdot CH_2 \cdot SiCl_3}$	Notes
MeSiHCl₂	10:1	100	4.4	70	2.0	15.3	No CH₂:CHF or CH₂F·CH₂·SiCl₂Me
Me₃SiH	10:1	50	0.93	100	-O-	0.93	No CH₂:CHF or CH₂F·CH₂·SiMe₃
Cl₃SiH	10:1	14 days	In the absence of light at 20°C.	0	-O-	-O-	-O-

It was possible during the investigation
of the abstraction reaction discussed above to
obtain by product analysis an approximate figure
for the relative rates of abstraction of α - and
β - chlorine.   It was found that β-chlorine
was removed in preference to α-chlorine in the ratio
of 3·5:1.   This appears at first sight to indicate
preferential formation of the primary free radical.

$$CH_2Cl \cdot CHF \cdot SiCl_3 \xrightarrow{\overset{\bullet}{Si}X_3} \overset{\bullet}{C}H_2 \cdot CHF \cdot SiCl_3 , k_1$$

$$CH_2F \cdot CHCl \cdot SiCl_3 \longrightarrow CH_2F \cdot \overset{\circ}{C}H \cdot SiCl_3, k_2$$
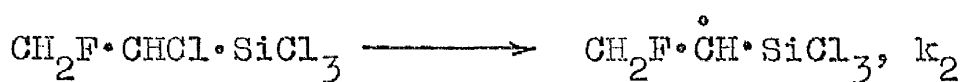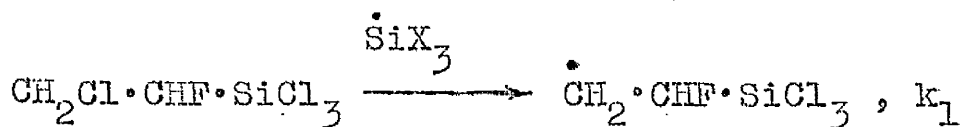
i.e., $k_1/k_2 = 3 \cdot 5$ (assuming that the abstraction
of chlorine is rate determining).

These results are analogous to the chlorination of
trichloroethylsilane under free radical conditions,
in which again the formation of the β-chloroethyl-
compound predominates over that of the α-chloroethyl-
compound.   This may be related to some form of
destabilisation of a radical by an α-silyl group,
the mechanics of which are difficult to visualise, or
simply to very definite steric requirements for the
reaction path.   Almost all the published work on
radical stability has been concerned with carbon

free radicals.   The effect of heteroatoms on
radical stability is a subject which has received
relatively little study.

Comparison of the reactivity of silanes with

fluoro-olefins.

A comparison of the percentages of
reactions of trichlorosilane, methyldichlorosilane
and trimethylsilane with vinyl fluoride shows
that the reactivity falls in the order
$Me_3SiH < MeSiHCl_2 \simeq SiHCl_3$.
In contrast to this the reactivity of trichlorosilane,
methyldichlorosilane and trimethylsilane towards
1-chloro-2-fluoroethylene and trifluoroethylene
falls in the order $SiHCl_3 \simeq MeSiCl_2H < Me_3SiH$.
A general decrease in the reactivity of the olefins
towards the trichlorosilane and trimethylsilane was
observed in the order $CH_2:CHF < CHF:CHCl < CHF:CF_2$.
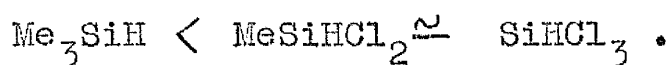
It must be pointed out however that
these generalisations are drawn from reactions
which are not strictly comparable, and only the
most obvious differences are worthy of further
consideration.   It would be necessary to carry
out competition reactions to gain more meaningfull
information.

TABLE 20	Comparison of percentages of reaction of silanes with fluoro-olefins.			
CH$_2$:CHF	Silane	SiHCl$_3$	MeSiHCl$_2$	Me$_3$SiH	Me$_3$SiH/Hg
	ratio	2:1	5:1	2:1	6:1
	time	100	120	100	300
	% reaction	30	56	18	80
CHF:CF$_2$	Silane	SiHCl$_3$	MeSiHCl$_2$	Me$_3$SiH	Me$_3$SiH
	ratio	5:1	5:1	5.5:1	5:1
	time	100	100	140	12
	% reaction	93	80	100	20
CFH:CHCl	Silane ratio	SiHCl$_3$ 5:1	SiHCl$_3$ 10:1	Me$_3$SiH 5:1	Me$_3$SiH 10:1
	time	100	100	100	100
	% reaction	67	98	50	100

An attempt to understand the comparative reluctance of trimethylsilane to react with vinyl fluoride was made by a consideration of the individual steps involved in the addition reaction. This approach was of value for all the photochemical reactions studied.

The initiation step in these photochemical addition reactions is thought to occur by the absorption of ultraviolet light by the silane which results in homolysis of the weak covalent silicon-hydrogen bond.

The electronegativities of silicon and hydrogen on the Pauling scale are 1·8 and 2·1 respectively. This would give a silicon-hydrogen bond with a difference of electronegativity of 0·3, i.e., ca. 2% ionic character in the direction $\overset{+}{Si} - \overset{-}{H}$. It is interesting to note that this is the reverse of the direction of polarisation of the carbon-hydrogen bond, $\overset{-}{C} - \overset{+}{H}$.

The ready reactivity of chlorosilanes in the free radical addition reaction has previously been explained in terms of an inductive effect of chlorine atoms which decreases the polarity of the silicon-hydrogen bond. Similarly, it might be expected that the polarisability of the methyl groups in trimethylsilane would allow greater polarity of the silicon-hydrogen bond and hence would decrease the tendency towards homolysis. This is equivalent to saying that the initiation and displacement steps would be slightly more endothermic in alkyl silanes.

Whilst this argument is in agreement with the reduced reactivity of trimethylsilane towards vinyl fluoride and vinylidene fluoride, it is at the most only a slightly contributing factor in view of the ease of reaction of trimethylsilane with

trifluoroethylene, chlorotrifluoroethylene, and
tetrafluoroethylene.[172]

The influence of this type of effect
should be concentrated in the displacement step.
Differences in the initiation step which may be
accounted for on this basis should show only small
contributions to the overall observed reactivity
for a reaction of high kinetic chain length.

If the differences in reactivity were due
to such bond polarities as described above, it would
also be expected that significant differences in the
infra-red stretching frequencies and in the
stretching force constants for the silicon-hydrogen
bond would be observed. A general trend is
observed (table 21   ), which suggests that a small
difference in reactivity may be related to differences
in bond dissociation energies.

TABLE 21	Stretching force constants, and infra-red stretching frequencies for Si – H bonds.		
Silane	f, mdyne/ mole ref.	V, cm.$^{-1}$ ref.	$r(Si-H), A^{O}$. Ref.
Me$_3$SiH	—	2118 [159]	1.489±0.001 [159]
Me$_2$SiH$_2$	2.6 [154]	2142 [158]	1.483±0.005 [159]
SiH$_4$	2.77 [155]	2180 [158]	1.46 – 48 [148]
SiH$_3$Cl	2.66 [156]	2201 [158]	1.476 [159]
SiHCl$_3$	2.92 [157]	2257 [158]	—

f = stretching force constant.
V = frequency
r = inter-atomic radius

It is possible therefore that the slow reaction of trimethylsilane with vinyl fluoride is due to a) a slow addition step and b) an inefficient initiation step. Each of these explanations has to be consistent with the rapid reaction of trimethylsilane with the more heavily fluorinated olefins.

a) Most of the reactions dealt with in this work were carried out in the presence of a large excess of the silane. This was a qualitative attempt to ensure that the addition step was rate determining, as mentioned in the introduction, pp. 37 , and the discussion, pp. 59 .

$$\overset{\bullet}{S}iX_3 + \overset{\diagup}{\underset{\diagdown}{C}} = \overset{\diagup}{\underset{\diagdown}{C}} \longrightarrow \bullet\overset{|}{\underset{|}{C}}\bullet\overset{|}{\underset{|}{C}}\bullet SiX_3,$$ the addition step.
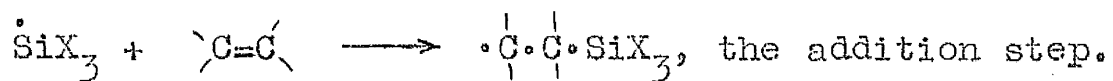
It has been concluded that free radicals are electrophilic in varying degrees by showing that the rates of addition of free radicals parallel the rates of ionic bromination, i.e., polarisable groups adjacent to the double bond release electrons into the π- system and facilitate attack by electrophilic radicals. The results on the orientation of free radical addition reactions obtained in this work, and elsewhere,[132] suggest that the replacement of groups with a strong $-I$ inductive effect (e.g., chlorine) by groups with a $+I$ effect (e.g., methyl-), will decrease the electrophilicity of the radical carrying those groups.

It may be argued, therefore, that the relatively more electrophilic trichlorosilyl radical is less discriminating in its reactions with olefins with which it can form a low energy transition state. This type of argument depends too much on conjecture and assumption in the present state of knowledge about free radical addition reactions and the properties of free radicals. It is, for example, clear that the trimethylsilyl radical is a much more efficient halogen abstractor than the trichlorosilyl radical; a

fact which cannot be satisfactorily explained.

(b)   It is possible that the low percentages
of reaction observed for trimethylsilane with vinyl
fluoride are related to a poor initiation step.   In
this case the ready reaction of trimethylsilane with
the more heavily fluorinated olefins is explained as
part of the initiation step.

An attempt to clarify this was made by
measuring the ultraviolet spectra of the reactants
as used in the photochemical reactions, i.e., on
samples shown to be pure by gas-liquid chromatography,
infra-red spectroscopy and molecular weight determination.
The results are, therefore, not quantitative as the
spectra were obtained on samples which were not ultra-
pure spectroscopically, i.e., no extra purifying
technique was used.   The absorption maxima and
extinction coefficients for the olefins and of
trichlorosilane and trimethylsilane are presented in
table 22 .   Tetrafluoroethylene and chlorotri-
fluoroethylene are included from published data[160] for
comparison with the olefins under investigation.

TABLE 22	Ultra-violet absorption spectra of some fluoro-olefins and silanes; not quantitative, (maxima only).	
Sample	absorption maxima cm^{-1}	Extinction coeficient,
$CH_2:CHF$	52,360 51,810	21 19
$CHCl:CHF$	52,900 52,360	655 658
$CF_2:CHF$ ref 160	52,360 --	995 --
$CF_2:CFCl$ ref 160	43,000 --	-- --
$CF_2:CF_2$	48,500 --	-- --
Me_3SiH	53,480 52,620	11.7 8.5
Cl_3SiH	51,010 35,720	6.0 4.9

The silica tubes used in the current work transmit light of shorter wavelength than 3000A$^{\circ}$, i.e., above 33,000 cm.$^{-1}$ and the lamps used produce intense irradiation at 39,400 cm.$^{-1}$ at 54,100 cm.$^{-1}$. It can be seen from the table that all the reactants are capable of absorbing ultra-violet light within the range transmitted by the reaction vessel and

that there will be some absorption of the
frequencies produced by the lamp.   It is
immediately apparent, however, that the silanes do
not differ greatly in their absorption (the peak
at 35,720 cm.$^{-1}$ is thought to be an impurity,
possibly of the type containing a $\equiv$Si - O - Si$\equiv$ bond).
Comparison of the data for the olefins indicates
that they absorb in the same region, but that the
extinction coefficient for vinyl fluoride is by
far the lowest of the olefins.

This allows speculation as follows.
The inital energy absorption is by the olefin with
transfer to either an excited singlet state or a
triplet state.   The former can cause the dissociation
of a molecule of the silane on collision.

$$\searrow C \overset{*}{=} C \nwarrow \; + \; SiHX_3 \longrightarrow \; \searrow C = C \nwarrow \; + \; \dot{S}iX_3 + \dot{H}$$
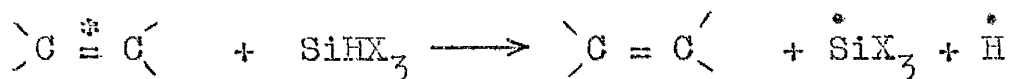
The latter can abstract hydrogen by reaction as a
free diradical.

$$- \dot{C} - \dot{C} - \; + \; SiHX_3 \longrightarrow -\dot{C} - \overset{|}{C} - H + \dot{S}iX_3$$
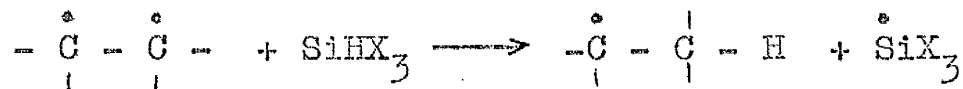
This approach does not necessarily rule out the
conventional description of the initiation by
dissociation of the silane.

$$SiHX_3 \; + \; h\nu \longrightarrow \dot{S}iX_3 + \dot{H}$$

It is possible, therefore, that the
initiation consists of two reactions, both
initiating the same chain reaction. It is not
possible to suggest how the actual initiation
is divided between these reactions, and it is not
possible, therefore, to compare reactivities of
various silanes as these may or may not be
completely masked by the olefin absorption. It
must also be pointed out that the absorption at a
particular wavelength and with a particular extinction
coefficient does not necessarily indicate that this
is associated with bond breaking relative to the
extinction coefficient.

Another approach to the problem of
initiation from the more practical point of view of
the separate irradiation of the reactants. The
reactants were separately irradiated for similar
periods, (table 23).

Compound	Time (hr).	Products.
$SiHCl_3$	90	H_2(1%); HCl (3%); recovered $SiHCl_3$ (97%)
Me_3SiH	100	H_2(1%); Me_3SiH recovered (98%).
CH_2:CHF	113	CH:CH(8%); CH_2:CHF recovered (90%).
CHCl:CHF	90	CH_2:CHF (2%); polymeric CHCl:CHF; CHCl:CHF recovered (16%)
CF_2:CHF	113	CHF:CF_2 recovered (84%); no other volatile product.

TABLE 23 The irradiation of silanes and olefins

It may be seen that all the reactants are capable of absorbing ultraviolet light and producing a reactive species, and that the percentage reaction of the olefins is higher than that of the silanes. This is probably because the olefins can still sustain a chain reaction once such a reaction has been initiated. The percentage reaction of trimethylsilane is much lower than the other compounds, and the use of mercury as a photosensitiser was investigated in an attempt to increase this figure.

Photosensitising agents are useful sources of radicals for compounds which do not absorb radiation of a convenient wavelength. Organic "dyes" may be used, but the most common agent used in conjunction with ultraviolet radiation from mercury resonance lamps is atomic mercury. The mercury may absorb energy and be promoted to a 6 $^3P_0$ state (i.e., a triplet state). Collision with another molecule brings about either electronic excitation (i) or dissociation (ii) in the quenching molecule.

$$Hg\ 6\ ^1S_0 \xrightarrow{\quad 2537A^{\circ} \quad} Hg\ 6\ ^3P_0 \quad \text{Excitation energy}$$
$$112\ kcal/g.atom.$$

$$Hg\ 6\ ^3P_0 + MH \longrightarrow MH^* + Hg\ 6\ ^1S_0 \qquad (i)$$

$$\longrightarrow \dot{M} + \dot{H} + Hg\ 6\ ^1S_0 \qquad (ii)$$
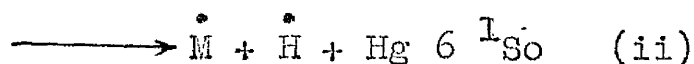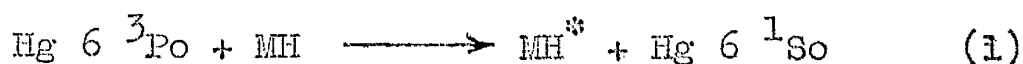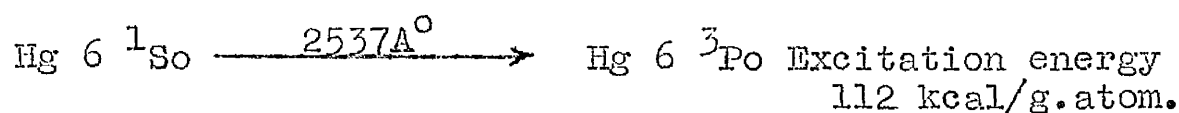
Quenching by silane (SiH_4) has been claimed to produce silyl radicals,[41] and quenching by ethylene resulted in the formation of cyclo-butanes, hydrogen, acetylene, and higher olefins.[61]

The possibility of photosensitisation by mercury in all the reactions carried out in this work can not be excluded because of the use of mercury manometers for pressure measurements. The extent

of this is probably quite low in view of the changes
wrought by the introduction of bulk mercury. For
example the production of vinyl fluoride ($\sim$96%) in
the irradiation of 1-chloro-2-fluoroethylene with
trimethylsilane in the presence of mercury as compared
to the formation of the 1:1 adduct, the 1:1 reduced
adduct, and vinyl fluoride ($\sim$4%) in the absence of
mercury. Irradiations of trimethylsilane in the
presence of mercury and in the absence of purposely
introduced mercury were carried out to investigate
this, (table 24)

TABLE 24		The effect of mercury on the photodissociation of trimethylsilane
Reactant	Time, hr.	Products.
Me_3SiH	100	H_2(1%), Me_3Si recovered (98%)
Me_3SiH/Hg	90	H_2(12%), Me_3SiH recovered (80%)

These results indicate the effectiveness
of mercury in promoting the photodissociation of
trimethylsilane.

It is interesting to note that the irradiation characteristics of the olefins are all different. This again suggests that it is not possible to draw any worthwhile conclusions from the varying percentages of reaction in the addition reactions. These reactions of the olefins were carried out to determine whether they were capable of initiating the reaction and consequently the mechanism of the photodissociation was not further investigated.

The hydrolysis of substituted alkyl silicon compounds.

Unsubstituted alkyl groups are not easily cleaved from silicon by nucleophilic reagents. There appears to be no example of such cleavage involving tetra-alkylsilanes. Cleavage of silicon-alkyl bonds by electrophilic reagents is more common.[162] The presence of almost any hetero-atom in an alkyl side-chain seems to increase the ease of cleavage by nucleophiles. Thus the hetero atom (which is generally more electronegative than hydrogen) increases the tendency of the alkyl group to separate with the electrons of the silicon-carbon bond. The low electronegativity of silicon and the ease with which it can increase its coordination number facilitate the approach of the nucleophile.

α-Halogenated alkyl groups attached to silicon are susceptible to nucleophilic attack, the ease which is dependent on the degree of substitution, i.e., $CCl_3 > CCl_2H > CClH_2$;[163,164]

e.g.

$$CCl_3 \cdot Si(OEt)_3 \xrightarrow{\text{NaOEt}} CHCl_3 + Si(OEt)_4 \quad \text{Ref}(165)$$

$$CF_3 \cdot SiCl_3 \xrightarrow{\text{OH}^-} CF_3H + SiO_2 \quad \text{Ref}(166).$$
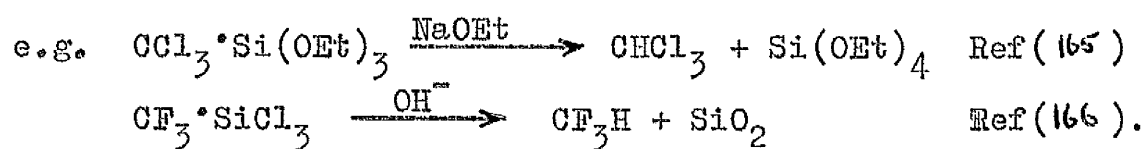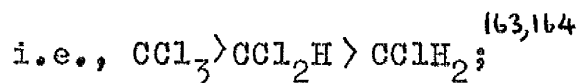
The mechanism of these reactions is thought to involve the displacement of a carbanion.

$$^-OH \quad \overset{}{\underset{}{\text{Si}}} - CF_3 \longrightarrow {}^-CF_3 + SiO_2$$

$$CF_3^- + H_2O \longrightarrow CF_3H + OH^-$$
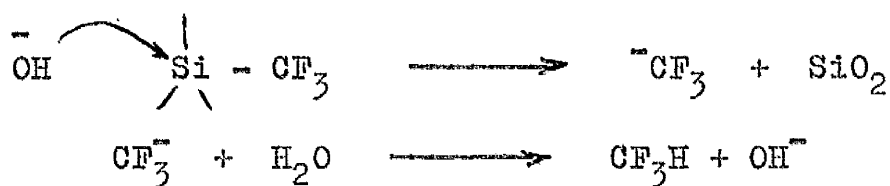
β-Chlorinated alkyl groups are much more easily cleaved from the silicon atom than their α-chlorinated counterparts. For example, the silicon carbon bond in α-chloroethyltrichlorosilane is stable in 40% ethanolic potassium hydroxide solution at 80° whereas β-chloroethyltrichlorosilane is cleaved by dilute aqueous sodium hydroxide solution.[142]

$$CH_3 \cdot CHCl \cdot SiCl_3 + KOH \longrightarrow (CH_3 \cdot CHCl \cdot SiO_{1.5})_n$$

$$CH_2Cl \cdot CH_2 \cdot SiCl_3 + NaOH \longrightarrow CH_2:CH_2 + SiO_2$$

A similar difference in stability is apparent in the action of Grignard reagents. Whereas α-chloroethyltrichlorosilane is readily methylated, β-chloroethyltrichlorosilane is cleaved to produce ethylene.[141]

The process of cleavage is thought to occur via a concerted elimination analogous to the E_2 elimination reaction of alkyl halides,[141]

$$^-OH \quad \text{Si-CH}_2 \cdot CH_2 - Cl \longrightarrow Si \cdot OH + CH_2:CH_2 + Cl^-$$

$$^-OH \quad H - CH_2 \cdot CH_2 - Cl \longrightarrow HOH + CH_2:CH_2 + Cl .$$
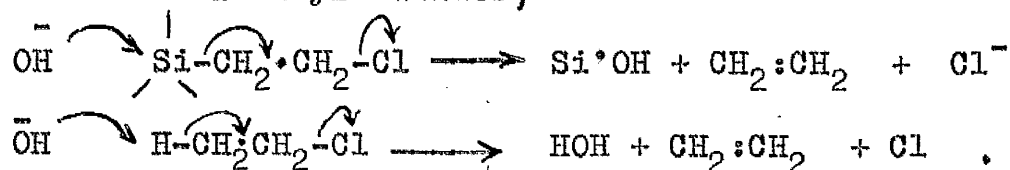
The process is evidently facilitated in the case of
silicon compounds by the lower electronegativity of silicon
compared to carbon (E.N., Si 1.8; C, 2.5; H, 2.1;) and its
ability to increase its coordinate number. The attack
occurs exclusively at the silicon atom, and not at the
α-hydrogen atoms as depicted below.

$$-\overset{|}{\underset{/}{Si}} - \overset{|}{\underset{\underset{OH^-}{H}}{CH}} CH_2 \cdot Cl \longrightarrow -\overset{|}{\underset{/}{Si}} \cdot CH = CH_2 + H_2O + Cl^-$$
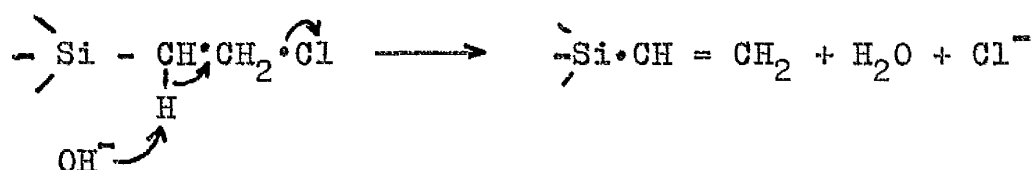
Many β-chlorinated compounds have been shown
to undergo this elimination.   In all cases the elimination
is so rapid that aqueous hydrolysis and titration of the
β-chlorine atom as well as of the silicon-bonded chlorine
atoms is possible.[167]   Because of this rapidity, kinetic
studies of the hydrolysis have not yet been carried out.

γ-Halogenated alkyl groups may be cleaved
from silicon with the formation of cyclopropane rings, or
dehydrohalogenation may occur without cleavage:[168]

$$OH^- \rightarrow \overset{Cl}{\underset{Cl \quad Cl}{\overset{|}{\underset{/ \backslash}{Si}}}} - CH_2 \cdot CH_2 \cdot CH_2 - Cl \longrightarrow \overset{CH_2}{\underset{CH_2 - CH_2}{/ \backslash}} + SiO_2 + Cl^- \quad Ref(168)$$

$$\overset{Me}{\underset{Me \quad Me}{\overset{|}{\underset{/ \backslash}{Si}}}} - CH_2 \cdot CH_2 \cdot CH_2 - Cl \xrightarrow{OH^-} Me_3Si \cdot CH_2 \cdot CH:CH_2 + HBr \quad ref(168)$$
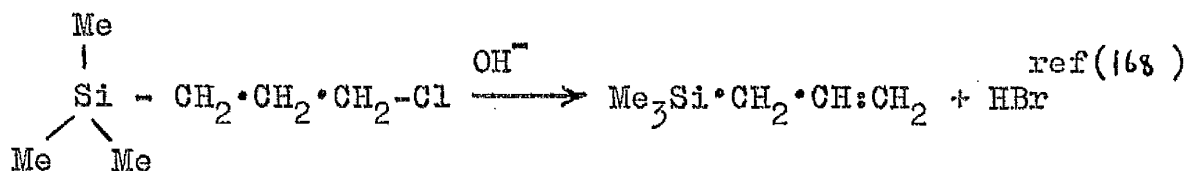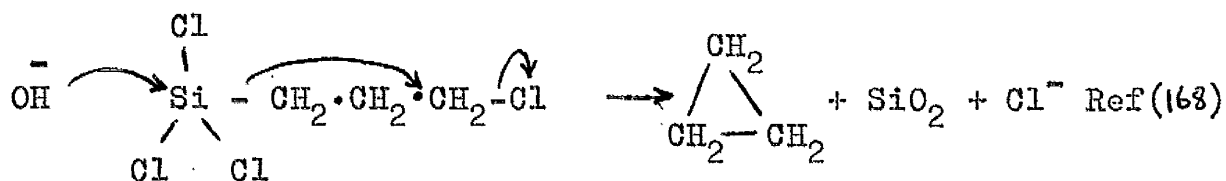
The compounds dealt with in this dissertation are all substituted ethyl groups, and γ-substituted compounds need by considered no further.

The substituted ethyl groups dealt with contain both c͟h͟lorine and fluorine in the 1-and 2-positions relative to silicon. A consideration of data from cleavage of other substituted ethyl groups, along with the observations recorded in this thesis allows certain general considerations to be drawn. β-Bromine and β-iodine atoms are eliminated in a similar manner to β-chlorine atoms, [169] and it is found that β-bromine atoms are removed in preference to β-chlorine atoms, e.g.,

$$CHBrCl \cdot CBrCl \cdot SiCl_3 \xrightarrow{OH^-} CBrCl{:}CClH. \qquad Ref. (170)$$
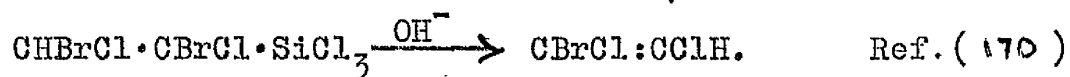
It has been suggested[171] that elimination of fluorine would not occur because of the strength of the C - F bond, and this suggestion was probably based on the observation that 1,1,2,2,tetrafluoroethyltrichlorosilane reacted with sodium hydroxide solution to give the saturated alkane.[60]

$$CF_2H \cdot CF_2 \cdot SiCl_3 \xrightarrow{OH^-} CF_2H \cdot CF_2H.$$

It is however important to note in this context that even a β-chlorine substituent in a similar compound, e.g., 2-chloro-1,1,2,2-tetrafluoroethyltrichlorosilane,

$CF_2Cl \cdot CF_2 \cdot SiCl_3$, is only removed by β-elimination
to an extent of 9%.[60]

$$CF_2Cl \cdot CF_2 \cdot SiCl_3 \xrightarrow{\ OH^-\ } CF_2H \cdot CF_2Cl \qquad (91\%)$$
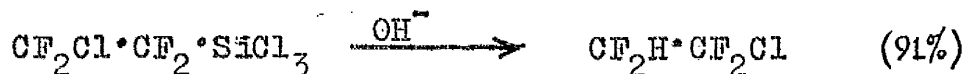
It has been found during this work that the
replacement of chlorine by fluorine in the monosubstituted
ethylsilanes leads only to the necessity of a stronger
nucleophile for β-elimination to occur.   Thus, both
β-chloro- and β-fluoro-ethylsilanes are readily cleaved
by hydroxide ions to give ethylene,   but the former is also
cleaved by water, whereas the latter is stable to water.
Both α-substituted compounds behave similarly, they are
not cleaved by aqueous solutions of base:

$$CH_2Cl \cdot CH_2 \cdot SiCl_3 \xrightarrow{\ NaOH\ } CH_2 : CH_2 \qquad (100\%)$$

$$CH_2F \cdot CH_2 \cdot SiCl_3 \xrightarrow{\ NaOH\ } CH_2 : CH_2 \qquad (100\%)$$

$$CH_3 \cdot CHX \cdot SiCl_3 \xrightarrow{\ NaOH\ } (CH_3 \cdot CHX \cdot Si(O)_{1.5})_n$$
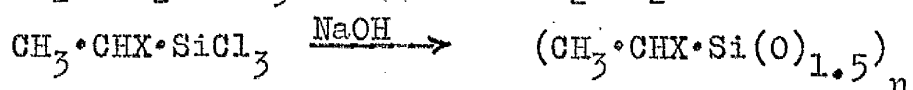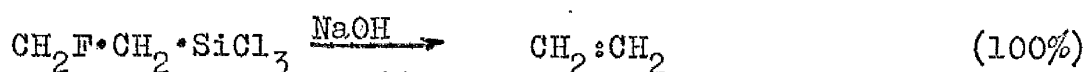
If both chlorine and fluorine are present hydrolysis takes
place similarly, again with elimination of the atom β- to
silicon, irrespective of whether it is chlorine or fluorine.
Again it is observed that aqueous sodium hydroxide is
necessary for the elimination of β-fluorine, whereas
β-chlorine is eliminated by water.

$$CH_2F \cdot CHCl \cdot SiCl_3 \xrightarrow{NaOH} CH_2:CHCl \qquad (100\%)$$

$$CH_2Cl \cdot CHF \cdot SiCl_3 \xrightarrow{H_2O} CH_2:CHF \qquad (100\%)$$
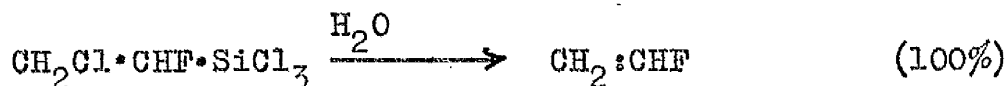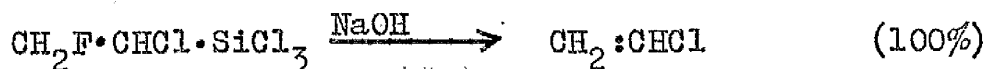
Hydrolysis of the adducts of silanes to trifluoroethylene gave the alkane and the olefins in varying percentages. It appears therefore that these adducts are possibly reacting by two mechanisms, corresponding to the two types discussed above. The various mechanisms possible will now be discussed to see which mechanism best fits the observed facts, and to determine the extent of the value of hydrolysis as a diagnostic method.

The various mechanisms are:

I) Carbanion displacement and alkane formation.

II) Carbanion displacement with elimination.

(III) Alkane formation as in (i) followed by E_2 elimination.

IV) Concerted β-elimination.

V) Dehydrohalogenation followed by carbanion displacement.

1) <u>Carbanion displacement and alkane formation.</u>
This is equivalent to an $S_{N}2$ reaction at the silicon atom in which the slow step is the formation of the carbanion. Because silicon can also have coordination numbers 5 and 6, bond formation and bond breakage need not be simultaneous.

$$\overset{\ominus}{OH} \overset{\frown}{\quad} \underset{|}{\overset{|}{Si}} - \underset{|}{\overset{|}{C}} - \underset{|}{\overset{|}{C}} - X \longrightarrow \quad - \underset{|}{\overset{|}{C}} = \underset{|}{\overset{|}{C}} - X$$

$$- \underset{|}{\overset{\ominus}{C}} - \underset{|}{\overset{|}{C}} - X + H_2O \longrightarrow H - \underset{|}{\overset{|}{C}} - \underset{|}{\overset{|}{C}} - X.$$
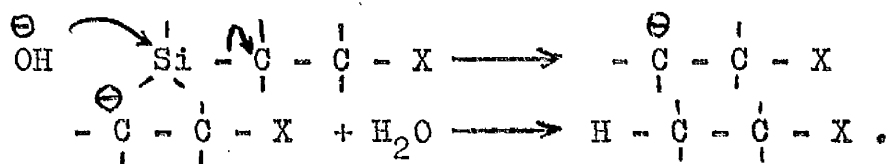
Alkanes were formed when the ethyl group carried three or four fluorine atoms. This observation has been made in this work and in other reported reactions.[60,146]

$$Cl_3Si \cdot CF_2 \cdot CF_2 \cdot H \xrightarrow{\quad OH^- \quad} HCF_2 \cdot CF_2H, \quad 100\%$$

$$Cl_3Si \cdot CF_2 \cdot CF_2Cl \xrightarrow{\quad OH^- \quad} HCF_2 \cdot CF_2Cl, \quad 91\%$$

$$Cl_3Si \cdot CF_2 \cdot CH_2F \xrightarrow{\quad OH^- \quad} HCF_2 \cdot CH_2F, \quad 99\%$$
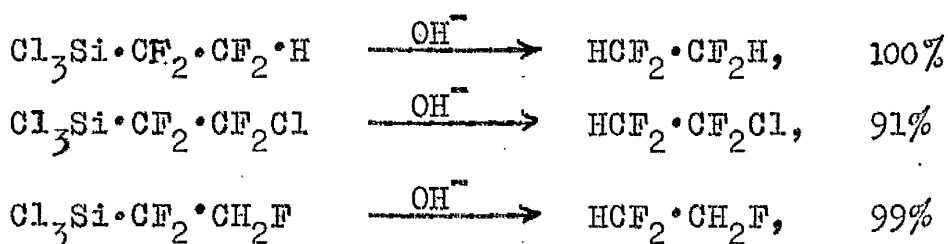
The compounds containing less heavily fluorinated ethyl groups gave 100% olefin formation[172]

$$Cl_3Si \cdot CH_2 \cdot CHF_2 \longrightarrow CH_2:CHF \quad 100\%$$

$$Cl_3Si \cdot CH_2 \cdot CH_2F \longrightarrow CH_2:CH_2 \quad 100\%$$
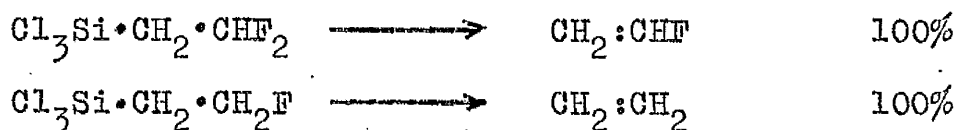
The observation that the isomers of trifluoroethyltrichloro-silanes give different percentages of olefin formation suggests that the presence of the α-fluorine atoms may play some part in determining the percentage olefin formation as against alkane formation, i.e., two α-fluorine atoms appear to favour alkane formation.

The presence of fluorine atoms on the α-carbon may a) facilitate nucleophilic attack on silicon or b) hinder or inhibit the electron shift which leads to elimination of the β-halogen atom.

$$\text{OH}^- \quad \overset{|}{\underset{/\backslash}{\text{Si}}} \longrightarrow \overset{|}{\underset{|}{\text{C}}} \longrightarrow \overset{|}{\underset{|}{\text{C}}} \longrightarrow \text{X}$$
$$\downarrow$$
$$\text{F}$$
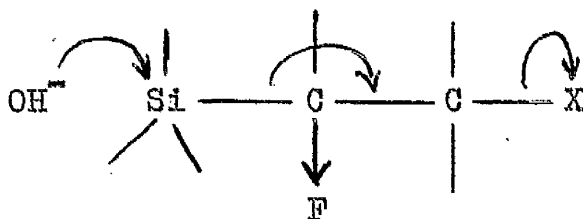
It is also of interest to note that the percentage alkane formation decreases $_\wedge^{as}$ silicon-chlorine bonds in the compound hydrolysed are replaced by silicon-methyl bonds. As silicon-halogen bonds are readily susceptible to nucleophilic attack this apparent order may be misleading, i.e., the comparison should be between Si - O - and Si - Me bonds.

The remaining reaction schemes are concerned with the olefin formation.

II) <u>Carbanion displacement with elimination.</u> This is equivalent to carbanion formation as in (I) followed by a unimolecular elimination from the conjugate base, as discussed by Ingold, $(E_1 cB)$.

$$- \overset{-}{\underset{|}{\text{C}}} - \overset{|}{\underset{|}{\text{C}}} - \text{X} \longrightarrow \hspace{-0.3em} \text{>} \text{C} = \text{C} \text{<} + \text{X}^-$$

Investigations of the corresponding reactions of organic halides (giving the same type of carbanion) by means of isotopic exchange methods suggest that the $E_1 cB$ mechanism is improbable. From the sparse information available it is thought that elimination from β -halogenocarbonyl compounds may involve this mechanism.

$$-\overset{|}{\underset{X}{C}}-\overset{\overset{S-}{\overset{O}{\|}}}{\underset{\underset{S+}{H}}{C}}-\overset{O}{\underset{}{\|}}{C}-\quad\xrightarrow{\;OH^{\ominus}\;}\quad -\overset{|}{C}-\overset{|}{C}-\overset{O}{\underset{}{\|}}{C}-\quad\longrightarrow\quad -C=\overset{|}{C}-\overset{O}{\underset{}{\|}}{C}-\;+\;X^{\ominus}$$
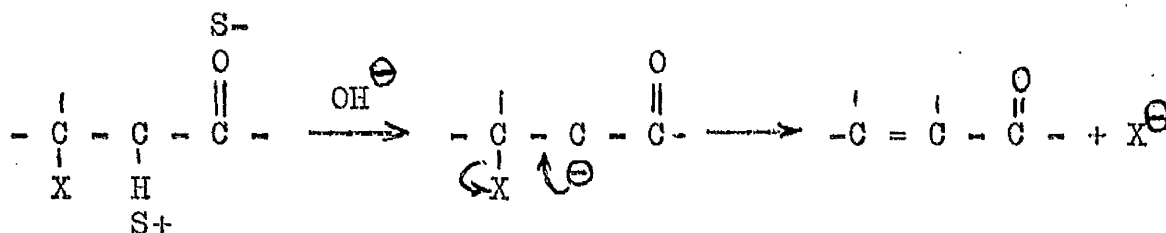
If this was the mechanism of olefin formation
from fluoroethylsilanes, alkane formation and olefin
formation should take place from the same carbanion. As
compounds with different adjacent groups attached to
silicon but the same fluoroalkyl group would hydrolyse
to give the same carbanion which would then react to give
the alkane or eliminate an ion to give the olefin the
effect of varying the adjacent groups on the percentage
alkane formation would not be expected.

$$CHF_2 \cdot CHF \cdot SiCl_3 \searrow$$
$$\xrightarrow{\;OH^-\;} CHF_2 \cdot \overset{-}{CHF} \longrightarrow \begin{cases} CHF_2 \cdot CH_2F \\ CHF:CHF + F^- \end{cases}$$
$$CHF_2 \cdot CHF \cdot SiMe_3 \nearrow$$
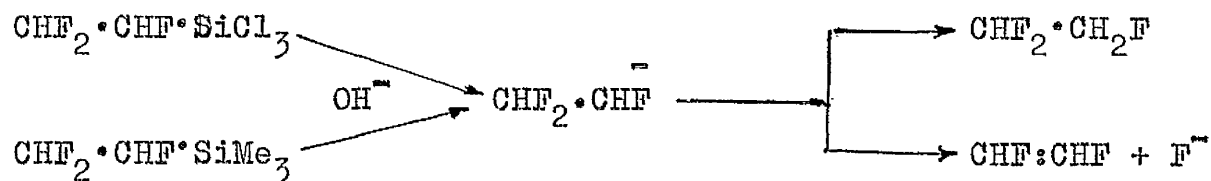
i.e., The same percentage of alkane and olefin formation
would be expected. As this was not so it is probable
that this mechanism does not apply.

III) <u>Alkane formation as in (I) followed by</u>
<u>E₂ elimination</u>

$$OH^- + H-\overset{|}{C}-\overset{|}{C}-X \longrightarrow \;\overset{\diagdown}{\diagup}C=C\overset{\diagup}{\diagdown}\; + H_2O + X^-$$

This mechanism was directly tested during the course of
the investigation by subjecting samples of the expected

alkane to attack by hydroxyl groups under the same
conditions as those used for the hydrolysis.   In the
case of ethyl fluoride, 1-chloro-2-fluoroethane, and
1,1,2-trifluoroethane no olefin formation was observed.
This mechanism was consequently discarded.

IV)   Concerted β-elimination.

This is visualised as a synchronous process
occurring simultaneously with the alkane formation.   The
machanism fits all the observed facts of loss of the
β-halogen atom during olefin elimination.   The varying
degress of olefin elimination can be visualised in terms
of the α-fluorine atom effect and the adjacent group effect.
It is possible that the first effect, as pointed out in (I),
reduces olefin formation by an inductive effect away from
the α-carbon and so impedes the electron shift to the
β-halogen atom, whereas the second effect assists this
shift by an inductive effect towards the silicon and the
carbon atom.

i.e.

$$\overset{-}{OH} \curvearrowright Si - \overset{\overset{\displaystyle F}{\uparrow}}{\underset{\underset{\displaystyle F}{\downarrow}}{C}} - C - X \longrightarrow CF_2H - CX$$

$$\overset{-}{OH} \curvearrowright \overset{+I}{Si} - \overset{+I}{C} - \overset{+I}{C} - X \longrightarrow \diagup C = C \diagdown .$$
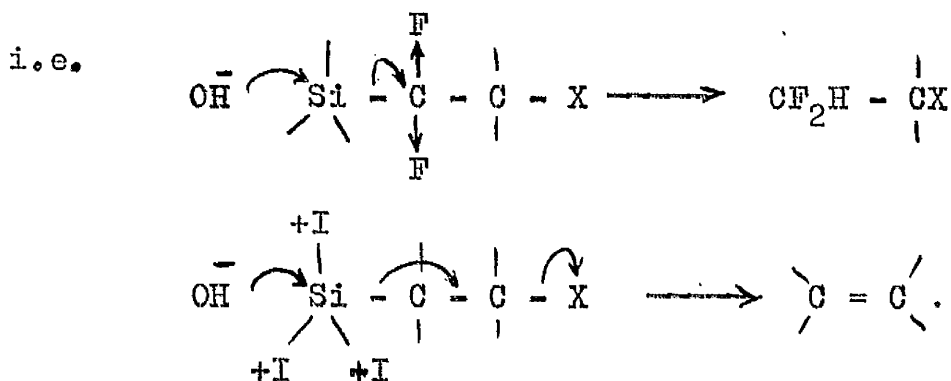
V) Dehydrohalogenation followed by carbanion displacement.

This scheme involves the formation of a vinyl silane by attack at either α or β hydrogen atoms.

$$OH^- \quad H - \underset{\underset{H}{|}}{\overset{\overset{\diagdown | \diagup}{Si}}{C}} - CH_2 - X \longrightarrow \underset{H}{\overset{\diagdown | \diagup}{Si}} C = CH_2 + H_2O + X^-$$

$$OH^- \quad H - CH_2 - \underset{\overset{\diagdown | \diagup}{Si}}{CH} - X \longrightarrow \underset{H}{\overset{\diagdown | \diagup}{Si}} C = CH_2 + H_2O + X^- \quad (\beta\text{- elimination})$$

$$(\alpha\text{- elimination}).$$

$$\overset{|}{\underset{\diagup \diagdown}{Si}} - CH = CH_2 \quad \xrightarrow{OH^-} \quad CH_2 = CH_2$$
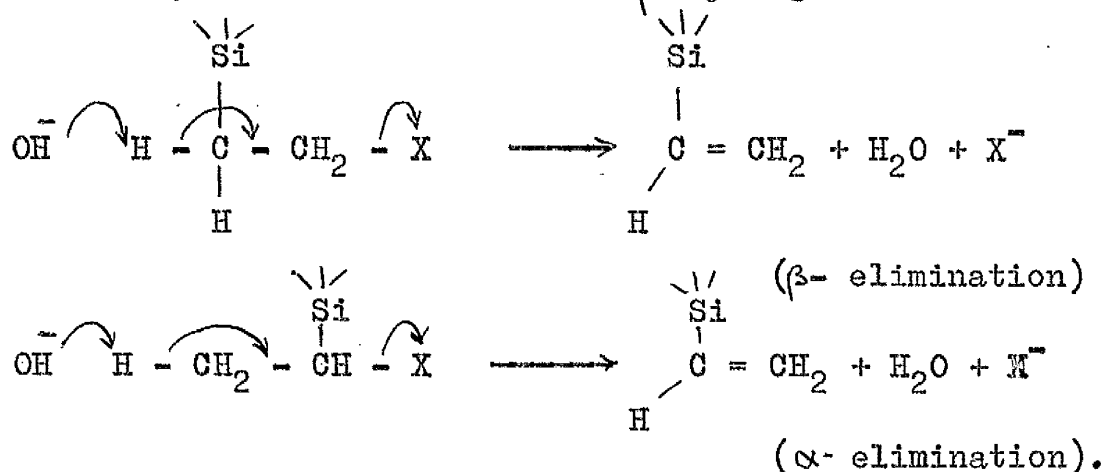
Breakdown of vinyl silanes has been shown to occur at 170° in 30% aqueous sodium hydroxide, [173] but fluorovinyl silicon compounds hydrolyse readily. The absence of vinyl compounds in the hydrolysis products is not, therefore, an indication of the absence of this mechanism.

The necessity of attack at the more electro-negative hydrogen instead of at silicon suggests that this mechanism is improbable, but it can not be completely discounted.

From the consideration of the extent to which the observed facts are consistent with the varying possible
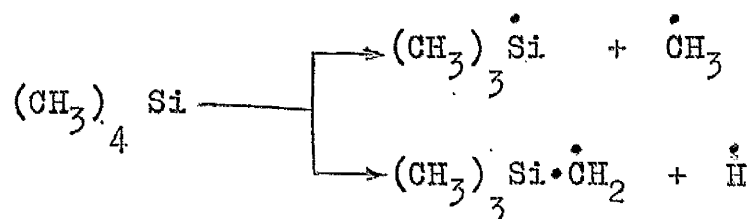
mechanisms it is clear that the most probable

mechanisms are (I) and (IV), i.e., carbanion

formation for the alkane and concerted β-elimination

for the olefin.   It is possible to generalise this

to the extent that β-chlorine is more easily eliminated

than β-fluorine;   and that alkane formation is

favoured by the presence of electron withdrawing groups

on both the α-carbon atom and the silicon atom.   The

observation that the degree of olefin formation increases

as the concentration of the nucleophile increases is in

agreement with these proposals.   It would be illuminating

to study the variation in the alkane itself, and not

only its concentration, but this was beyond the scope of

this work.   It was apparent, however, during reactions of

fluoroalkyl chlorosilanes with methyl magnesium iodide,

and with lithium aluminium hydride, that considerable

β-elimination was taking place even at reduced

temperatures (0°).   Attempts to carry out this type of

reaction with the exclusion of β-elimination were made by

reacting 1,1,2-trifluoroethyltrimethylsilane,

$CH_2F \cdot CF_2 \cdot SiMe_3$, with water in the presence of aluminium

amalgam.   No silicon-carbon cleavage was observed.   It

is interesting to note that both α-chloro- and α-fluoro-

ethyl silanes are not cleaved under the mild conditions

which effect β-elimination and alkane formation.
It is not possible to rationalise this with the
observed alkane formations, i.e., one could argue
that in the absence of a β-group the alkane should be
formed as with trichloromethyl and trifluoromethyl
silanes. This may however be merely a question of
using more extreme conditions.

From the above discussion of the hydrolysis
mechanism it is apparent that the method is of no
diagnostic value when alkane formation occurs. In
the event of exclusive olefin formation, however, it is
possible to deduce the structures and ratios of possible
isomers from the various olefins, provided that
β-elimination is assumed. Although it has not been
rigorously demonstrated that β-elimination is the
mechanism of hydrolysis it is felt by the author that
the most of the experimental evidence is in agreement
with this mechanism.

Pyrolysis of substituted alkyl silicon compounds.

The thermal decomposition of tetraalkylsilanes occurs at 580 - 700°,[174] and kinetic studies have shown that homogeneous unimolecular decomposition proceeds at pressure down to 10 cm. of mercury. It has been shown that both silicon-carbon and carbon-hydrogen bond fission is proceeding, and that these reactions are followed by further free radical reactions to give complex mixtures of products.[175]

$$(CH_3)_4 Si \longrightarrow \begin{cases} (CH_3)_3 \overset{\bullet}{Si} + \overset{\bullet}{CH_3} \\ (CH_3)_3 Si \cdot \overset{\bullet}{CH_2} + \overset{\bullet}{H} \end{cases}$$

Tetraethylsilane decomposes at slightly lower temperatures (540-600°) than tetramethylsilane, (660-720°) but the introduction of a chlorine atom β- to the silicon in tetraethylsilane causes a marked decrease in stability;[176] e.g.,

$$Et_3Si \cdot CH_2 \cdot CH_2Cl \xrightarrow{ca. \ 80°} CH_2:CH_2 + Et_3SiCl$$

However; the analogous compound 2-chloroethyltrichlorosilane, $CH_2Cl \cdot CH_2 \cdot SiCl_3$, is stable up to at least 400°, but slow decomposition occurs at about 550°.

Complete decomposition of 2-chloroethyltrichlorosilane at 610° indicates the possibility of two simultaneous mechanisms.[170]

$$CH_2Cl \cdot CH_2 \cdot SiCl_3 \xrightarrow{610^o} CH_2 : CH_2, SiCl_4, CH_2 : CH \cdot SiCl_3.$$
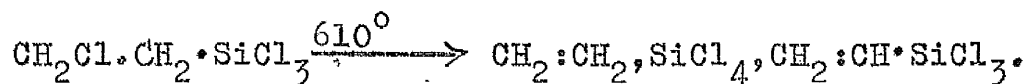
Vinyltrichlorosilane is stable at the temperature of
the decomposition.   This indicates that ethylene and
vinyltrichlorosilane are formed by different processes.
Kinetic studies[177] indicated that the process is a
unimolecular first order reaction and not a free radical
reaction.   The data are consistent with the formation of
4-centre transition states similar to that proposed for
the decomposition of secondary and tertiary alkyl bromides.[178]

$$
\begin{array}{ccc}
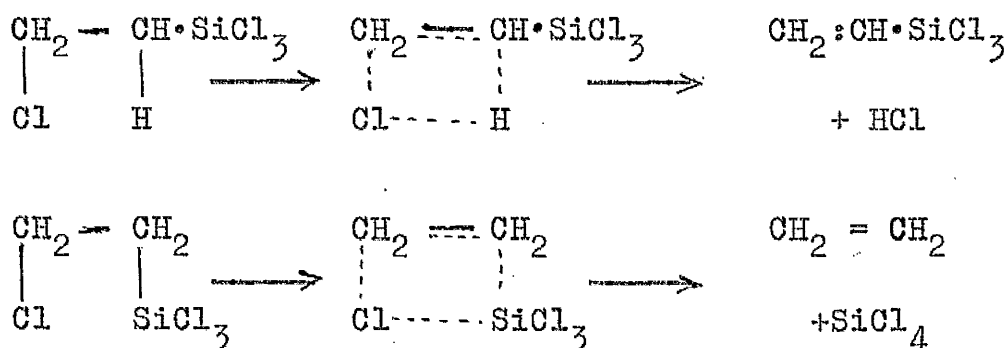CH_2 - CH \cdot SiCl_3 & CH_2 --- CH \cdot SiCl_3 & CH_2 : CH \cdot SiCl_3 \\
| \quad\quad | \longrightarrow & \vdots \quad\quad \vdots \longrightarrow & \\
Cl \quad\quad H & Cl ----- H & + HCl
\end{array}
$$

$$
\begin{array}{ccc}
CH_2 - CH_2 & CH_2 --- CH_2 & CH_2 = CH_2 \\
| \quad\quad | \longrightarrow & \vdots \quad\quad \vdots \longrightarrow & \\
Cl \quad\quad SiCl_3 & Cl ----- SiCl_3 & + SiCl_4
\end{array}
$$

It was originally thought that the introduction of
fluorine atoms into the organic side chain might confer
the stability of fluorocarbons on the fluoroalkylsilicon
compound.   This has not been generally found to be the
case, for although γ-trifluoroalkylsiloxanes show good
thermal stability (decomposition occurs only above 400°),
α- or β- fluoroalkylsiloxanes decompose above 200°,[179]
e.g., $CHF_2 \cdot CH_2 \cdot SiCl_3 \longrightarrow CHF : CH_2 + SiFCl_3$

The driving force for the decomposition reaction is probably the change in enthalpy which accompanies the reaction. In the example shown a carbon-fluorine and a carbon-silicon bond are broken (this requires the input of 76 + 116 = 192 kcal/mole of energy), while a silicon-fluorine and a carbon-carbon π-bond are formed (this results in the evolution of 64 + 135 = 119 kcal/mole). Hence there is a net evolution of 10 kcal/mole of energy.

The reaction analogous to the formation of vinyl silanes from β-chloroalkylsilanes has not been observed with fluoroalkylsilanes.

$$CH_2F \cdot CH_2 \cdot SiCl_3 \longrightarrow\!\!\!\!\!\times\ CH_2:CH \cdot SiCl_3$$

A typical pyrolytic reaction of a fluoroalkylsilane is:[60]

$$CF_2H \cdot CF_2 \cdot SiCl_3 \xrightarrow{220\text{-}5^\circ} CF_2:CFH + SiCl_3F$$
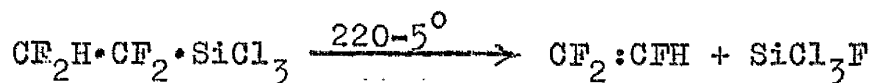
In this example trifluoroethylene can be formed by two possible elimination reactions. The first of these is a β-elimination directly analogous to that described above for the chloroalkyl compound:

$$
\begin{array}{ccc}
CHF & \text{---} & CF_2 \\
| & \nwarrow & | \\
F & \longrightarrow & SiCl_3
\end{array}
\qquad \longrightarrow \qquad CHF:CF_2 + SiCl_3F
$$
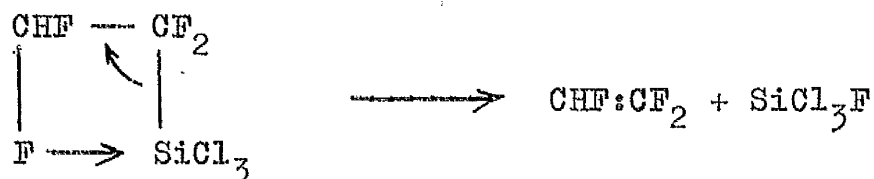
The alternative mechanism involves an α-fluorine elimination to give a carbene and a silicon halide. The carbene is able to rearrange by hydrogen or fluorine migration to give trifluoroethylene.

$$CHF_2 \cdot CF - SiCl_3 \xrightarrow{\Delta} CHF_2 \cdot \ddot{C}F + SiCl_3F$$

$$CHF_2 \cdot \ddot{C}F \xrightarrow{\text{H or F migration}} CHF:CF_2 \quad .$$
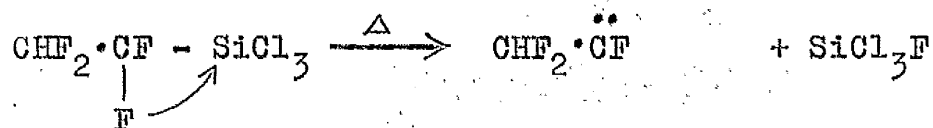
Experimental evidence suggests that α-elimination is the basic step in compounds containing two α-fluorine atoms.[146] The presence of a carbene intermediate has been demonstrated by the formation of a cyclopropane in the presence of isobutene,[146]

e.g.,
$$(CH_3)_2 C:CH_2 + CH_2F \cdot \ddot{C}F \longrightarrow (CH_3)_2 C \underset{CF}{\overset{CH_2}{\diagdown \diagup}}$$
$$\underset{CH_2F}{\overset{|}{CF}}$$
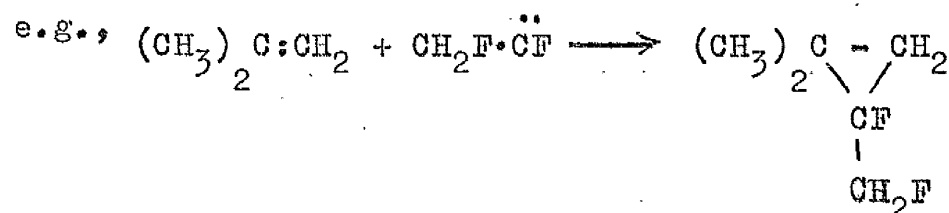
Other workers have shown that the thermal decomposition is a unimolecular first order process.[172,180]

It has been found that olefins which are more highly chlorinated than the original side chain are sometimes formed during the pyrolysis of substituted ethyltrichloro-silanes;[146]

e.g. $CHF_2 \cdot CF_2 \cdot SiCl_3 \xrightarrow[\text{16 hr.}]{225^\circ} CHF:CF_2, CHCl:CF_2, CHF:CCl_2$
$$\quad\quad 29\% \quad\quad 21\% \quad\quad 22\%$$
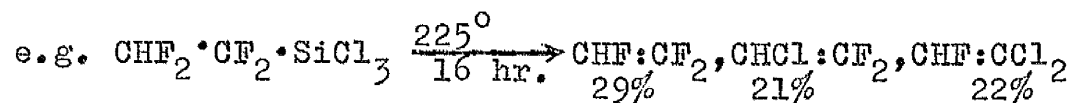
The reaction of trichlorofluorosilane with trifluoroethylene to give chlorotrifluoroethylene and dichlorofluorosilane is energetically feasible, but it has been shown not to occur under the conditions of the pyrolyses.[146]

$$SiCl_3F + CHF{:}CF_2 \xrightarrow{\hspace{1cm}} \big\backslash\!\big/ \; CF_2{:}CFCl + SiHCl_2F$$
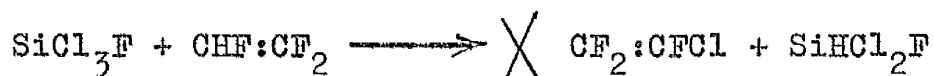
This evidence indicates that the chlorinated olefins do not result from a secondary reaction of this type.

An intensive study of the pyrolyses of fluoroalkylsilicon compounds[146] has shown that the formation of the more heavily chlorinated olefins occurs simultaneously with the α-elimination mechanism. The possible mechanisms are described below.

i) <u>Carbene formation followed by an insertion reaction.</u> Insertion of the carbene into a silicon-chlorine bond could give a new substituted ethyl group

e.g., $CH_2F{\cdot}\overset{\bullet\bullet}{C}F + SiFCl_3 \xrightarrow{\hspace{1cm}} CH_2F{\cdot}CFCl{\cdot}SiFCl_2,$

e.g., $CHF_2{\cdot}\overset{\bullet\bullet}{C}F + SiFCl_3 \xrightarrow{\hspace{1cm}} CHF_2{\cdot}CFCl{\cdot}SiFCl_2$
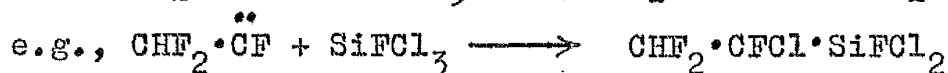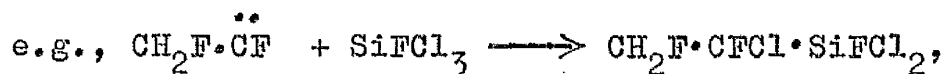
A similar insertion reaction with an undissociated molecule of the original silicon compound would produce a new compound, which could breakdown in the same way as the insertion product from the tetrahalosilane.

$$CH_2F{\cdot}\overset{\bullet\bullet}{C}F + CH_2F{\cdot}CF_2{\cdot}SiCl_3 \xrightarrow{\hspace{1cm}} \begin{array}{c} CH_2F{\cdot}CF_2 \\ \diagdown \\ \diagup \\ CH_2F{\cdot}CFCl \end{array}\!\!SiCl_2$$
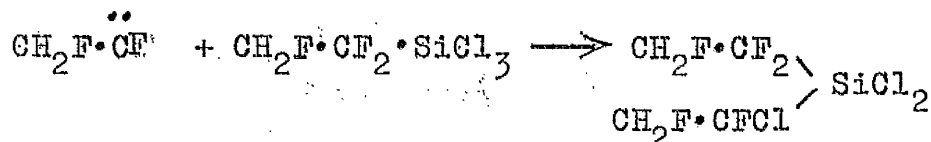
The postulated reactions are similar to the observed reactions

of methylene with carbon-halogen,[181] and with silicon-halogen bonds;[182]

e.g., $SiCl_4 + \overset{\bullet\bullet}{C}H_2 \longrightarrow Cl_3Si \cdot CH_2Cl$
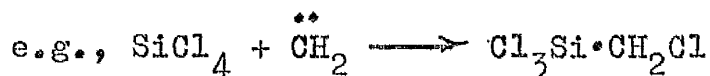
The new compounds formed in this way would contain α-carbon-chlorine bonds. They could decompose by α-fluorine elimination to give an olefin containing an extra chlorine atom;

e.g., $CH_2F \cdot CFCl \cdot SiFCl_2 \longrightarrow CH_2F \cdot \overset{\bullet\bullet}{C}Cl + SiF_2Cl_2$

$CH_2F \cdot \overset{\bullet\bullet}{C}Cl \xrightarrow{\text{H migration}} CHF:CHCl$
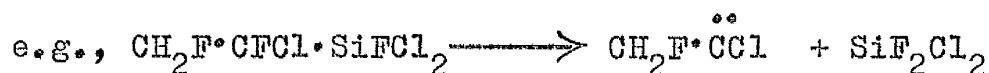
The new carbene, $CH_2F \cdot \overset{\bullet\bullet}{C}Cl$, could also repeat the insertion reaction with dichlorodifluorosilane to give a product which could decompose by a process of β-elimination to give a third olefin.

$CH_2F \cdot \overset{\bullet\bullet}{C}Cl + SiF_2Cl_2 \longrightarrow CH_2F \cdot CCl_2 \cdot SiF_2Cl$

$CH_2F \cdot CCl_2 \cdot SiClF_2 \xrightarrow[\beta\text{ elimination}]{} CH_2:CCl_2 + SiF_3Cl$
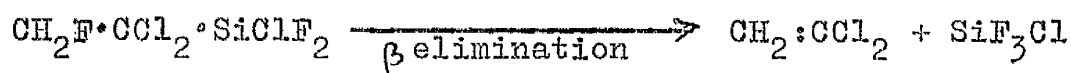
That the insertion process is improbable has been shown by demonstrating the absence of insertion products when a substituted ethyltrifluorosilane is pyrolysed in the presence of a large excess of silicon tetrachloride.[146]

$CH_2F \cdot CF_2 \cdot SiF_3 \xrightarrow[\text{excess of } SiCl_4]{225^\circ/16 \text{ hr.}} CHF:CHF \quad 96\%$

c.f., $CH_2F \cdot CF_2 \cdot SiF_3 \xrightarrow[\text{no added } SiCl_4]{225^\circ/16 \text{ hr.}} CHF:CHF \quad 98\%$
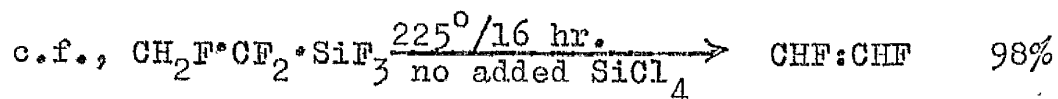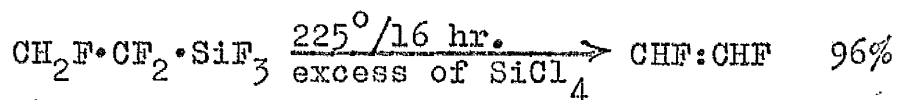
ii) <u>α-halogen exchange.</u>   Since the mechanism for the formation of the chlorinated olefins during pyrolysis does not involve a carbene insertion reaction, it has been suggested that attack by the α-fluorine atom on silicon occurs simultaneously with an attack by a silicon-bonded chlorine on the α-carbon:[146]
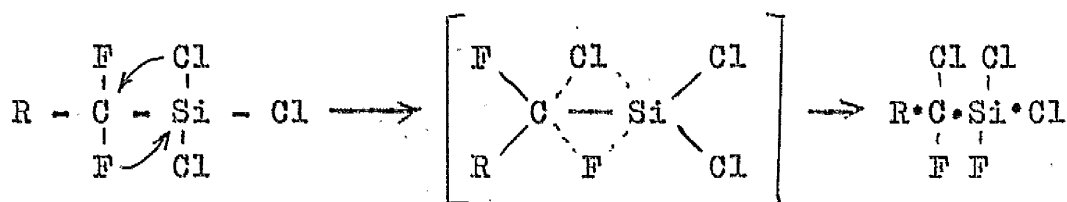
The rearranged silicon compound can then decompose by an α-fluorine elimination reaction to give an olefin containing one more chlorine atom than the original side chain.

$$CHF_2 \cdot CF_2 \cdot SiCl_3 \xrightarrow{\alpha\text{-exchange}} CHF_2 \cdot CFCl \cdot SiCl_2F$$

$$CHF_2 \cdot CFCl \cdot SiCl_2F \xrightarrow{\alpha\text{-elimination}} CHF_2 \cdot \overset{\bullet\bullet}{C}Cl + SiCl_2F_2$$

$$CHF_2 \cdot \overset{\bullet\bullet}{C}Cl \xrightarrow{H\text{-migration}} CF_2 : CHCl$$
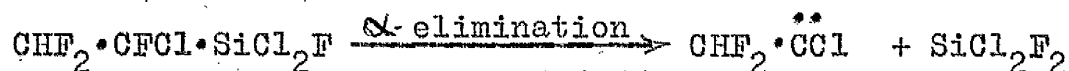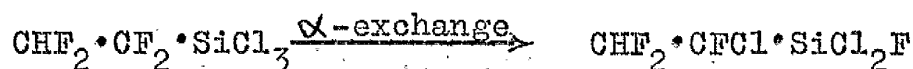
The rearranged silicon compound can also undergo a further α-halogen exchange reaction, and the product can decompose by a β-elimination reaction.

$$CHF_2 \cdot CFCl \cdot SiCl_2F \xrightarrow{\alpha\text{-exchange}} CHF_2 \cdot CCl_2 \cdot SiClF_2$$

$$CHF_2 \cdot CCl_2 \cdot SiCl_2F \xrightarrow{\beta\text{-elimination}} CHF : CCl_2 + SiClF_3$$
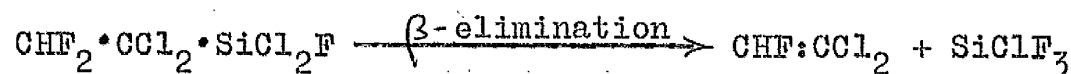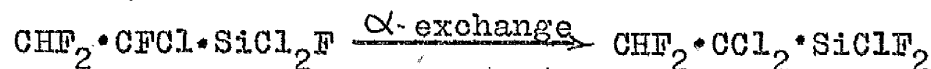
It has been shown that this mechanism fits the known facts for the thermal decomposition of fluoroalkyl-silicon compounds containing two α-halogen atoms.[146]

The results obtained from the pyrolyses of some of the compounds dealt with in this thesis (Table 25) can be rationalised in terms of the reaction schemes discussed above.

It is clear that only in the case of 2-fluoroethyltrichlorosilane, $CH_2F \cdot CH_2 \cdot SiCl_3$, is β-elimination the only possible mechanism.

$$
\begin{array}{ccc}
\begin{array}{c} CH_2 \\ | \\ F \end{array} \! \! \! \begin{array}{c} CH_2 \\ | \\ SiCl_3 \end{array} \longrightarrow
\left[\begin{array}{c} CH_2 \text{---} CH_2 \\ \vdots \qquad \vdots \\ F \text{-----} SiCl_3 \end{array} \right] \longrightarrow
\begin{array}{c} CH_2 : CH_2 \\ \\ SiCl_3F \end{array}
\end{array}
$$
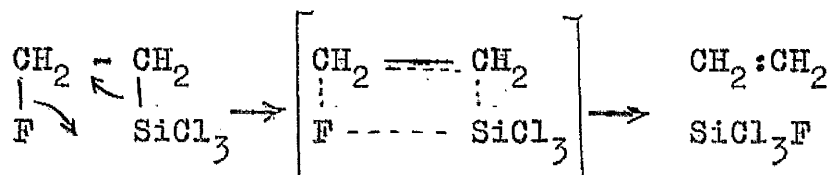
However the products of the pyrolyses of the 1,2,2-trifluoro-ethylsilanes could be produced by either an α- or a β-fluorine elimination reaction.

$\underline{\alpha - \text{elimination:}}$

$$CHF_2 \cdot \underset{\underset{F}{|}}{CH} \cdot SiCl_3 \longrightarrow CHF_2 \cdot \overset{\bullet\bullet}{CH} + SiCl_3F$$

$$CHF_2 \cdot \overset{\bullet\bullet}{CH} \xrightarrow{\text{F-migration}} CHF : CHF$$

$\underline{\beta - \text{elimination:}}$

$$
\begin{array}{ccc}
\begin{array}{c} CHF \\ | \\ F \end{array} \! \! \! \begin{array}{c} CHF \\ | \\ SiCl_3 \end{array} \longrightarrow
\left[\begin{array}{c} CHF \text{---} CHF \\ \vdots \qquad \vdots \\ F \text{-----} SiCl_3 \end{array} \right] \longrightarrow
\begin{array}{c} CHF : CHF \\ \\ + \; SiCl_3F \end{array}
\end{array}
$$
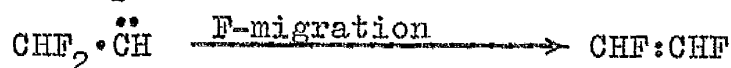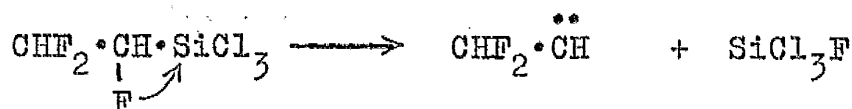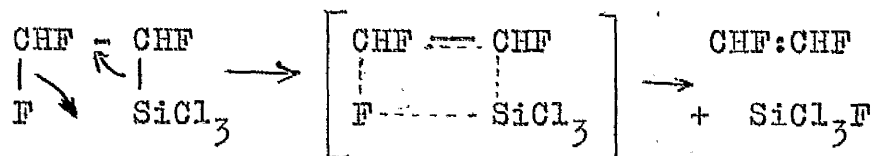
Chlorine-containing olefins were not detected in the pyrolysis products of the compounds which contained an α-fluorine atom. This suggests that the α-fluorine-chlorine exchange may be inhibited in some way by the

α-hydrogen atom so that the other reactions compete successfully with it. This conclusion requires considerably more experimental evidence before it can be confirmed.

The mobility order for atoms in carbenes has been shown to be $F < H < Cl$ by a study of the pyrolyses of a series of substituted-ethyl silicon compounds.[146] If the pyrolysis of 1,2,2-trifluoroethyltrichlorosilane, $CHF_2 \cdot CHF \cdot SiCl_3$, occurs by an α-elimination then fluorine must migrate in preference to hydrogen to give the observed product, 1,2-difluoroethylene;

$$CHF_2 \cdot CHF \cdot SiCl_3 \longrightarrow CHF_2 \cdot \overset{\cdot\cdot}{CH}$$

$$CHF_2 \cdot CH \left\{ \begin{array}{ll} \longrightarrow X \quad CF_2:CH_2 & \text{(H-migration)} \\ \longrightarrow CHF:CHF & \text{(F-migration)} \end{array} \right.$$
$$(50\%)$$

The low yield of organic products ($< 50\%$) resulted from heavy carbonisation during the pyrolyses.

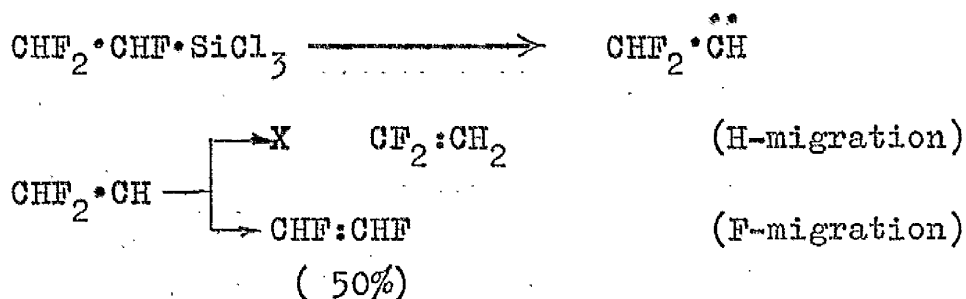This is contrary to the previously established order of mobility and hence it appears likely that 1,2,2-trifluoroethyltrichlorosilane decomposes thermally by a β-fluorine elimination rather than by an α-fluorine elimination. This conclusion is not firmly based since the total yield of organic products from the pyrolysis was only 49%. Olefin formation was accompanied by heavy carbonisation.

A high yield of organic products (99%) was obtained when 1,2,2-trifluoroethylmethyldichloro-silane, $CHF_2 \cdot CHF \cdot SiCl_2Me$, containing a little ($< 5\%$) of the isomer 1,1,2-trifluoroethylmethyldichlorosilane, $CH_2F \cdot CF_2 \cdot SiCl_2Me$, was pyrolysed. The organic products were 1,2-difluoroethylene (95%) and 1,1-difluoroethylene (5%).

$$CHF_2 \cdot CHF \cdot SiCl_2Me \quad (95\%)$$
$$+$$
$$CH_2F \cdot CF_2 \cdot SiCl_2Me \quad (5\%) \xrightarrow[\text{18 hr.}]{280^\circ} \quad CH_2{:}CF_2 \quad (5\%)$$
$$CHF{:}CHF \quad (95\%)$$
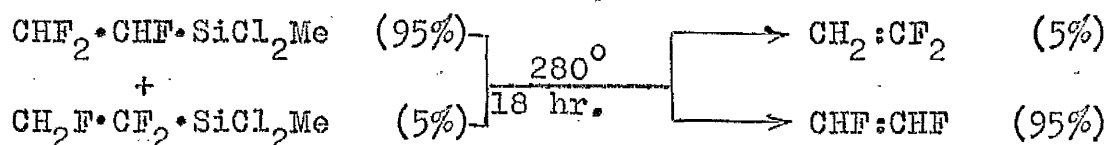
Both starting materials could decompose by either β- or α-elimination:

$$CHF_2 \cdot CHFiSiCl_2Me \quad \xrightarrow{\beta-} \quad CHF{:}CHF$$
$$\xrightarrow{\alpha-} \quad CHF_2 \cdot \overset{\bullet\bullet}{CH} \quad \xrightarrow{\text{H-shift}} \quad CF_2{:}CH_2$$
$$\xrightarrow{\text{F-shift}} \quad CHF{:}CHF$$

$$CH_2F \cdot CF_2 \cdot SiCl_2Me \quad \xrightarrow{\beta-} \quad CH_2{:}CF_2$$
$$\xrightarrow{\alpha-} \quad CH_2F \cdot \overset{\bullet\bullet}{CF} \quad \xrightarrow{\text{H-shift}} \quad CHF{:}CHF$$
$$\xrightarrow{\text{F-shift}} \quad CH_2{:}CF_2.$$
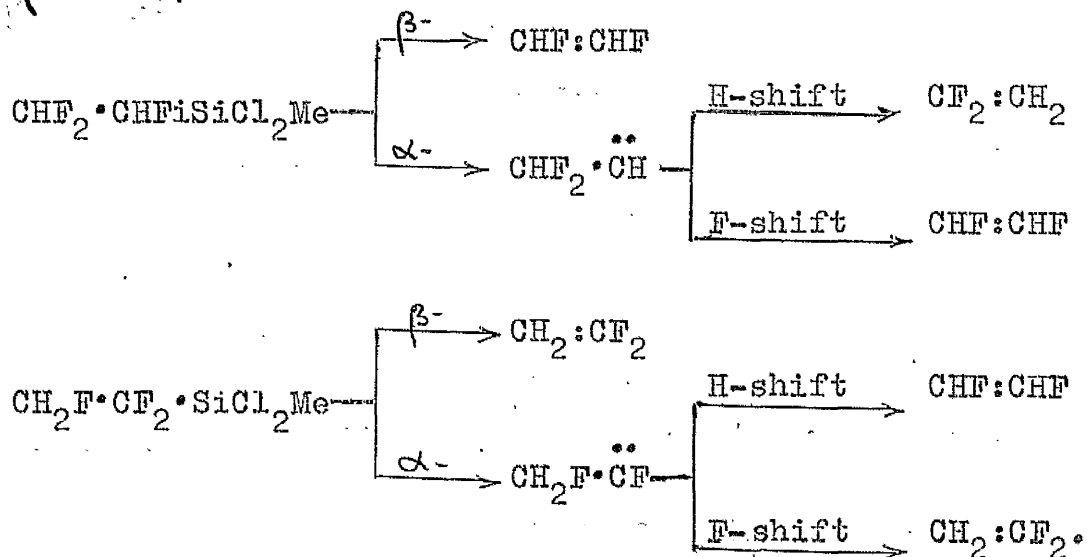
It is probably fortuitous, therefore, that the percentage composition of the mixture of olefins produced is approximately the same as that of the mixture of starting materials. The high yield of 1,2-difluoroethylene (95%) may indicate that a) the compound $CHF_2 \cdot CHF \cdot SiCl_2Me$

decomposes by β-fluorine elimination   b) the compound decomposes by α-fluorine elimination, but the mobility order previously observed does not apply in this case, or c) α- and β- fluorine elimination occur simultaneously.

The pyrolysis of fluoro-alkylsilicon compounds is clearly interesting mechanistically. It is equally clear that, in many cases, the pyrolysis products do not allow unambiguous conclusions to be drawn about either the homogeneity of a product or the percentage composition of a mixture of isomers.

An example of the care which must be taken in interpreting the results of pyrolysis experiments is provided by the isomeric pair of compounds 2-fluoroethyl-trichlorosilane, $CH_2F \cdot CH_2 \cdot SiCl_3$, and 1-fluoroethyltrichloro-silane, $CH_3 \cdot CHF \cdot SiCl_3$.

$$CH_2F \cdot CH_2 \cdot SiCl_3 \xrightarrow[\text{24 hr.}]{220^0} CH_2{:}CH_2 \qquad (97\%)$$

$$CH_3 \cdot CHFSiCl_3 \xrightarrow[\text{24 hr.}]{250^0} CH_2{:}CH_2 \qquad (23\%)$$

The production of ethylene from the first compound, $CH_2F \cdot CH_2 \cdot SiCl_3$, is presumably _via_ a simple β-fluorine elimination, whereas an α-fluorine elimination must have occurred in the second case.

$$CH_3 \cdot CHF \cdot SiCl_3 \xrightarrow[\text{elimination}]{\alpha\text{-Fluorine}} CH_3 \cdot \overset{\cdot\cdot}{C}H \xrightarrow[\text{Shift}]{\text{Hydrogen}} CH_2{:}CH_2$$

α-Fluorine-chlorine exchange should also be possible for

1-fluoroethyltrichlorosilane to give 1-chloroethyltrichloro-silane.

$$CH_3 \cdot CH \cdot SiCl_2 \xrightarrow{} CH_3 \cdot CHCl \cdot SiCl_2F$$

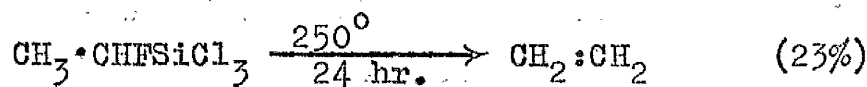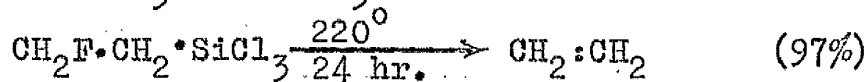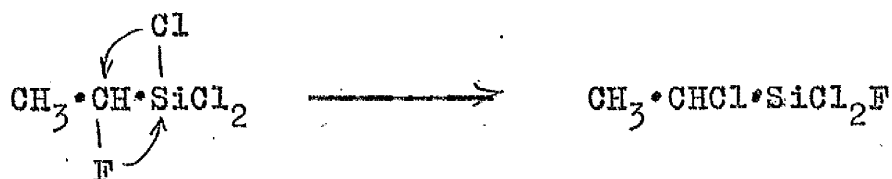However, in the case of the pyrolysis of 1,2,2-trifluoro-ethylmethyldichlorosilane, $CHF_2 \cdot CHF \cdot SiCl_2Me$, which also contains an α-CHF group, α-fluorine-chlorine exchange did not occur as shown by the absence of chlorine containing olefins and the high yield of 1,2-difluoroethylene (95%).

It has been reported that 1-chloroethyltrichloro-silane is stable to 620°. Therefore if the exchange took place no further decomposition would occur under the reaction conditions, and the yield of ethylene would be low. The yield of ethylene would similarly be low in the event of incomplete decomposition of the starting material. The experimental procedure used could not distinguish between these two possibilities.

Difficulty would arise if an attempt was made to assess the percentage composition of a mixture of monofluoroethyltrichlorosilanes on the basis of the amount of ethylene produced during pyrolysis. A quantitative yield of ethylene would indicate the presence of 2-fluoroethyltrichlorosilane, lower yields of ethylene

would require more careful interpretation.   This

particular problem could be overcome by a preliminary

separation of the most volatile products (ethylene and

the chlorofluorosilanes) from the less volatile products

(unconsumed starting materials and 1-chloroethyldichloro-

fluorosilane).   An analysis of the latter would permit

a quantitative interpretation of the results.

The behaviour of the two isomeric trifluoro-

ethyltrichlorosilanes illustrates this problem in a

more acute form.

$$CHF_2 \cdot CHF \cdot SiCl_3 \xrightarrow[16 \text{ hr.}]{225^{\circ}} \quad CHF\!:\!CHF \quad + \text{ carbonisation}$$
$$(47\%) \qquad \text{products}$$

$$CH_2F \cdot CF_2 \cdot SiCl_3 \xrightarrow[16 \text{ hr.}]{225^{\circ}} \quad CH_2\!:\!CH_2 + CHF\!:\!CHF + CHF\!:\!CHCl^{146}$$
$$(60\%) \qquad (19\%) \qquad (7\%)$$
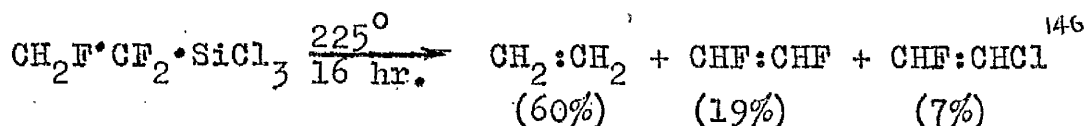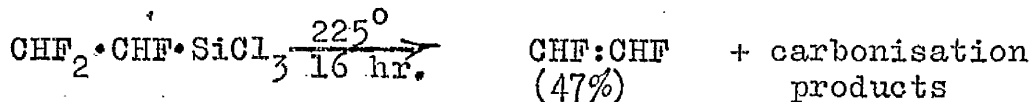
If a pyrolysis of a mixture of the isomers

had been carried out without previous knowledge of the products

from the pyrolyses of the individual isomers, interpretation

of the results would have been difficult, if not impossible

as it would not be clear whether one or both isomers

underwent carbonisation.

Since the object of obtaining isomer ratios

from studies of pyrolyses was to provide this information

when individual isomers were not obtained, it is clear that

the technique must be used with extreme care.   Isomer

ratios obtained by this method cannot be considered to be

unambiguous unless they are supported by evidence from

such other sources as gas-liquid chromatography,

nuclear magnetic resonance spectroscopy, and possibly

hydrolysis studies.

Compound	Pyrolysis conditions	Yield of organic products (%)
TABLE 25		The pyrolysis of fluoroethylsilanes
$CH_2F \cdot CH_2 \cdot SiCl_3$	$220^{\circ}/24$ hr.	$CH_2:CH_2$, 97%
$CH_3CHF \cdot SiCl_3$	$250^{\circ}/24$ hr.	$CH_2:CH_2$, 23% [**]
$CH_2F \cdot CH_2 \cdot SiCl_3$	$450^{\circ}/24$ hr.	$CH_2:CH_2$, 78%
$CHF_2 \cdot CHF \cdot SiCl_3$	$280^{\circ}/18$ hr.	$CHF:CHF$, 49% [+]
$CHF_2 \cdot CHF \cdot SiCl_2Me$ $CH_2F \cdot CF_2 \cdot SiCl_2Me$ ratio ca. 95:5	$280^{\circ}/18$ hr.	99% decomposition to $CHF:CHF$, 95%; $CH_2:CF_2$, 5%
$CHF_2CHF \cdot SiCl_3$	$225^{\circ}/16$ hr.	$CHF:CHF$, 47% [+]
$CH_2F \cdot CF_2 \cdot SiCl_3$ [*]	$225^{\circ}/16$ hr.	$CH_2:CCl_2$, 60%; $CHF:CHF$, 19%; $CHCl:CHF$, 7%

* Reference 146.

** Yield of organic product after hydrolysis with distilled water.

+ The poor mass balance results from heavy carbonisation during the reaction.

Orientation in free radical addition reactions.

It has been previously mentioned that the direction of addition of free radicals to polarised olefins is determined primarily by the relative stability of the two possible intermediate free radicals, and that bidirectional addition is possible when these stabilities are sufficiently similar to each other.

The addition of silyl radicals to vinyl fluoride has been shown to proceed with exclusive addition at the $=CH_2$ group of the olefin to produce a series of 2-fluoroethylsilanes. This is the same as the direction of addition of bromine atoms and trifluoromethyl radicals. A report of the possible bidirectional addition reaction of trifluoroiodomethane with vinyl fluoride has appeared in the literature. This has been criticised at the opening of the discussion section. It appears therefore that the addition of trichlorosilyl-methyldichlorosilyl-, and trimethylsily - radicals to vinyl fluoride produces the more stable radical, $\overset{\bullet}{C}HF.CH_2.Si\equiv$ as opposed to $\overset{\bullet}{C}H_2.CHF.Si\equiv$.

There is little published work on ionic addition reactions to vinyl fluoride. In the absence of published data on the ionic addition reaction of hydrogen chloride and of hydrogen fluoride to the olefin it is necessary to use the published data on the ionic addition reaction of nitrosyl chloride with vinyl fluoride to indicate polarisation of this olefin.[139]

Nitrosyl chloride adds to unsaturated compounds in the direction called for by the polarisation of the bond;

$$e.g., \quad \underset{Cl \; - \; NO}{\underset{-\qquad +}{Me_2 \; - \; CH = CHMe}} \quad \xrightarrow{\hspace{1cm}} \quad \underset{Cl \quad NO}{Me - \overset{Me}{\underset{|}{C}} - \overset{H}{\underset{|}{C}} - Me} \longleftrightarrow \underset{Cl}{Me - \overset{Me}{\underset{|}{C}} - \overset{Me}{\underset{|}{C}} = NOH}$$
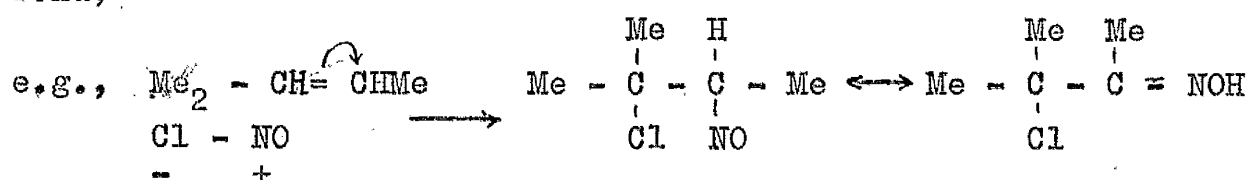
The result of addition reaction of nitrosyl chloride with vinyl fluoride at room temperature suggests that the olefin is polarised in the following manner,

$$\overset{s-}{} \quad \overset{s+}{}$$
$$CH_2 : CHF$$

$$\underset{\underset{+\qquad -}{NO - Cl}}{\overset{CH_2 = CHF}{+}} \quad \xrightarrow{\hspace{1cm}} \quad CHClF \cdot CH_2 \cdot NO. \quad (54\%)$$
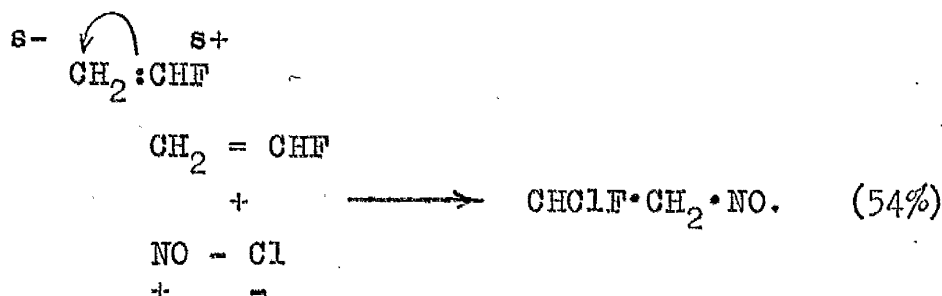
The yield of the adduct is low (54%) because further reaction of the adduct with nitrosyl chloride takes place and chlorine is formed. The chlorine then adds to any unreacted olefin to give the compound $CH_2Cl \cdot CHClF$.

$$2CHClF \cdot CH_2 \cdot NO + 2NOCl \longrightarrow 2CHClF \cdot CH_2 \cdot NO_2 + N_2 + Cl_2$$

$$CH_2 : CHF + Cl_2 \longrightarrow CH_2Cl \cdot CHClF.$$
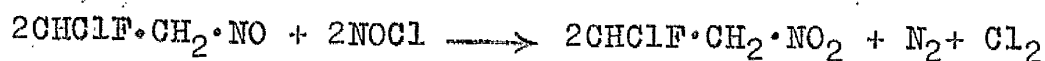
Because of the low yield of the 1:1 adduct from the reaction of nitrosyl chloride with vinyl fluoride evidence on the direction of polarisation derived from this source must be used with caution. However, it would appear that the polar and radical stability factors operate in the same direction for vinyl fluoride.

homolytic,

$$SiX_3 + CH_2:CHF \longrightarrow \overset{\bullet}{C}HF \cdot CH_2 \cdot SiX_3$$

$$\overset{\bullet}{C}HF \cdot CH_2 \cdot SiX + SiHX_3 \longrightarrow CH_2F \cdot CH_2 \cdot SiX_3 + \overset{\bullet}{S}iX_3$$
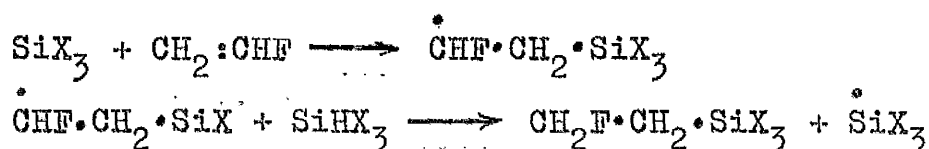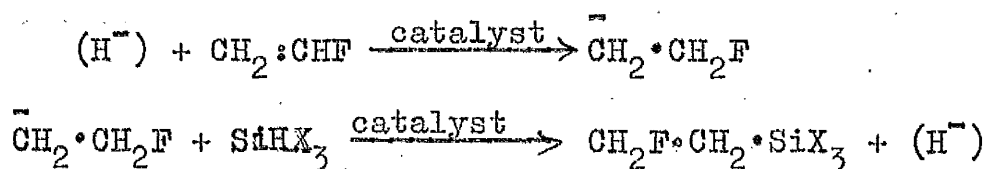
heterolytic,

$$(H^-) + CH_2:CHF \xrightarrow{catalyst} \overset{-}{C}H_2 \cdot CH_2F$$

$$\overset{-}{C}H_2 \cdot CH_2F + SiHX_3 \xrightarrow{catalyst} CH_2F \cdot CH_2 \cdot SiX_3 + (H^-)$$

It is usually assumed that heterolysis of the silicon-hydrogen bond is in the sense $Si^+ H^-$.

The addition reaction of trichlorosilane with 1-chloro-2-fluoroethylene has been shown to be bidirectional. The relative percentages of the 1:1 adducts determined were found to vary because of an abstraction of chlorine atoms by an excess of trichlorosilane. The ratio for attachment to the = CHF and = CHCl groups was 1:4.4 for a reaction in which the abstraction was minimised. This reaction necessarily entailed some telomerisation. The intermediate radicals $\overset{\bullet}{C}HCl \cdot CHF \cdot SiCl_3$ and $\overset{\bullet}{C}HF \cdot CHCl \cdot SiCl_3$

could initiate telomerisation at different rates. The observed ratio of the 1:1 adducts will obviously be dependent on this difference and a true indication of the percentages of actual attack at the various groups cannot be obtained unless telomerisation is absent. Measurement of such differences is beyond the scope of this work.

The addition of trimethylsilane to 1-chloro-2-fluoroethylene was similarly complicated by the abstraction reaction on the one hand and the telomerisation on the other. It was possible to deduce from the experimental data that under conditions where no telomerisarion occurred, the addition reaction proceeded exclusively ($>$ 98%) at the =CHF group of the olefin.

The theory of radical stability would predict the greater stability of the intermediate radical $\overset{\circ}{C}HCl \cdot CHF \cdot SiX_3$ as opposed to $\overset{\circ}{C}HF \cdot CHCl \cdot SiX_3$. Steric factors would predict the same direction of addition but the ionic addition of nitrosyl chloride to 1-chloro-2-fluoroethylene indicates polarisation in the direction $\overset{\delta-}{C}HCl = \overset{\delta+}{C}HF$. The same uncertainty arises about the olefin polarisation for this data as for the analogous data from the reaction of nitrosyl chloride with vinyl fluoride. The reaction with 1-chloro-2-fluoroethylene gave a yield of only 45% of the 1:1 addition product. The results may now be
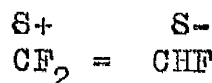
rationalised if it is postulated that the chlorine atoms on the trichlorosilyl radical lower the electron density at the silicon centre and so make the radical more electrophilic. There will, therefore, be a definite tendency for the trichlorosilyl radical to add onto the electron rich centre of the olefin. This explains the orientation of the isomers resulting from addition of trichlorosilyl radicals to the = CHF and = CHCl groups. The exclusive attack of trimethylsilyl radicals on the =CHF group of the olefin indicates that these radicals are considerably less electrophilic than trichlorosilyl radicals.

The addition reaction of silyl radicals to trifluoroethylene has been shown to be unidirectional for trichlorosilyl radicals and bidirectional for methyldi-chlorosilyl radicals and trimethylsilyl radicals. An initial reaction with silyl radicals ($\overset{\bullet}{S}iH_3$) indicated the possible bidirectionality of the addition reaction, but the results were obtained from gas-liquid chromatography only and no verification of the retention times was obtained. The figures are included for comparison but are not strictly related to the other ratios of the 1:1 adducts as considerable reaction of other silicon-hydrogen bonds of the 1:1 adduct had taken place.

TABLE 26   The addition reaction of silanes with trifluoroethylene.

Silane	% addition at =CHF	% addition at =CF$_2$
SiHCl$_3$	98	—
MeSiHCl$_2$	95	5
SiH$_4$	(88)	(12)
Me$_3$SiH	65	35

It appears that the percentage of addition at the =CF$_2$ group increases as the electron withdrawing properties of the substituents on silicon decreases. The nucleophilic addition of ethoxide ion indicates that the direction of polarisation in trifluoroethylene is $\overset{\delta+}{CF_2} = \overset{\delta-}{CHF}$. It is thus possible to suggest the order of electrophilicity $Me_3\overset{\bullet}{Si} < \overset{\circ}{SiH_3} < Me\overset{\bullet}{SiCl_2} < \overset{\circ}{SiCl_3}$. In this case it appears that the "normal" case for addition to trifluoroethylene is bidirectional, e.g., $Br^{\bullet}$ and $\overset{\bullet}{CF_3}$. More electrophilic radicals will show a distinct preference for addition to the = CHF group as found in the present work. This is also in agreement with work on the addition of thiols to trifluoroethylene carried out in this department.

CONCLUSION.

The research described in this thesis has shown that it is possible to explain the variations in the isomer ratios obtained from the bidirectional addition reaction of alkyl-, alkylhalo-, and halo-silanes to fluoro-olefins in terms of the structure of the silyl radical and the possible carbon radicals produced on addition of the silyl radical to a vinylic carbon atom. The order of electrophilicity of the silyl radicals was found to be $Me_3Si < SiH_3 < MeSiCl_2 < SiCl_3$, which is in agreement with previous work on the addition reactions of silanes with hexafluoropropene.

It has been shown that side reactions which accompany the addition reaction may be of major importance in reactions of silanes with olefins containing chlorine atoms. Careful product analysis must be carried out to determine the effect of such side reactions if meaningful comparisons of isomer ratios are to be made. If this is not done the application of the previously derived theory of radical addition reactions is neither easy nor precise.

The major difficulty found by previous workers in this field has been the separation and characterisation of the isomer formed in the lower percentage during the addition reaction. By using the ability of silyl radicals to abstract chlorine atoms, a pure sample of the minor adduct can be obtained,

e.g., $CH_2:CHF + SiHCl_3 \longrightarrow CH_2F \cdot CH_2 \cdot SiCl_3$

$CHCl:CHF + SiHCl_3 \longrightarrow CH_2Cl \cdot CHF \cdot SiCl_3$

$CH_2Cl \cdot CHF \cdot SiCl_3 + SiHCl_3 \longrightarrow CH_3 \cdot CHF \cdot SiCl_3 + SiCl_4$
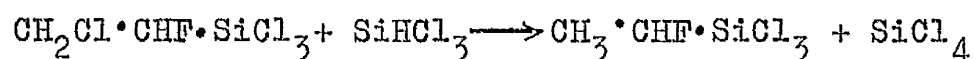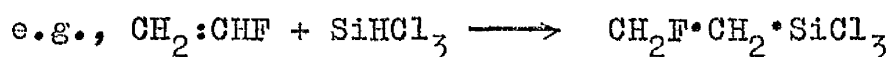
In this way pure samples of the expected isomers may be prepared and actual physical separation of the isomers can be limited to small scale gas-chromatographic separation.

The stabilising effect of hetero-atoms on free radicals has received little study. The halogen abstraction reaction dealt with in this work provides a means of studying such effects. This is of particular interest since intermediate radicals which cannot be formed during an addition reaction may be formed during an abstraction reaction. A series of monochlorinated silanes, studied by competitive techniques, may provide valuable information on the stabilising effect of various

substituted silyl groups on an alkyl radical. An
investigation of the relative ease with which different
silyl radicals abstract halogen would also be of value
if a correlation between structure and reactivity could
be obtained. A more detailed study of the mechanism
and the kinetics of the reaction would go some way
towards solving this problem.

The anomalous reaction of trimethylsilane
with 1-chloro-2-fluoroethylene in the presence of
mercury to give vinyl fluoride is deserving of further
study as it is not clear whether this is a true anomaly
or one of a series of similar reactions with other
chlorinated olefins.

Long range couplings of hydrogen to fluorine
in the nuclear magnetic resonance spectrum of fluoroalkyl-
silicon compounds of the type reported in this thesis have
not previously been described. It would be of interest
to establish similar long range coupling in other silicon
compounds, and also to study the temperature dependence of
this effect. If this coupling is present at high
temperatures ($\sim 200^{\circ}$), this approach may be of use in
understanding the behaviour of fluoroalkylsilicon compounds
during pyrolysis.

EXPERIMENTAL.

EXPERIMENTAL SECTION

General Techniques

Many of the compounds dealt with in this work are either gases or volatile liquids at room temperatures. Consequently manipulations of these materials were carried out where possible in a conventional vacuum system to enable air and moisture to be excluded from the compounds, many of which are readily hydrolysed, and to allow quantitative handling of gaseous materials to be carried out. The vacuum system was constructed of "Pyrex" glass and consisted of a series of storage bulbs (1 litre to 20 litres in capacity), a fractional condensation train, and a Regnault molecular weight apparatus. Standard vacuum taps and joints were used throughout. The fractionation traps and storage bulbs were calibrated against a molecular weight bulb of known volume, and pressure measurements were taken with mercury manometers. The system was evacuated by means of an Edwards two-stage "Speedivac" pump which gave pressures of ca. 10^{-3}mm. of mercury, and with a mercury diffusion pump for pressures down to 10^{-4}mm. when required.

Except where otherwise stated, all photochemical reactions

were carried out in sealed silica tubes at pressures up to 8 atmospheres. The tubes were flamed out under vacuum to remove traces of moisture, and the reactants were condensed into the tube by cooling the latter to -196°. The tubes were both sealed and opened <u>in vacuo</u> by means of a 2 cm. constriction in the neck of the tube, used in conjunction with thick walled rubber tubing. Photolysis was carried out at a distance of 10 cm. from a "Hanovia" 500 watt lamp, with vigorous shaking of the tube, except where otherwise stated.

Partial separation of the products was carried out by means of vacuum fractionation. In this technique the vapours from the condensed reaction products were allowed to pass slowly through a series of traps maintained at progressively lower temperatures at a pressure of not more than 5 mm. of mercury. Constant low temperatures were maintained by means of organic "slush baths", i.e., equilibrium mixtures of solid and liquid solvent obtained by periodically cooling the solvent with liquid nitrogen. Gases remaining non-condensable at -196° were absorbed on to activated charcoal cooled to -196°. Commonly employed "slush bath" solvents are

listed below.

Carbon tetrachloride,	-24°
Dichloroethane,	-36°
Chlorobenzene,	-46°
Chloroform,	-64°
Methylated spirits and solid carbon dioxide,	-78°
Toluene,	-95°
Diethyl ether,	-120°
$30\text{-}40^{\circ}$ Petroleum ether,	-130°
Liquid nitrogen.	-196°

Mixtures containing components boiling within 30° could not be fully separated in this manner. Analysis of such mixtures was carried out by the use of calibrated gas-liquid chromatography columns (Perkin Elmer "Vapour Fractometer" models 451 and 452) or by normal distillation techniques. Gases were identified by the use of infra-red spectroscopy (Perkin Elmer models 21 and 137 ("Infracord")) and by molecular weight determinations, and their purity was assessed by means of gas liquid chromatography by comparison with authentic samples. Infra-red spectra are recorded in the form of band tables for which the following symbols have been used for absorption, w = weak, m = medium, s = strong, vw = very weak, vs = very strong. Liquid samples were investigated by gas

liquid chromatography using a 4 metre x 5 mm. metal column packed with "Celite" impregnated (30-40%) with a stationary phase of silicone oil (M.S. 550). The column was operated at temperatures from 100° to 150°, and the separated components were detected with thermistors. Similar columns containing a stationary phase of polymeric chlorotrifluoroethylene (Kel-F oil) or of a squalane/silicone oil mixture were used for gaseous samples.

Throughout this work, whenever chlorosilanes were used, the chlorosilane was stored frozen down when possible (unless stored in an ampoule) as the "Apiezon" grease used on the taps and joints of the vacuum system is susceptible to attack by chlorosilanes. When this was not possible, slow transport of the grease to the bottom of the traps occurred, leading to leaking and eventual siezing up of the ground glass joints.

Preparation of Starting Materials

The chlorosilanes used in this work were commercial samples purified by fractionation through a 50 cm. vacuum jacketed column packed with glass helices. The purified samples were stored in "Pyrex" ampoules. The vinyl fluoride used was a commercial sample, purified by double vacuum fractionation through traps cooled to -36, -78, -120 and -196°. The vinyl fluoride condensed in the trap cooled to -196°, and was stored in the vacuum system.

Alkyl silanes can be most conveniently prepared by the reduction of the readily available chloroalkylsilanes with lithium aluminium hydride. A typical example is the preparation of trimethylsilane.

The Preparation of Trimethylsilane (Me$_3$SiH)

Lithium aluminium hydride [8.0 g., 0.21 mole] and dry di-n-butyl ether (300 ml.) were introduced into a 500 ml. round-bottomed flask fitted with a dropping funnel and a double surface condenser leading to two traps cooled to -78°. Nitrogen was blown through the apparatus, and the openings to the atmosphere were closed with drying tubes. The nitrogen flow was stopped and chlorotrimethylsilane [81.0 g., 0.75 mole] in dry di-n-butyl ether (50 ml.) was added dropwise to the

stirred slurry of lithium aluminium hydride at room temperature. As the reaction is very exothermic the addition was carried out over a period of one hour, after which the stirred mixture was slowly brought to the reflux temperature, and maintained at this temperature for a further two hours. The gases which had collected in the cold traps were transferred to the system under vacuum. They were then fractionated in vacuo to give pure trimethylsilane [47.5 g., 0.64 mole, equivalent to 88% conversion], M = 73.9, Calc. for $C_3H_{10}Si$, M = 74.0, identified by infra-red spectroscopy. The purity was checked before use by gas chromatography.

The Preparation of Silane (SiH_4)

Gaseous silane reacts explosively with oxygen at room temperature, and ignites spontaneously in air at -196°. Consequently all seals and joints used in its preparation must be completely air-tight. The apparatus used consisted of a 500 ml. flask fitted with a dropping funnel, a double surface condenser, a nitrogen inlet and a magnetic stirrer. Provision was made for external cooling. The condenser was connected to three external traps via a short length of thick walled rubber tubing, and the last trap was connected to a mercury lute at a depth of ca. 5 mm. beneath the surface

of the mercury. The first two traps were arranged with the central tube at the exit side of the system to reduce the possibility of blockage. The nitrogen inlet and the dropping funnel nitrogen lead were both connected via thick walled rubber tubing to a T-piece lute at a depth of ca. 10 mm. In the event of blockages the silane would be able to escape from this lute. Two screw clips were placed about one inch apart on the rubber tubing at the entrance and exit of the reaction vessel to allow for its safe isolation (by tightening the clips and cutting between them) after completion of the reaction. All joints were wired together and the apparatus was evacuated and vacuum tested. The apparatus was filled with nitrogen, and nitrogen was blown through for 24 hr. before the reaction.

Silicon tetrachloride [11.0 g., 0.06 mole] in dry di-n-butyl ether (70 ml.) was added dropwise over a period of two hours to a stirred slurry of lithium aluminium hydride [4.5 g., 0.12 mole] in dry di-n-butyl ether (140 ml.) at 0° with a slow feed rate of nitrogen through the apparatus. The addition must be carried out slowly otherwise the back pressure from the evolution of silane will blow a mixture of silane and nitrogen out through the inlet lute. When the addition was complete the bath was allowed to warm to room

temperature and then slowly warmed to 30° for two hours
after which heating was discontinued and nitrogen was passed
through for a further two hours whilst the reaction vessel
cooled to room temperature. The silane collected in the
traps was transferred to the vacuum system and was shown to
be pure by infra-red spectroscopy and molecular weight
determination. M = 32, Calc. for H_4Si, M = 32.

Preparation of 1,1,2-trichloro-2-fluoroethane

Symmetrical tetrachloroethane [504 g., 3.0 mole] antimony
trifluoride [270 g., 1.52 mole] and antimony pentachloride
[40 g., 0.13 mole] were stirred and slowly totally distilled
from a 2 l. three-necked flask fitted with an oil-seal
stirrer and a Liebig condenser. The distillate was washed
respectively with 2N. sodium hydroxide solution, 2N.
hydrochloric acid, saturated sodium carbonate solution, and
water. The liquid was dried over anhydrous magnesium
sulphate for five days. The crude product was filtered into
a 500 ml. flask and fractionated from a small amount of
phosphorus pentoxide through a 400 x 10 mm. vacuum jacketed
column packed with glass helices and fitted with a partial
reflux take-off head. A fraction boiling at $90\text{-}110^{\circ}$ was
collected. This was then refractionated from phosphorus

pentoxide to give a fraction collected at 101-3°, which was shown to be pure 1,1,2-trichloro-2-fluoroethane [130 g., 0.87 mole, 30% yield]. The purity was checked by gas-liquid chromatography and infra-red spectroscopy.

Preparation of 1-chloro-2-fluoroethylene

A 500 ml. three-necked flask equipped with a mercury-seal stirrer, dropping funnel, and a reflux condenser leading to two external traps cooled to -78°, and fitted with phosphorus pentoxide drying tubes, was flushed out overnight with dry nitrogen. Zinc dust [75 g., 1.15 mole] was activated by washing with dilute hydrochloric acid and rinsing twice with dry ethyl alcohol. It was then added to 175 ml. ethyl alcohol contained in the 500 ml. flask. The zinc-ethyl alcohol mixture was brought to the reflux temperature and stirred vigorously, while 1,1,2-trichloro-2-fluoroethane [130 g., 0.87 mole] was added over a period of two hours. The apparatus was again flushed out with dry nitrogen, and the condensed gases which had collected in the cooled traps were transferred to the system under vacuum. The product was fractionated under vacuum through traps cooled to -45, -78, -120, and -196° to give 1-chloro-2-fluoroethylene [49 g., 0.61 mole, 70% yield], which condensed in the trap at

-120°. Found: C, 29.4; H, 2.2%; M = 80.2, Calc. for

C_2H_2ClF; C, 29.6; H, 2.48%; M = 80.5; . The purity was

checked by gas liquid chromatography and infra-red

spectroscopy.

The Preparation of 1-Bromo-2-chloro-1,1,2-trifluoroethane

Chlorotrifluoroethylene [47.4 g., 0.4 mole] and hydrogen

bromide [32.4 g., 0.4 mole] were introduced into a 20 l. bulb

fitted with a mercury manometer and a silica insert for

ultraviolet irradiation. The reactants were irradiated by

means of a 500 watt "Hanovia" lamp for two hours and the

reaction was seen to proceed after a short induction period

by the reduction in the pressure in the bulb. The products

of the reaction were transferred to the system under vacuum

and fractionated through traps maintained at -24, -63, -95, and

-196°. The product was found to have condensed in the trap

at -63°. This fraction was then transferred to a 150 ml.

flask and fractionated at atmospheric pressure through a 250 mm.

vacuum jacketed packed column fitted with a partial reflux

take-off head to give a major fraction boiling at $51-54^{\circ}$.

The product was shown to be 1-bromo-2-chloro-1,1,2-trifluoroethane

[65.5 g., 0.328 mole , equivalent to 82%] bp. $52.8^{\circ}/760$

(lit. 52.5°), by infra-red spectroscopy. A higher boiling

fraction [5.3 g.] was not investigated.

The Preparation of trifluoroethylene

Zinc dust [196 g., 3.0 mole] contained in a 500 ml. three-necked flask was activated with 5N. hydrochloric acid and washed three times with dry ethanol. The flask was fitted with a dropping funnel and a double-surface condenser leading to two external traps cooled to -120°. Outlets to the atmosphere were closed with drying tubes and the flask was fitted for magnetic stirring. Dry ethanol (150 ml.) was added to the zinc in the flask and the mixture was heated to the reflux temperature over an oil bath. 1-Bromo-2-chloro-1,1,2-trifluoroethane [200 g., 1.0 mole] in dry ethanol (50 ml.) was slowly added dropwise to the stirred refluxing mixture over a period of two hours, after which the reaction mixture was heated at the reflux temperature for a further two hours. The product which condensed in the cooled traps were transferred to the vacuum system and were fractionated *in vacuo* to give a major fraction condensing at -120°. This was shown to be pure trifluoroethylene [72.2 g., 0.88 mole, equivalent to 88% yield] by infra-red spectroscopy, gas-liquid chromatography and molecular weight determination.

ADDITION REACTIONS OF SILANES WITH VINYL FLUORIDE
AND THE PROPERTIES OF THE ADDUCTS

Photochemical reactions were carried out in sealed silica tubes (volume 300 ml. unless otherwise stated) which were filled _in vacuo_ and irradiated at a distance of 10 cm. from a "Hanovia" 500 watt ultraviolet lamp at the temperature in the vicinity of the lamp (_ca._ 35°). The reactant ratio and the time of irradiation were varied to determine the most favourable conditions for conversion to the 1:1 adduct with as little telomer formation as possible.

Reaction of Trichlorosilane with Vinyl Fluoride

A typical example is the reaction with a silane/olefin ratio of 5:1. Results with different ratios have been tabulated (Table 27).

Trichlorosilane [39.0 g., 0.29 mole] and vinyl fluoride [2.65 g., 0.058 mole] in a silica tube were shaken and irradiated for 100 hr. Fractionation _in vacuo_ gave vinyl fluoride [1.205 g., 0.026 mole equivalent to 54% conversion], a liquid which condensed in a trap cooled to -24°, unreacted trichlorosilane, and a trace of high boiling material which remained in the tube at 100° under vacuum. The -24° fraction was combined with a similar fraction from an identical reaction

and fractionated under nitrogen in a 20 ml. pear-shaped
flask fitted with a 130 x 8 mm. vacuum jacketed column,
packed with glass helices, and fitted with a partial reflux
take-off head, to give an adduct of trichlorosilane and vinyl
fluoride[2 x 5.02 g., 2 x 0.0276 mole, equivalent to 88% on
olefin consumed], bp. 118°/760 mm. The adduct was identified
by infra-red spectroscopy and elemental analysis.

Found: C, 13.4; H, 1.9; Cl, 59.4%;

$C_2H_4Cl_3FSi$ requires   C, 13.2; H, 2.2; Cl, 58.8%.

Chlorine was determined as hydrolysable halogen by acid-base
titration at pH7 using bromo-thymol blue as an indicator. The
fore-runnings consisted of a mixture of trichlorosilane and
a trace of the adduct, and the pot-residue consisted of a small
quantity of polymeric material [0.34 g.]. The infra-red
spectrum of the adduct indicated that it was free from
trichlorosilane by the absence of the Si - H stretching
frequency 4.6μ. The infra-red spectra of both the pot-residue
and the high boiling tube residue were essentially similar to
that of the adduct.

Infra-red band table for 2-fluoroethyltrichlorosilane

$$\underline{CH_2F.CH_2.SiCl_3}$$
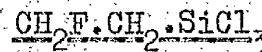
3.34 s	7.76 m	10.20 vs
3.40 s	7.95 vw	10.60 vs
5.05 w	8.22 vs	12.95 ⎫
6.26 m	8.39 ⎫	13.25 ⎬ s
6.95 w	9.00 ⎬ s	13.95 ⎫
7.09 m	9.60 vs	14.15 ⎬ vs
7.20 vs	10.00 vs	

The adduct was investigated by gas-liquid chromatography using
a Perkin Elmer vapour "Fractometer" (model 116) fitted with a
thermistor detector. The column used was constructed from
4 metres of 5 mm. tubing containing silicone oil (M.S. 550)
supported on "Celite". A single peak for the adduct was obtained
with a retention time of 15.9 min. at $150°$ and a nitrogen flow
rate of 68 ml./min. at 1 kg./cm^2. The retention time of
1-fluoroethyltrichlorosilane, isomeric with the expected adduct,
was 12.6 min. under the same conditions, suggesting that
1-fluoroethyltrichlorosilane was not present in the adduct.
The adduct was shown to be 2-fluoroethyltrichlorosilane by
nuclear magnetic resonance spectroscopy, (see appendix).
The sample of 1-fluoroethyltrichlorosilane was prepared by the
addition reaction of trichlorosilane with 1-chloro-2-

fluoroethylene followed by dechlorination <u>in situ</u> by the

trichlorosilane, .

TABLE 27

The Photochemical Reaction of
Trichlorosilane with Vinyl Fluoride

moles of olefin	mole ratio silane/ olefin	time (hr.)	olefin consumed (%)	1:1 adduct based on olefin consumed (%)	lamp wattage
0.055	1:1	100	18	40	250
0.07	1:1	150	2	-	250(a)
0.07	2:1	70	21	80	500
0.07	2:1	100	30	75	500
0.055	2:1	150	95	73	500(b)
0.039	2:1	200	22	95	500(c)
0.057	5:1	100	54	88	500
0.057	8:1	170	96	91	500
0.07	1:1	336	0	0	500(d)

(a) Tube Stationary

(b) ~1% Hydrogen detected

(c) Vapour phase shielded

(d) Reaction in the absence of light

Reaction of Methyldichlorosilane with Vinyl Fluoride

Methyldichlorosilane [35.05 g., 0.302 mole] and vinyl
fluoride [2.71 g., 0.059 mole] were sealed in a silica tube
and were shaken and irradiated before a "Hanovia" 500 watt
ultraviolet lamp for 100 hr. Fractionation of the products
in vacuo gave vinyl fluoride [1.11 g., 0.024 mole, equivalent
to 56% conversion], a liquid which condensed in a trap cooled
to -24° [5.55 g.] of which the infra-red spectrum indicated
the presence of the adduct of methyldichlorosilane with vinyl
fluoride together with a small percentage of unreacted
methyldichlorosilane; unreacted methyldichlorosilane
[31.0 g., 0.027 mole] containing a trace of the adduct; and
a high boiling material [0.1 g.]. Combined product fractions
from a similar tube were fractionated in a 20 ml. pear-shaped
flask fitted with a 130 x 8 mm. vacuum jacketed column packed
with glass helices, and fitted with a partial reflux take-off
head to give an adduct of methyldichlorosilane to vinyl
fluoride [2 x 5.05 g., 2 x 0.0314 mole, equivalent to 95% on
olefin consumed] bp. 120/760 mm.

Found: C, 23.0; H, 4.0%;

$C_3H_7Cl_2FSi$ requires,   C, 22.2; H, 4.3%.

The fore-runnings consisted of methyldichlorosilane and a

trace of the adduct $\left[0.4 \text{ g.}\right]$ and the pot-residue consisted of a trace of polymeric material $\left[0.6 \text{ g.}\right]$ of which the infra-red spectrum was essentially similar to that of the adduct.

Infra-red band table for 2-fluoroethylmethyldichlorosilane
$\underline{CH_2F.CH_2.SiCl_2Me}$

3.43 m	7.95 s	11.15 w
3.50 m	8.35 m	11.40 w
6.80 w	8.00 m	12.30 s
7.05 w	9.10 m	12.65 s
7.16 m	9.68 s	13.30 m
7.28 m	10.20 s	14.20 m
7.75 m	10.70 s	

The adduct was investigated by gas-liquid chromatography using a Perkin Elmer "Vapour Fractometer" (model 452) fitted with a 4 m. silicone column as described previously. A single peak was obtained from the adduct with a retention time of 15.6 minutes at a temperature of 150° and a column pressure of 1 kg./cm^2 and a nitrogen flow of 68 ml./min.

TABLE 28

The Photochemical Reaction of Methyldichlorosilane
with Vinyl Fluoride

moles of olefin	mole ratio silane/ olefin	time (hr.)	olefin consumed (%)	1:1 adduct based on olefin consumed (%)	lamp wattage
0.059	5:1	100	57	95	500
0.059	8:1	120	68	95	500

The isomeric compound, 1-fluoroethylmethyldichlorosilane, was not prepared but the structure of the adduct was shown to be 2-fluoroethylmethyldichlorosilane by nuclear magnetic resonance spectroscopy.

The Reaction of Trimethylsilane with Vinyl Fluoride

A typical experiment is the reaction with a silane/olefin ratio of 4:1. Results with different ratios are given in table 29.

Trimethylsilane [14.8 g., 0.20 mole] and vinyl fluoride [2.3 g., 0.05 mole] in a silica tube were irradiated with shaking for 90 hr. Fractionation in vacuo gave unreacted vinyl fluoride [1.38 g., 0.03 mole, equivalent to 40% reaction of the olefin], unreacted trimethylsilane [13.0 g., 0.18 mole], a liquid condensing at -36° [2.1 g.], and a high boiling yellow

oil which remained in the tube $\left[\text{0.45 g.}\right]$. The unreacted

starting materials were identified by infra-red spectroscopy,

molecular weight determination, and gas-liquid chromatography.

The liquid condensing at -36° was recognised by infra-red

spectroscopy and elemental analysis as an adduct of

trimethylsilane with vinyl fluoride containing a trace of

trimethylsilane, bp. $70^{\circ}/760$ mm. The structure of the major

component ($>95\%$) was shown to correspond to

2-fluoroethyltrimethylsilane by nuclear magnetic resonance

spectroscopy.

Found: C, 50.0; H, 10.4%;

$C_5H_{13}FSi$ requires,   C, 50.0; H, 10.8%.

Infra-red band table for 2-fluoroethyltrimethylsilane,
$\underline{CH_2F.CH_2.SiMe_3}$

3.43 vs	8.02 vs	10.45 m
3.53 s	8.5 w	10.7 w
3.6 w	8.7 m	11.02 m
6.9 w	8.95 s	11.04 s
6.98 w	9.5 s	11.85 vs
7.15 w	9.75 m	12.0 broad
7.3 m	9.9 m	13.25 s
7.46 w	10.3 w	14.55 m
7.75 w		

The adduct was investigated by gas-liquid chromatography using a Perkin Elmer "Vapour Fractometer" (model 154B) fitted with a thermistor detector and a 4 m. x 5 mm. column containing silicone oil (M.S. 550) supported on "Celite." A single peak for the adduct was obtained with a retention time of 10.6 min. at 90° and with a nitrogen flow of 78 ml./min. The retention time of 1-fluoroethyltrimethylsilane, isomeric with the expected adduct, was 9.4 min. under the same conditions, suggesting that this compound was not present in the adduct.

TABLE 29

The Photochemical Reaction of Trimethylsilane
with Vinyl Fluoride (500 watt Ultraviolet Lamp)

moles of olefin	mole ratio silane/olefin	time (hr.)	% reacted	yield 1:1 adduct %
0.05	2:1	100	18	11 (a)
0.05	4:1	100	40	87 (b)
0.05	6:1	300	80	90 (c)

(a) Telomeric material [0.6 g.] bp. 110°.

(b) Telomeric material [0.4 g.].

(c) Mercury photosensitisation used. A trace of ethylene ($<1\%$) was detected by infra-red spectroscopy.

The Reaction of Dimethylsilane with Vinyl Fluoride

Dimethylsilane and vinyl fluoride with a silane/olefin ratio of 4:1 were irradiated under standard conditions for 100 hr. and for 200 hr. Both reactions gave 100% consumption of vinyl fluoride but produced 2.5% and 18% ethylene respectively. The liquid products, on examination by gas-liquid chromatography, indicated the presence of four new components in addition to unreacted dimethylsilane. The reaction is not suitable for the purpose of the investigation and was not further investigated.

The Reaction of Trimethylsilane with Vinyl Fluoride in the presence of Azobisisobutyronitrile

Trimethylsilane [18.4 g., 0.249 mole], vinyl fluoride [2.855 g., 0.062 mole] and azobisisobutyronitrile [.2 g., 1.3 mmole, ca. 2% on vinyl fluoride, 0.5% on trimethylsilane] were sealed in vacuo in a "Dreadnought" tube and shaken for 2 weeks in the absence of light. Fractionation in vacuo gave a gas condensing at -46° [0.062 mmole], molecular weight 78, (calc. for $C_3H_{10}Si$, M = 74), which was mainly trimethylsilane plus a trace of the adduct of trimethylsilane with vinyl fluoride (estimated at ~10% of the gas). This gives approximately 0.01% reaction to the adduct. The reactants were recovered unchanged (>99%). The amount of adduct formed was much too small to allow

investigation by gas-liquid chromatography.

Trimethylsilane [17.13 g., 0.23 mole], vinyl fluoride [2.665 g., 0.057 mole] and azobisisobutyronitrile [0.226 g., 1.4 mmole] were sealed in a "Dreadnought" tube *in vacuo* and shaken at 85° for 24 hr. Fractionation *in vacuo* gave nitrogen [0.0195 g., 1.4 mmole, equivalent to 103% theoretical nitrogen as measured] M = 28, (calc. for N_2, M = 28), vinyl fluoride [2.46 g., 0.053 mole, equivalent to 92% recovery], trimethylsilane [16.63 g., 0.225 mole, equivalent to 97% recovery] and an adduct of trimethylsilane with vinyl fluoride [0.35 g., 2.9 mmole, equivalent to 5% reaction of the olefin or 62% of the olefin consumed]. Unchanged starting materials and the adduct were identified by infra-red spectroscopy, molecular weight determination, and gas-liquid chromatography. The adduct had a retention time identical with that of the adduct from the photochemical reaction. No attempt was made to detect the initiator residue.

Trimethylsilane and azobisisobutyronitrile were sealed *in vacuo* in a "Pyrex" ampoule to check the miscibility of the initiator and the reactant. The initiator was seen to be immiscible with the trimethylsilane (liquefied under pressure).

REACTIONS OF SILANES WITH TRIFLUOROETHYLENE

The Reaction of Trichlorosilane with Trifluoroethylene

Trichlorosilane [37.6 g., 0.2775 mole] and

trifluoroethylene [4.55 g., 0.0555 mole] in a silica tube

was shaken and irradiated for 100 hr. Fractionation in vacuo

gave unreacted trifluoroethylene [0.319 g., 3.88 mmole,

equivalent to 93% conversion] unreacted trichlorosilane

[22.01 g., 0.1626 mole] and a liquid condensing in a trap

cooled to -24°, [19 g.]. The contents of the -24° trap were

combined with a similar fraction from an identical reaction

and fractionated at atmospheric pressure under nitrogen in a

20 ml. pear-shaped flask fitted with a 130 x 8 mm. vacuum

jacketed column packed with glass helices and fitted with

a partial reflux take-off head to give a 1:1 adduct of

trichlorosilane with trifluoroethylene [16.53 g., 0.0763 mole,

equivalent to 75% of the olefin reacted], b.p. 102-4°/760 mm.

The fore-runnings consisted of a mixture of trichlorosilane

and the adduct [0.4 g.] and unreacted trichlorosilane. The

pot-residue consisted of a small quantity of dark brown

material [~1 g.]. The absence of the Si-H stretching frequency

at 4.6 μ in the infra-red spectrum of the adduct indicated

that it was free from trichlorosilane.

Found: C, 11.2;   H, 0.95;   Cl, 49.1%;

$C_2H_2Cl_3F_3Si$ requires,   C, 11.1;   H, 0.95;   Cl, 49.2%.

Infra-red band table for 1,2,2-trifluoroethyltrichlorosilane
($\underline{CHF_2.CHF.SiCl_3}$)

μ		μ		μ	
3.40	w	8.20	m	10.22	s
7.20	s	8.70	vs	11.00	m
3.39	m	8.95	vs	12.65	s
7.65	vw	9.15	vs	13.80	m
7.83	w	9.45 ⎫	vs		
8.03	m	9.55 ⎭	doublet		

The infra-red spectrum of the pot-residues was essentially
similar to that of the adduct, hydrolysable chlorine of the
residue indicated an average of ~2 olefin units per silane unit.

Found: Cl, 36.1%;

$C_4H_3Cl_3F_6Si$ requires,   Cl, 38.0%.

The adduct was investigated by gas-liquid chromatography
using a "4 m. silicone" (M.S.550) column. A single peak for
the adduct was obtained with a retention time of 14.2 min. at
150° and a nitrogen flow rate of 74 ml./min. at 1 kg./cm^2. The
retention time of the compound isomeric with the expected adduct,

1,1,2-trifluoroethyltrichlorosilane,* $CH_2F.CF_2.SiCl_3$, was

12.9 min. under the same conditions. The adduct was shown to

be 1,2,2-trifluoroethyltrichlorosilane by nuclear magnetic

resonance spectroscopy. A mixture of 1,2,2-

trifluoroethyltrichlorosilane and 1,1,2-trifluoroethyltrichloro-

silane (92% and 8% respectively) was investigated by gas-liquid

chromatography under the same conditions. It gave two well

distinguished peaks at 12.9 min. (7.5% by area), and 14.2 min.

(92.5% by area).

The Reaction of Methyldichlorosilane with Trifluoroethylene

Methyldichlorosilane [37.3 g., 0.275 mole] and

trifluoroethylene [4.55 g., 0.0555 mole] in a silica tube were

shaken and irradiated for 100 hr. Fractionation in vacuo gave

unreacted trifluoroethylene [0.91 g., 0.0111 mole, equivalent

to 80% conversion], unreacted methyldichlorosilane, and a

liquid condensing in a trap cooled to -24° [10.4 g.]. The

contents of the -24° trap were combined with a similar fraction

from an identical reaction and fractionated at atmospheric

pressure in a 20 ml. pear-shaped flask fitted with a 130 x 8 mm.

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* Prepared by Dr. W.I. Bevan by the addition reaction of

trichlorosilane with chlorotrifluoroethylene followed by

dechlorination in situ. by the trichlorosilane.

vacuum jacketed column packed with glass helices and fitted
with a partial reflux take-off head to give unreacted
methyldichlorosilane containing a trace of the adduct, a
fraction collected at 110-12° [8.69 g.], and a fraction
collected at 113-4° [5.1 g.]. The last two fractions were
found to be identical and to consist of a 1:1 adduct of
methyldichlorosilane with trifluoroethylene [13.79 g., 0.07 mole,
equivalent to 80% of the olefin reacted] b.p. 112-3°/760 mm.
The pot-residues consisted of a dark brown viscous material
[2.5 g.] of which the infra-red spectrum was essentially
similar to that of the adduct. It was found to contain
26.1% chlorine; $C_5H_6Cl_2F_3Si$ requires Cl, 25.5%. The adduct
was shown to be free of methyldichlorosilane by the absence
of the Si-H infra-red stretching frequency at 4.6 μ and was
recognised as the 1:1 adduct by elementary analysis for
carbon, hydrogen and chlorine.

Found: C, 18.7;   H, 2.5;   Cl, 35.9%;

$C_5H_5Cl_2F_3Si$ requires,   C, 18.3;   H, 2.5;   Cl, 36.0%.

Infra-red band table for 1,2,2-trifluoroethylmethyldichlorosilane, ($CF_2H.CFH.SiCl_2Me$) (purity 95%)

μ	μ	μ
3.41 w	7.92 s	9.60 vs, broad
3.50 vw	8.10 w	10.30 m
6.94 vw	8.25 w	11.00 m
7.25 m	8.79 s	12.55 vs
7.40 m	8.95 m	13.23 s
7.70 vw	9.25 vs, broad	14.45 m

The adduct was investigated by gas-liquid chromatography using a "4 m. silicone" (M.S.550) column. A main peak with a retention time of 17.3 min. was observed with a small shoulder to the main peak at 16.7 min. ($\sim$5%) at 150° with a nitrogen flow rate of 74 ml./min. at 1 kg./cm^2. The adduct was shown to consist mainly of 1,2,2-trifluoroethylmethyldichlorosilane by nuclear magnetic resonance spectroscopy. Traces of a compound corresponding to 1,1,2-trifluoroethylmethyldichlorosilane were detected in concentrations less than 5% by nuclear magnetic resonance spectroscopy.

The Reaction of Trimethylsilane with Trifluoroethylene

Trimethylsilane [22.0 g., 0.30 mole] and trifluoroethylene [4.43 g., 0.054 mole] with mercury (2 ml.) in a silica tube were shaken and irradiated for 140 hr. Fractionation in vacuo gave unreacted trimethylsilane [18.76 g., 0.252 mole, equivalent to 96% reaction (excluding the 4 molar excess of trimethylsilane] and a liquid which condensed in a trap cooled to -24°, [7.5 g.]. A small quantity of high boiling liquid [0.1805 g.] remained in the tube under vacuum. The infra-red spectrum of the latter was identical with that of the liquid which condensed at -24° apart from the Si-H stretching frequency at 4.6 μ in the -24° fraction. No olefins were detected. The liquid condensing at -24° was investigated by infra-red spectroscopy, gas-liquid chromatography and elemental analysis for carbon and hydrogen. It was shown to be a 1:1 adduct of trimethylsilane with trifluoroethylene [7.42 g., 0.0475 mole, equivalent to 89% of the olefin consumed], together with a trace of trimethylsilane [0.08 g., 1.1 mmole].

Found: C, 38.2; H, 7.0%;

$C_5H_{11}F_3Si$ requires,   C, 38.5; H, 7.1%.

Infra-red band table for 1,2,2-trifluoroethyltrimethylsilane, ($CF_2H.CHF.SiMe_3$)

μ	μ	μ
3.34 s	7.38 w	10.97 s
3.42 m	7.95 vs	11.74 vs
6.85 w	8.82 m	13.17 m
7.03 w	9.45 vs	13.24 m
7.25 w	9.53 vs	15.07 w
7.34 w	10.28 w	

The adduct was intensively investigated by gas-liquid chromatography on a laboratory built machine using a squalane/silicone (M.S.550) column and a series of different temperatures. A very small peak (less than 0.001% of the total peak area) with a retention time corresponding to that of an authentic sample of 1,1,2-trifluoroethane was detected when the volume of sample injected was approaching the upper limits of the machine. During the investigation it was found that the main peak (i.e. the adduct) was resolved into two components in approximate percentages 35% and 65% (i.e. relative peak areas) in order of increasing retention time. The identities of these peaks were found to be 1,1,2-trifluoroethyltrimethylsilane, $CH_2F.CF_2.Si(CH_3)_3$, and

1,2,2-trifluoroethyltrimethylsilane, $CF_2H.CHF.Si(CH_3)_3$,
respectively by calibrating for retention time against
independently prepared samples of the two compounds (see pp. 288).
It was later shown (p. 242) that differences in thermal
conductivity of these two compounds (assessed by quantitative
calibration with a synthetic mixture of known composition) were
insignificant for the purpose of determining the isomer ratio.

The reaction was repeated in the absence of mercury with
irradiation for 250 hr. Trimethylsilane [22 g., 0.297 mole]
and trifluoroethylene [4.43 g., 0.054 mole] in a silica tube
were shaken and irradiated for 250 hr. Fractionation in vacuo
gave a non-condensable gas (M = 3.8) assumed to be hydrogen
[0.00232 g., 1.16 mmole, equivalent to 0.004 % of the
trimethylsilane before reaction], trimethylsilane [17.7 g.,
0.239 mole, equivalent to 125% consumption based on the
olefin] and liquids condensing at -63° and -78°, combined,
[9.103 g.]. The combined liquids were investigated by infra-red
spectroscopy and shown to contain a trace of trimethylsilane,
trimethylfluorosilane, and an adduct of trimethylsilane with
trifluoroethylene (by comparison with the spectra of authentic
samples). The liquids were investigated by gas-liquid

chromatography using a "4 m. silicone" column at 120° at

0.5 kg./cm^2. and a nitrogen flow of 40 ml./min. Peaks

corresponding to trimethylsilane (minute trace),

trimethylfluorosilane 11.5% , an unidentified compound 6.6%

and the adduct pair 88% were obtained in order of elution.

The relative percentages of the adduct peaks was $41\pm 2\%$ and

$59\pm 2\%$. Quantitative calibration was not carried out

(see below). No olefinic products were detected.

The Low Conversion Reaction of Trimethylsilane with Trifluoroethylene

Trimethylsilane [7.4 g., 0.1 mole] and trifluoroethylene

[1.64 g., 0.02 mole] in a silica tube were shaken and irradiated

for 12 hr. Fractionation in vacuo gave fractions condensing

at -45, -63, -78, -96, -120 and -196°. The fractions

condensing at -45, -63 and -78° were combined and the fraction

condensing at -96° was refractionated, the -45, -63 and -78°

fractions again being combined and transferred to the first

combined products. This procedure gave unreacted trifluoroethylene

[1.31 g., 0.016 mole, equivalent to 20% reaction of the

olefin] and the total liquid products (at ambient temperatures)

along with much unreacted trimethylsilane. Investigation of

the liquid products by gas-liquid chromatography using a

"4 m. silicone" column at 50° and with a pressure of 0.5 kg./cm^2, and a nitrogen flow of 42 ml./min. gave three peaks only, corresponding to trimethylsilane and the adduct pair. Duplicate runs gave the following percentages.

retention time, (t) min.	peak-weight g.	%	t	peak-weight	%	identity
3.0	--	--	3.0	--	--	Me$_3$SiH
13.0	0.1965	34	13.1	0.1289	34.8	isomer I
15.4	0.3816	66	15.4	0.2415	65.2	isomer II

Authentic samples of 1,1,2-trifluoroethyltrimethylsilane, $CH_2F.CF_2.Si(CH_3)_3$, and 1,2,2-trifluoroethyltrimethylsilane, $CHF_2.CHF.Si(CH_3)_3$, in a mixture of known percentage gave the following results.

compound	retention time, (min.)	weight	%	weight of peak	%(peak)
$CH_2F.CF_2.Si(CH_3)_3$	13.0	0.259	38	0.1351	38.2
$CF_2H.CHF.Si(CH_3)_3$	15.5	0.424	62	0.2200	61.8

It can be seen from the above results that isomer I corresponds

to 1,1,2-trifluoroethyltrimethylsilane, $(CH_2F \cdot CF_2 \cdot Si(CH_3)_3)$,

and that isomer II corresponds to 1,2,2-trifluoroethyltri-

methylsilane, $(CF_2H \cdot CHF \cdot Si(CH_3)_3)$. It is also apparent

that the correction to the isomer ratio due to differences in

thermal conductivity is not significant here.

The Reaction of Trichlorosilane with Trifluoroethylene in the Absence of Light

Trichlorosilane [1.125 g., 8.3 mmole] and

trifluoroethylene [0.34 g., 4.15 mmole] were sealed in a silica

tube _in vacuo_ and shaken at room temperature in the absence of

light for 14 days. Fractionation _in vacuo_ gave trichlorosilane

[1.090 g., 8.05 mmole] and a fraction condensing at -120°

shown to consist of trifluoroethylene [0.34 g., 4.15 mmole,

100% recovery] contaminated with a small quantity of

trichlorosilane [0.03 g., 0.22 mmole]. No other components

were found. Identification was by infra-red spectroscopy and

gas-liquid chromatography. The reaction was repeated at 85°

for 100 hr. and the same procedure was used for investigation

of the products. The reactants were again recovered

quantitatively. No reaction had taken place in either case.

ADDITION REACTIONS OF SILANES WITH
1-CHLORO-2-FLUOROETHYLENE.

Reaction of trichlorosilane with 1-chloro-2-fluoroethylene.

a) In the absence of light. Trichlorosilane
[135.5 g., 1.00 mole] and 1-chloro-2-fluoroethylene [8.05 g.,
0.10 mole] were sealed in a silica tube and left in a dark
cupboard at room temperature for fourteen days. Fractionation
in vacuo, followed by quantitative gas-liquid chromatography on
a 4 m. silicone column (M.S.550) at 80°, gave 1-chloro-2-
fluoroethylene [8.05 g., 0.10 mole] and trichlorosilane
[134.9 g., 0.99 mole] only. The infra-red spectrum of the
contents of the tube showed no peaks other than those ascribable
to the reactants. No reaction was detected.

b) The photochemical reaction with a silane/olefin ratio
of 2.5:1. Trichlorosilane [135.5 g., 1.00 mole] and 1-chloro-
2-fluoroethylene [34.0 g., 0.4 mole] were irradiated with
shaking for 116 hr. before a 500 watt ultraviolet lamp.
Fractionation in vacuo gave 1-chloro-2-fluoroethylene [9.2 g.,
1.12 mole, equivalent to 73% reaction of the olefin] , excess
of trichlorosilane, and a pale yellow liquid which remained in
the reaction tube at room temperature. Fractionation under
nitrogen in a 20 ml. pear-shaped flask, fitted with a 130 x 8 mm.

vacuum jacketed column, packed with glass helices, and fitted

with a partial reflux take-off head, gave trichlorosilane

b.p.33°, a fraction collected at 100-102°, [0.834 g.] which

was shown to be 1-fluoroethyltrichlorosilane, containing a

trace of 2-fluoroethyltrichlorosilane ($\sim$ 5%), and a fraction

collected at 140-6° [13.67 g.] , which was shown to be a

mixture of the isomeric adducts of trichlorosilane to 1-chloro-

2-fluoroethylene and traces of both fluoroethyltrichlorosilanes

($\sim$ 5%). A refractionated sample of the adduct gave a

fraction free from the impurity of the fluoroethylsilanes, and

was recognised as the adduct of trichlorosilane with

1-chloro-2-fluoroethylene by elemental analysis for carbon,

hydrogen and chlorine.

Found: C, 11.3; H, 1.39; Cl, 65.3%;

$C_2H_3Cl_4FSi$ requires, C, 11.1; H, 1.4; Cl, 65.5%.

A high boiling viscous material [16 g.] which was not

distillable at atmospheric pressure remained in the flask.

Percentages were obtained by means of gas-liquid chromatography

as indicated below and the overall yields (table 12) are based

on these results.

c) **The photochemical reaction with a silane/olefin ratio of** 5:1. Trichlorosilane [14.0 g., 0.1 mole] and
1-chloro-2-fluoroethylene [5.32 g., 0.066 mole] were

irradiated in a silica tube with shaking for 100 hr.

Fractionation in vacuo gave unreacted 1-chloro-2-fluoroethylene

[1.75 g., 0.028 mole, equivalent to 67% reaction of the olefin],

unreacted trichlorosilane, and a high boiling liquid [13.4 g.]

which remained in the tube at room temperature under vacuum.

Fractionation under nitrogen in a 20 ml. pear-shaped flask

fitted with a 130 x 8 mm. vacuum jacketed column packed with

glass helices, and fitted with a partial reflux take-off head

gave fractions at 35-95°, shown to be a mixture of trichloro-

silane and silicon tetrachloride; 95-114° [1.6 g.] , shown to

be silicon tetrachloride and 1-fluoroethyltrichlorosilane (51%);

and 140-6° [10.7 g.] shown to be the isomeric 1:1 adducts of

trichlorosilane with 1-chloro-2-fluoroethylene.   A small

quantity of high boiling material ($\sim$ 0.3 g.) remained in the

flask.

d)   The photochemical reaction with a silane/olefin ratio

of 10:1.   Trichlorosilane [135.5 g., 1.0 mole] and

1-chloro-2-fluoroethylene [8.05 g., 0.10 mole] were irradiated

with shaking in a silica tube for 100 hr.   Fractionation

in vacuo gave unreacted 1-chloro-2-fluoroethylene [0.16 g.,
0.002 mole, equivalent to 98% reaction of the olefin], unreacted
trichlorosilane containing traces of silicon tetrachloride,
and a high boiling material [16.7 g.] which remained in the
tube at room temperature under vacuum. Fractionation of
11.5 g. of this high boiling material under nitrogen in a
20 ml. pear-shaped flask as described above gave fractions at
33-100°, [2.52 g.] shown to be trichlorosilane and silicon
tetrachloride; 102-104°, [6.81 g.] shown to be
1-fluoroethyltrichlorosilane containing a small quantity of
2-fluoroethyltrichlorosilane (~ 10%); 106-114°, [0.35 g.]
shown to be a mixture of 1-fluoroethyltrichlorosilane (31%) and
2-fluoroethyltrichlorosilane (68%); 114-120°, [0.97 g.] shown
to be 2-fluoroethyltrichlorosilane; and fractions at 134°,
[0.98 g.] and 140-50° [1.02 g.] which were both shown to be
isomeric mixtures of the 1:1 adducts of trichlorosilane with
1-chloro-2-fluoroethylene. A viscous brown liquid [0.8 g.]
remained in the flask.

Identification and evaluation of the components of the
    fractions from the reactions of trichlorosilane with
    1-chloro-2-fluoroethylene.

The fractions were investigated by means of gas-liquid
chromatography using a 4 m. silicone "(M.S.550)" column at 150°

with an inlet pressure of 1 kg./cm^2. on a Perkin Elmer "Fractometer" model 452 fitted with thermistor detectors. Samples for the calibration of the column for 2-fluoroethyltrichlorosilane and 1-fluoroethyltrichlorosilane were obtained respectively from the reaction of trichlorosilane with vinyl fluoride and from the 102-4° fraction from the reaction of trichlorosilane with 1-chloro-2-fluoroethylene with a silane/olefin ratio of 10:1. Pure samples of the isomeric chlorofluoroethyltrichlorosilanes were obtained by preparative gas-liquid chromatography. Structures were assigned on the basis of elemental analysis for carbon and hydrogen; nuclear magnetic resonance spectroscopy and hydrolysis data, (table 30).

TABLE 30

Identification of the adducts required for gas-liquid
chromatographic calibrations.

Compound	Source	C (%)	H (%)	Hydrolysis
$CH_2F.CH_2.SiCl_3$	$SiHCl_3$ + $CH_2:CHF$ (118°)	13.4	1.9	$CH_2:CH_2$
$CH_2F.CH_2.SiCl_3$	$SiHCl_3$ + $CHCl:CHF$ (114–120°)	13.4	2.2	$CH_2:CH_2$
$CH_3.CHF.SiCl_3$	$SiHCl_3$ + $CHCl:CHF$ (102–104°)	13.4	2.4	No olefin
$H(CHCl.CHF)SiCl_3$ isomeric mixture	$SiHCl_3$ + $CHCl:CHF$ (140–146°)	11.3	1.4	$CH_2:CHF$ $CH_2:CHCl$
1st peak (140–146°)	"	-	-	Not carried out
2nd peak (140–146°)	"	11.3	1.6	Not carried out
	$C_2H_4Cl_3FSi$ requires $C_2H_3Cl_4FSi$ requires	13.2 11.1	2.2 1.4	

The infra-red spectra of the fractions obtained by preparative gas-liquid chromatography indicate that separation had been achieved.

Infra-red band table for 1-chloro-2-fluoroethyl-trichlorosilane,

$CH_2F.CHCl.SiCl_3$

2.78	m	7.15	m	90.0	s
3.00	m	7.46	m	10.64	s
3.37	}w	8.25	s	11.07 }s	
3.42		8.9	vs	11.18	
6.20	vw	9.45	vs	12.7	m
7.02	w				

Infra-red band table for 2-chloro-1-fluoroethyl-trichlorosilane,

$CH_2Cl.CHF.SiCl_3$

2.90	m	7.7	}m	11.79	s
3.37	m	7.75		11.84	s
3.58	w	7.925	m	12.38	m
6.15	w	8.2	m	12.55	s
6.75	vw	8.55	}s,	13.05	s
6.84	vw	8.9	}broad	13.6	}m
6.90	w	9.2		13.65	
7.02	m	9.47		13.85	
7.525	m	9.86	s	14.65	w
7.65	m	10.88	m	15.46	m

Percentages were obtained by means of relative peak areas corrected for small differences in thermal conductivity in the

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following manner.   A known mixture of A and B of molar

composition A' and B' gives peak areas "a" and "b".   The true

"area" of "a" for comparison with "b" should be $\frac{bA'}{B'}$,

therefore any other peak of compound A must be corrected by a

factor $\frac{A'b}{B'a}$ for comparison with any other peak B in the same

mixture.   Thus a 1:1 mixture of 1-fluoroethyltrichlorosilane

and 2-fluoroethyltrichlorosilane gave peak areas in the ratio

1:1.02 respectively;   therefore the factor for

1-fluoroethyltrichlorosilane is 1.02.   Similarly, a mixture of

2-chloro-1-fluoroethyltrichlorosilane [0.60 g.] and

1-chloro-2-fluoroethyltrichlorosilane [0.262 g.] gave peak

areas in the ratio 32.29:14.44, therefore the factor for

1-fluro-2-chloroethyltrichlorosilane is 0.969.   Retention times

under the conditions stated above are given below.

$$SiHCl_3 \qquad\qquad 3.9 \text{ min.}$$
$$SiCl_4 \qquad\qquad 5.0 \text{ "}$$
$$CH_3 \cdot CHF \cdot SiCl_3 \qquad 12.4 \text{ "}$$
$$CH_2F \cdot CH_2 \cdot SiCl_3 \qquad 15.0 \text{ "}$$
$$CH_2F \cdot CHCl \cdot SiCl_3 \qquad 25.6 \text{ "}$$
$$CH_2Cl \cdot CHF \cdot SiCl_3 \qquad 31.4 \text{ "}$$

Each fraction from the reactions was investigated

in this way and overall percentages of both the 1:1 adduct and

the dechlorinated 1:1 adduct were obtained, (table 13).

Isomer ratios for the adduct were obtained, but only in the

reaction with a silane/olefin ratio of 10:1 was the percentage of 2-fluoroethyltrichlorosilane significant.

The photochemical reaction of the adduct of trichlorosilane to 1-chloro-2-fluoroethylene with methyldichlorosilane.

A sample of the adduct of trichlorosilane to

1-chloro-2-fluoroethylene was investigated by quantitatively

calibrated gas-liquid chromatography and shown to consist

of the two isomers 1-chloro-2-fluoroethyltrichlorosilane,

$CH_2F.CHCl.SiCl_3$, and 2-chloro-1-fluoroethyltrichlorosilane,

$CH_2Cl.CHF.SiCl_3$, in the ratio 1:4.38.   A sample of the adduct

$\left[3.0 \text{ g.}, 13.9 \text{ mmole} \right]$ was photolysed with methyldichlorosilane

$\left[16.0 \text{ g.}, 139 \text{ mmole} \right]$ for 100 hr. before a 500 watt "Hanovia"

ultraviolet lamp.   The tube was opened in vacuo connected to

a volume of ca. 80 ml. and the contents of the tube were

allowed to warm up to room temperature.   The 80 ml. trap

was also at room temperature and not at -196° as is normally

the case.   At room temperature (the pressure was not greater

than 10 cm. of mercury) the tube was isolated from the gases

in the trap and the contents of the trap were investigated by

infra-red spectroscopy and shown to consist of methyldichloro-

silane.   No olefinic compound was detected.   The liquid in

the tube was investigated by gas-liquid chromatography on a

4 m. silicone (M.S.550) column at 150° with the flow rate

adjusted to allow good separation of all the expected products.

Retention times were checked with authentic samples before and after the reaction mixture was investigated, and the column was quantitatively calibrated for the four substituted ethyl silanes. Peaks were obtained corresponding to methyldichlorosilane and methyltrichlorosilane, (these were not measured quantitatively), the isomeric fluoroethylsilanes, $CH_2F.CH_2.SiCl_3$ and $CH_3.CHF.SiCl_3$, in the ratio 1:15.3, and the isomeric chlorofluoroethyltrichlorosilanes, $CH_2F.CHCl.SiCl_3$ and $CH_2Cl.CHF.SiCl_3$ in the ratio 1:1.19, (the ratios quoted are peak areas corrected to molar ratios). The compound 2-fluoroethylmethyldichlorosilane, $CH_2F.CH_2.SiCl_2Me$, was not detected in the reaction mixture although the peak due to this compound in the synthetic mixture was easily identifiable.

These ratios allow the calculation of the percentage reaction of each isomer of the adduct and they also give an approximation to the relative rate of halogen abstraction.

Let the isomer ratio of the adduct before reaction be expressed in terms of x, after the reaction in terms of y, and the ratio of the reduced adduct in terms of z.

i.e., $CH_2F.CHCl.SiCl_3/CH_2Cl.CHF.SiCl_3$ = 4.38x (before reaction)

$CH_2F.CHCl.SiCl_3/CH_2Cl.CHF.SiCl_3$ = 1.19y (after reaction)

$CH_3.CHF.SiCl_3/CH_2F.CH_2.SiCl_3$ = 15.3z (after reaction)

Then $x = y + z$ (for the α -F isomers)

and $4.38x = 1.19y + 15.3z$ (for the β -F isomers).

It follows that $y = 4.78z$

therefore, % reaction of

$$CH_2F.CHCl.SiCl_3 \quad = \quad \frac{1}{5.78} \quad = \quad 17.3\%$$

and of $CH_2Cl.CHF.SiCl_3 \quad = \quad \frac{15.3}{24.56} \quad = \quad 61.5\%$

The relative rate of dehalogenation is approximately $\frac{\beta Cl}{\alpha Cl} = 3.55$

for chlorine abstraction.

The relative rate, but not the percentages can be arrived at

by a simple comparison of the ratio of the dehalogenated

adducts.   Thus the ratio of $\beta : \alpha$ chlorine abstraction

equals $\frac{15.3}{4.38}$:1 or   3.5:1, indicating an error of 1.4% in the

measurement and evaluation of peak areas.

The reaction of the adduct of trichlorosilane to 1-chloro-2-fluoroethylene with trichlorosilane in the absence of light.

The adduct of trichlorosilane to 1-chloro-2-fluoro-

ethylene $\begin{bmatrix} 0.2605 \text{ g.}, \ 2.25 \text{ mmole} \end{bmatrix}$ and trichlorosilane $\begin{bmatrix} 2.7 \text{ g.}, \end{bmatrix}$

$20.0 \text{ mmole} \end{bmatrix}$ were shaken at the ambient temperature of the

ultraviolet lamp (35-40°) in the absence of light for

14 days.   Investigation by gas-liquid chromatography gave

peaks attributable to trichlorosilane and the isomeric adducts

($CH_2Cl.CHF.SiCl_3$ and $CH_2F.CHCl.SiCl_3$) only.   Reaction had

not taken place to any significant extent.

The photochemical reaction of the adduct of trichlorosilane to 1-chloro-2-fluoroethylene with trimethylsilane.

A sample of the adduct of trichlorosilane with

1-chloro-2-fluoroethylene was investigated by quantitatively

calibrated gas-liquid chromatography and shown to consist of

the two isomers 1-chloro-2-fluoroethyltrichlorosilane

$CH_2F.CHCl.SiCl_3$ and 2-chloro-1-fluoroethyltrichlorosilane

$CH_2Cl.CHF.SiCl_3$ in the ratio 1:1.07.   A sample of this

adduct [0.864 g., 4.0 mmole] and trimethylsilane [2.96 g.,

40.0 mmole] were photolysed for 50 hr. before a 500 watt

"Hanovia" ultraviolet lamp.   The tube was opened in vacuo to

a volume of ca. 1 litre and the volatile components allowed

to vaporise at room temperature.   The tube was isolated from

the 1 litre bulb, and the contents of the bulb were shown by

infra-red spectroscopy and gas-liquid chromatography indicated

the presence of trimethylchlorosilane [0.430 g., 39.7 mmole,

equivalent to 99% reaction based on the adduct] , the isomeric

fluoroethyltrichlorosilanes [0.715 g., 3.94 mmole ,

equivalent to 98% reaction] , and excess trimethylsilane.

1-Fluoroethyltrichlorosilane, $CH_3.CHF.SiCl_3$, and

2-fluoroethyltrichlorosilane, $CH_2F \cdot CH_2 \cdot SiCl_3$ were found to be in

the ratio 1.07:1 (identical with the original adduct ratio)

by quantitatively calibrated gas-liquid chromatography.   The

original adduct could not be detected in the reaction products.

Neither vinyl fluoride nor an adduct of trimethylsilane to

vinyl fluoride was detected among the reaction products.

REACTION OF TRIMETHYLSILANE WITH
1-CHLORO-2-FLUOROETHYLENE

Reaction of Trimethylsilane with 1-chloro-2-fluoroethylene under Reduced Pressure

Trimethylsilane [12.6 g., 0.17 mole] and 1-chloro-2-fluoroethylene [13.66 g., 0.17 mole] were allowed to expand into an evacuated 20 l. bulb fitted with a water cooled silica insert for ultraviolet irradiation and with a mercury manometer. The pressure at room temperature was ca. 300 mm. The contents of the bulb were irradiated for 10 hr. after which they were transferred to the vacuum system and fractionated in vacuo. Fractionation gave a gaseous mixture of trimethylsilane and 1-chloro-2-fluoroethylene [0.306 mole] of molecular weight 78.0 (calc. for Me_3SiH = 74, CHCl:CHF = 80.5), indicating a mixture of approximately 50% of each component. Infra-red spectroscopy indicated the presence of trimethylsilane and 1-chloro-2-fluoroethylene along with traces (estimated at less than 1%) of vinyl fluoride. Investigation by gas-liquid chromatography was not carried out. An approximate estimation of the percentage reaction of the olefin based on molecular weight is 8%. A liquid condensing at $-36°$ was investigated by infra-red spectroscopy and gas-liquid chromatography. It was shown to consist of trimethylchlorosilane [1.4 g., 13.0 mmole, equivalent

to ca. 95% of the olefin reacted] and a compound with the same
retention time as l-fluoroethyltrimethylsilane [1.5 g., 8.5 mmole,
equivalent to ca. 60% of the olefin reacted].

Reaction of Trimethylsilane with l-chloro-2-fluoroethylene in the Presence of Mercury

Trimethylsilane [15.25 g., 0.23 mole] and l-chloro-2-
fluoroethylene [2.095 g., 0.026 mole] in a silica tube with ca.
2 g. mercury were irradiated with shaking for 144 hr. Fractionation
in vacuo gave vinyl fluoride [1.065 g., 0.023 mole, equivalent
to 89% reaction of the olefin], containing a trace of ethylene
(<1%) identified by infra-red spectroscopy and gas-liquid
chromatography, trimethylchlorosilane [2.7 g., 0.025 mole,
equivalent to 96% reaction of the olefin] identified by infra-
red spectroscopy and gas-liquid chromatography, and a compound
having a retention time similar to that of a fluoroethyltri-
methylsilane (ca. 4% based on this assumption), along with
unreacted trimethylsilane.

A duplicate reaction was carried out for 96 hr. to give
vinyl fluoride (90%), trimethylchlorosilane (96%) and the
possible fluoroethyltrimethylsilane (ca. 4%). No unreacted
l-chloro-2-fluoroethylene was detected in either reaction.
At the time of the experiment only one isomer of the

monofluoroethyltrichlorosilanes was available and it was

impossible to determine which isomer was present among the

reaction products.

The Reaction of Trimethylsilane with 1-chloro-2-fluoroethylene (1:1)

Trimethylsilane [1.48 g., 20.0 mmole] and 1-chloro-2-

fluoroethylene [1.61 g., 20.0 mmole] were irradiated with shaking

for 90 hr. in a silica tube (volume ca. 20 ml.). Fractionation

in vacuo gave vinyl fluoride [0.0039 g., 0.085 mmole, equivalent

to ca. 4% of the olefin], unreacted trimethylsilane [0.533 g.,

7.2 mmole, equivalent to 36% recovery], and trimethylchlorosilane

[0.24 g., 2.3 mmole, equivalent to 18% of the trimethylsilane

reacted or 11.1% of the trimethylsilane originally present].

Identification was by infra-red spectroscopy and gas-liquid

chromatography. A high boiling liquid remained in the tube

[2.6 g.] which on prolonged heating (hot air blower temperatures)

in vacuo released a further sample which was shown to consist

of trimethylsilane [0.0296 g., 0.4 mmole, equivalent to 2%

of the trimethylsilane originally present] and trimethylchloro-

silane [0.0123 g., 0.12 mmole, equivalent to ca. 0.6% of the

trimethylsilane originally present] identified by gas-liquid

chromatography. The remaining viscous yellow oil had an infra-

red absorption spectrum corresponding to that of the high

boiling oil from the irradiation of 1-chloro-2-fluoroethylene

alone, together with some possible silicon containing adduct.

Found: C, 39.1; H, 3.6; Cl, 25.3%;

$C_9H_{17}Cl_2F_3$ requires,   C, 38.6; H, 6.0; Cl, 25.4%.

This suggests that the average number of olefin units per

silyl group is of the order of 3. The structure can not be

defined from this data.

A sample of the high boiling oil [0.0983 g.] was transferred

to a hydrolysis bulb, and hydrolysed in vacuo with freshly

prepared 10% aqueous sodium hydroxide solution. Fractionation

of the products gave a gas condensing at -196° which was shown

by infra-red spectroscopy to be vinyl fluoride [0.00145 g.,

0.031 mmole] as the only volatile component. The liquid was

presumed to be mainly a polymer of 1-chloro-2-fluoroethylene

and was not further investigated.

The Reaction of Trimethylsilane with 1-chloro-2-fluoroethylene
(10:1)

Trimethylsilane [3.06 g., 41.5 mmole] and 1-chloro-2-

fluoroethylene [0.333 g., 4.15 mmole] were irradiated with

shaking for 200 hr. in a silica tube (volume ca. 20 ml.).

Fractionation in vacuo gave unreacted trimethylsilane

[2.32 g., 31.4 mmole, equivalent to 75% recovery] and a liquid

[1.073 g.] remaining in the reaction tube at room temperature.

The trimethylsilane was identified by infra-red spectroscopy and gas-liquid chromatography. Vinyl fluoride was not detected in the gaseous products. Investigation of the liquid by means of gas-liquid chromatography indicated the presence of trimethylsilane (18% by peak areas) and another component with a retention time identical with both trimethylchlorosilane and 1-fluoroethyltrimethylsilane. A peak corresponding to 2-fluoroethyltrimethylsilane was not detected. The liquid was transferred to a hydrolysis bulb and hydrolysed _in vacuo_ with 10% aqueous sodium hydroxide solution. The hydrolysis products were transferred to the vacuum system through a tube loosely packed with glass wool and phosphorous pentoxide and fractionated _in vacuo_ to give trimethylsilane [0.013 g., 1.7 mmole, equivalent to 4.1% recovery], 1-fluoroethyltrimethylsilane [0.7 g., 4.1 mmole, equivalent to 98% based on the olefin] and hexamethyldisiloxane [0.025 g., 1.7 mmole, equivalent to 83% recovery based on olefin consumed]. Ethylene and vinyl fluoride could not be detected in the hydrolysis products.

The Reaction of Trimethylsilane with 1-chloro-2-fluoroethylene (5:1)

Trimethylsilane [1.48 g., 0.201 mole] and 1-chloro-2-fluoroethylene [0.322 g., 0.0394 mole] were irradiated with shaking for 100 hr. in a silica tube (volume _ca._ 20 ml.).

Fractionation in vacuo gave vinyl fluoride [0.008 g., 0.7 mmole,

equivalent to 2% of the original olefin, 4% of the olefin

reacted], 1-chloro-2-fluoroethylene [0.162 g., 0.0198 mole,

equivalent to a recovery of 50%] and trimethylsilane [1.302 g.,

0.176 mole, equivalent to a 4 molar excess plus 40% recovered,

based on the olefin], along with a liquid [0.254 g.] remaining

in the tube at room temperature. The gases were identified and

estimated by gas-liquid chromatography and infra-red spectroscopy.

Investigation of the liquid by gas-liquid chromatography on a

Perkin Elmer "Vapour Fractometer" (model 116) using a 4 m.

silicone column at 100° with a nitrogen flow of 70 ml./min.

indicated the presence of a trace of trimethylsilane (less

than 0.5%) and two other components with peak areas in the ratio

4:1. The retention time of the first peak corresponded to that

of trimethylchlorosilane, but calibration runs with

ethyltrimethylsilane, trimethylchlorosilane and 1-fluoro-

ethyltrimethylsilane indicated that even though the retention

times are slightly different, a mixture of any two of these

compounds is not resolved on the column. Attempts to achieve

a separation by reducing both the temperature and the flow-rate

of the nitrogen carrier gas were not successful. A sample

of the high boiling liquid [0.2054 g.] was hydrolysed <u>in vacuo</u>

with 10% aqueous sodium hydroxide solution to give

trimethylsilane [0.0036 g., 0.486 mmole] vinyl fluoride

[0.0138 g., 3.0 mmole], and 1-fluoroethyltrimethylsilane [0.0786 g.,

6.56 mmole], identified and estimated by infra-red spectroscopy,

molecular weight determination, and gas-liquid chromatography.

If it is assumed that the vinyl fluoride arose from hydrolysis

of 2-chloro-1-fluoroethyltrimethylsilane (the validity of this

assumption is discussed on page 173) this allows the estimation

of the weight of trimethylchlorosilane by difference, i.e. 3.0 mmole

of vinyl fluoride is equivalent to 3.0 mmole of 2-chloro-1-

fluoroethyltrichlorosilane, or 0.0466 g. leaving a deficit of

0.0766 g., 7.1 mmole if the remainder is assumed to be

trimethylchlorosilane not contaminated with any telomeric

material. This now allows the estimation of the following total

percentages; trimethylchlorosilane [0.0967 g., 8.9 mmole,

equivalent to 45.4% of the olefin reacted], 1-fluoroethyl-

trimethylsilane [0.0985 g., 8.2 mmole, equivalent to 42%

reaction of the olefin], and 2-chloro-1-fluoroethyltrimethylsilane

[0.0589 g., 3.78 mmole equivalent to 19.4% reaction of the

olefin]. The compound assumed to be 2-chloro-1-

fluoroethyltrimethylsilane was not separately identified.

The Reaction of Trimethylsilane with 1-chloro-2-fluoroethylene in the Absence of Light at 85°

Trimethylsilane [0.614 g., 8.30 mmole] and 1-chloro-2-fluoroethylene [0.333 g., 4.15 mmole] were sealed in a silica tube (20 ml.) _in vacuo_ and maintained at 85° for 100 hr. in the absence of light. As the reactants are not separable by vacuum fractionation they were transferred to the system and investigated by infra-red spectroscopy and gas-liquid chromatography. The products were found to consist of a gas [293.5 ml. at 20° equivalent to 0.01240 mole or 98% recovery] containing three components by gas-liquid chromatography. Calibration with authentic samples indicated the presence of cis-1-chloro-2-fluoroethylene, trimethylsilane, and trans-1-chloro-2-fluoroethylene. As no other components were observed and the peaks found overlapped, individual percentages were not determined.

HYDROLYSIS,PYROLYSIS AND FLUORINATION REACTIONS

Hydrolysis of the Adduct $H(CH_2.CHF)SiCl_3$

A freshly prepared 10% aqueous sodium hydroxide
solution was slowly added through the tap of a hydrolysis
bulb into which the adduct [0.2238 g., 1.23 mmole] had
previously been introduced. A vigorous reaction took place
which appeared to be complete after 30 seconds. The bulb
was shaken for 5 min. and the volatile products were
transferred to the vacuum system. Fractionation in vacuo
gave one fraction only, which condensed in a trap at -196°,
along with water which condensed in a trap at -24°. The -196°
fraction was identified by infra-red spectroscopy and
molecular weight determination as ethylene [0.0056 g., 1.22
mmole, equivalent to 99% recovery], M = 28, calc. for C_2H_4,
M = 28. Fluoride ions were shown to be present in the aqueous
residues remaining in the bulb by the AlizarinS-Zirconium
nitrate test.   Attempted hydrolysis with distilled water
gave only the white polysiloxane.

Pyrolysis of the Adduct $H(CH_2.CHF)SiCl_3$

The adduct [0.4038 g., 2.22 mmole] was pyrolysed in vacuo
in a silica tube at 450° for 24 hr. The products were

transferred to the vacuum system and fractionated through traps at -24, -120, and -196°. Most of the product was found to have condensed in the trap at -196° $\left[89.62 \text{ ml. at } 21°\right]$ with only a small percentage in the trap at -120° $\left[3.21 \text{ ml.}\right.$ at 21°$\left.\right]$. The trap at -24° was empty. The -196° fraction was identified as a chlorofluorosilane and ethylene, and the -120° fraction as a chlorofluorosilane by infra-red spectroscopy. The fractions were combined and the average molecular weight found to be 96.82 (theoretical average for C_2H_4 and $Cl_3FSi = 90.7$). The gases were condensed in a hydrolysis bulb and shaken with fresh 5% aqueous sodium hydroxide solution and fractionated in vacuo to give ethylene $\left[0.00486 \text{ g., } 1.74 \text{ mmole, equivalent to } 78\% \text{ recovery}\right]$. The aqueous residues contained both chloride and fluoride ions. An attempt to increase the yield of ethylene was made by pyrolysis at a lower temperature.

The adduct $\left[0.5124 \text{ g., } 2.83 \text{ mmole}\right]$ was pyrolysed as above at 220° for 24 hr. to give a gas $\left[130.2 \text{ ml. at } 23°\right]$, M = 89.8 which on shaking with water gave ethylene $\left[0.076 \text{ g., } 2.74 \text{ mmole,}\right.$ equivalent to 97% theoretical$\left.\right]$ identified by its infra-red spectrum and molecular weight (28.1).

Fluorination of the Adduct $H(CH_2.CHF)SiCl_3$

Fluorination was first attempted by means of antimony trifluoride activated by antimony pentachloride. Thus the adduct [1.65 g., 9.08 mmole] was passed under vacuum through a 400 x 20 mm. tube packed loosely with antimony trifluoride and glass wool, and activated by a few drops of antimony pentachloride. After six passes the volatile material was transferred to the system and fractionated to give silicon tetrafluoride [0.838 g., 0.00805 mole, equivalent to 88.5% reaction] and ethylene [0.234 g., 0.00835 mole, equivalent to 92% reaction], identified by infra-red spectroscopy and average molecular weight.

The fluorination was repeated using antimony trifluoride which had been activated by passing chlorine gas through it for 30 seconds. Thus, the adduct [1.963 g., 10.8 mmole] was passed under vacuum through a 400 x 20 mm. tube packed loosely with activated antimony trifluoride and glass wool. After six passes the volatile material was transferred to the system to give a fluorinated adduct (of trichlorosilane) [0.856 g., 6.5 mmole, equivalent to 60% recovery], condensing in a trap cooled to -78°, and a mixture of silicon

tetrafluoride and ethylene $\left[\text{1080 ml. at 19}^{\text{o}}, \text{4.5 mmole}\right]$ condensing in a trap cooled to -196°. The fluorinated adduct was recognised by its molecular weight and analysis for carbon and hydrogen.

Found: C, 18.7; H, 3.1%; M, 131 ;

$C_2H_4F_4Si$ requires,   C, 18.9; H, 3.1%; M, 132.

Infra-red band table for 2-fluoroethyltrifluorosilane
$(\underline{CH_2F.CH_2.SiF_3})$

3.34 s	7.01 m	10.2 vs
3.40 m	7.15 s	11.24 ⎫
4.28 ⎫ w	7.62 vs	11.30 ⎬ vs
4.32 ⎭	8.22 s	11.38 ⎭
4.88 ⎫	8.35 vs	11.80 s
4.96 ⎪	8.50 s	12.25 m
5.08 ⎪ w	8.90 s	12.99 s
5.24 ⎬	9.15 m	13.44 s
5.27 ⎪	9.45 s	13.88 s
5.37 ⎭	9.67 ⎫	14.25 s
6.28 w	9.72 ⎬ vs	14.90 ⎫ m
6.83 m	9.80 ⎭	14.98 ⎭

The compound slowly decomposed at room temperature in a "Pyrex" ampoule, releasing silicon tetrafluoride and ethylene.

Hydrolysis of the Adduct $H(CH_2.CHF)SiCl_2Me$

A freshly prepared 10% aqueous sodium hydroxide solution was slowly added through the tap of a hydrolysis bulb into which the adduct [0.6096 g., 3.79 mmole] had previously been condensed. The bulb was shaken for 5 min. and the volatile products transferred to the vacuum system and fractionated to give one fraction only condensing in a trap cooled to 196°, molecular weight 28.1, which was shown to be ethylene [0.0108 g., 3.86 mmole, equivalent to 100% recovery] by infra-red spectroscopy, along with water which condensed in a trap cooled to -24°. Fluoride ions were detected in the aqueous residues by the AlizarinS-Zirconium nitrate test. Attempted hydrolysis with water gave no readily volatile products.

Hydrolysis of the Adduct $H(CH_2.CHF)Si(CH_3)_3$

A freshly prepared 10% aqueous sodium hydroxide solution was slowly added through the trap of a hydrolysis bulb into which the adduct [0.1468 g., 1.223 mmole], containing a 2% impurity of trimethylsilane, had previously been introduced. A vigorous reaction took place. The bulb was shaken for 10 min. and allowed to stand overnight, after which the volatile

products were transferred to the vacuum system.

Fractionation _in vacuo_ through traps cooled to -24, -36, -96, and -196° gave a main fraction condensing at -196°, molecular weight 28.4, identified as ethylene [0.0329 g., 1.17 mmole, equivalent to 96% conversion] by infra-red spectroscopy. A trace of trimethylsilane was detected in the trap at -96°, and water and any higher boiling products were condensed in the trap at -24°. Fluoride ions were detected in the aqueous residue remaining in the bulb by the AlizariuS-Zirconium nitrate test.

Hydrolysis of 1-fluoroethyltrichlorosilane, $CH_3.CHF.SiCl_3$

A freshly prepared 20% aqueous sodium hydroxide solution was slowly added through the tap of a hydrolysis bulb into which 1-fluoroethyltrichlorosilane [0.5136 g., 2.82 mmole] had previously been introduced. A vigorous reaction took place, and the bulb was shaken for 10 min. The bulb was then opened _in vacuo_ and any volatiles were transferred to a trap at -196°. The tap was then closed and the bulb immersed in boiling water for three hours, periodically opening the tap to allow any volatiles to be condensed into the cold trap. Examination of the contents of the trap

indicated the presence of water only. Fluoride ions could

not be detected in the aqueous residues remaining in the bulb

after hydrolysis.

Pyrolysis of 1-fluoroethyltrichlorosilane, $CH_3.CHF.SiCl_3$

1-fluoroethyltrichlorosilane $\left[0.655 \text{ g., } 3.61 \text{ mmole}\right]$

was pyrolysed in vacuo in a silica tube at 250° for 24 hr.

The products were transferred to the vacuum system and the

presence of ethylene and an unidentified silicon compound was

indicated by infra-red spectroscopy. A trace of a pale brown

solid residue remained in the tube. The volatile products

were transferred to a hydrolysis bulb and shaken with degassed

distilled water. Fractionation of the contents of the bulb

in vacuo through traps maintained at -24, -96, and -196°

gave a major fraction condensing at -196°, shown to be

ethylene $\left[0.00231 \text{ g., } 0.825 \text{ mmole, equivalent to } 23\% \text{ conversion}\right]$

by molecular weight and infra-red spectroscopy. The minor

fraction condensing at -24° was shown to be water. No attempt

to identify the siliceous material was made.

Hydrolysis of the Adduct $H(CF_2.CHF)SiCl_3$

The adduct of trichlorosilane with trifluoroethylene

$\left[0.1773 \text{ g., } 0.82 \text{ mmole}\right]$ in a hydrolysis bulb was hydrolysed

in vacuo with an excess of freshly prepared 10% aqueous
sodium hydroxide solution. The bulb was shaken for 5 min.
and the contents were transferred to the vacuum system to
give a gas [0.82 mmole, equivalent to 100% conversion].
Fractionation in vacuo allowed only partial separation into
the components which were recognised as 1,1,2-trifluoroethane
and 1,2-difluoroethylene by infra-red spectroscopy and molecular
weight determination. 1,1-difluoroethylene could not be
detected by infra-red spectroscopy. The fractions were
recombined and investigated by gas-liquid chromatography
using an 8 m. "Kel-F oil" column under conditions set to
separate a synthetic mixture of the isomeric difluoroethylenes.
The gaseous mixture was found to consist of 1,1,2-
trifluoroethane (80%) and cis- and trans-1,2-difluoroethylene
(20%). Again no 1,1-difluoroethylene was detected.

The hydrolysis was repeated using 1% sodium hydroxide
and carrying out the investigation as above to give 100%
conversion to a gas shown to consist of 1,1,2-trifluoroethane
(87.5%) and cis- and trans-1,2-difluoroethylene (12.5%).
Fluoride ions were detectable in both the above hydrolyses.
An attempted hydrolysis with water gave no volatile products

along with the white polysiloxane.

Hydrolysis of the Adduct H(CF$_2$.CHF)SiCl$_2$Me

The adduct of dichloromethylsilane with trifluoroethylene [0.1307 g., 6.64 mmole] in a hydrolysis bulb was hydrolysed in vacuo with an excess of freshly prepared 10% aqueous sodium hydroxide solution. The bulb was shaken for 5 min. and the contents were transferred to the system to give a gas [6.57 mmole, equivalent to 99% conversion]. Fractionation in vacuo followed by infra-red spectroscopy and molecular weight determination indicated the presence of 1,1,2-trifluoroethane and 1,2-difluoroethylene, and that complete separation had not been achieved. 1,1-difluoroethylene was not detectable by infra-red spectroscopy. Investigation of the products, after recombination, by gas-liquid chromatography using an 8 m. "Kel-F oil" column at room temperature indicated the presence of 1,1,2-trifluoroethane (57%), 1,2-difluoroethylene (40.8%) and 1,1-difluoroethylene (2.2%).

The hydrolysis was repeated using 1% sodium hydroxide solution, carrying out the investigation as above, to give 99% conversion to a gas shown to consist of 1,1,2-trifluoroethane

(84%), 1,2-difluoroethylene (15.5%), and 1,1-difluoroethylene

(0.5%) by gas-liquid chromatography. Fluoride ions were

detected in both the above hydrolyses. An attempted

hydrolysis with water gave no volatile products along with

the formation of chloride ions.

Hydrolysis of the Adduct $H(CF_2 \cdot CFH)Si(CH_3)_3$

The adduct of trimethylsilane with trifluoroethylene

formed after irradiation for 140 hr. [0.2031 g., 1.30 mmole]

was hydrolysed in vacuo with an excess of freshly prepared 10%

aqueous sodium hydroxide solution. The bulb was shaken for

5 min. and allowed to stand overnight, after which the contents

of the bulb were transferred to the vacuum system and

fractionated in vacuo to give an incompletely separated

mixture of 1,1,2-trifluoroethane, 1,2-difluoroethylene and

1,1-difluoroethylene, [1.28 mmole, equivalent to 98.5%

conversion]. The fractions were recombined and shown by infra-

red spectroscopy and gas-liquid chromatography to consist of

1,1,2-trifluoroethane (43%), cis- and trans-1,2-difluoroethylene

(41%), and 1,1-difluoroethylene (16%). Fluoride ions were

detected in the aqueous residues. An attempted hydrolysis

with water gave no volatile products.

Pyrolysis of the Adduct $H(CF_2.CFH)SiCl_2Me$

The adduct of dichloromethylsilane with trifluoroethylene [0.1865 g., 0.9475 mmole] was pyrolysed in a silica tube in vacuo at 280° for 18 hr. The reaction products were transferred to the vacuum system and found to be a gas [1.868 mmole] the infra-red spectrum of which indicated the presence of 1,2-difluoroethylene and a chlorofluorosilicon compound. The gas was transferred to a hydrolysis bulb and shaken with distilled water, giving a decrease in volume of approximately half. The remaining gas had a molecular weight of 65.1 (CHF:CHF requires 64), and an infra-red spectrum corresponding mainly to 1,2-difluoroethylene, but with unidentified bands which did not correspond to $CH_2:CF_2$, CHCl:CHF, $CHF:CF_2$, or $CHClF.CF_2H$.

The pyrolysis was repeated at 225° for 16 hr. The adduct [0.3013 g., 1.53 mmole] was pyrolysed in a silica tube in vacuo at 225° for 16 hr. to give a gas [3.02 mmole] which was shown to be 1,2-difluoroethylene with a trace of 1,1-difluoroethylene, along with a chlorofluorosilicon compound. The gas was transferred to a hydrolysis bulb and shaken with distilled water to remove the hydrolysable

silicon compound. The gas was fractionated in vacuo to give a gas condensing at -196° [1.51 mmole, equivalent to 99% reaction] which was shown to be 1,2-difluoroethylene (95%) and 1,1-difluoroethylene (5%) by infra-red spectroscopy, gas-liquid chromatography, and molecular weight determination. Chlorine-containing olefins were not detected.

Pyrolysis of the Adduct H(CF$_2$.CFH)SiCl$_3$

The adduct of trichlorosilane with trifluoroethylene [0.3258 g., 1.5 mmole] was pyrolysed in a silica tube in vacuo at 250-255° for 18 hr. in a "Wild-Barfield" furnace. The reaction products were transferred to the vacuum system and were found to be a gas [1.49 mmole], having an average molecular weight of 107, and with an infra-red spectrum which indicated the presence of 1,2-difluoroethylene and a chlorofluorosilicon compound. The gas was transferred to a hydrolysis bulb and shaken with degassed distilled water, whereupon transfer to the system gave a gas [0.75 mmole, equivalent to 50% of the adduct]. Investigation of the gas by molecular weight determination, infra-red spectroscopy, and gas-liquid chromatography indicated that it was 1,2-difluoroethylene [0.043 g., 0.75 mmole]. 1,1-Difluoroethylene

was not detected. A minute trace of a compound similar
to 1-chloro-2-fluoroethylene was discernible in the infra-red
spectrum of the gas but this was not detected by gas-liquid
chromatography. It is presumed that it was at a very low
concentration (<0.5%). A black insoluble residue remained
in the tube after the pyrolysis.

The pyrolysis was repeated for 16 hr. at 225° for
comparison with the adduct $H(CF_2.CHF)SiCl_2Me$. Treatment
of the products in an identical manner gave 1,2-difluoroethylene
(47%), along with a black insoluble residue, and a volatile
hydrolysable siliceous material.

Hydrolysis of the Adduct of Trichlorosilane with 1-chloro-2-fluoroethylene

The adduct of trichlorosilane with 1-chloro-2-fluoroethylene
was investigated by gas-liquid chromatography and shown to
consist of 2-chloro-1-fluoroethyltrichlorosilane, $CH_2Cl.CHF.SiCl_3$,
and 1-chloro-2-fluoroethyltrichlorosilane, $CH_2F.CHCl.SiCl_3$,
in the ratio 3:1. The isomers could not be separated by
fractional distillation.

The adduct mixture [0.1822 g., 0.838 mmole] was
introduced into a hydrolysis bulb, and hydrolysed in vacuo
with fresh 10% aqueous sodium hydroxide solution. Fractionation

in vacuo gave vinyl fluoride [0.0285 g., 0.62 mmole, equivalent to 74.7% conversion] and vinyl chloride [0.0123 g., 0.197 mmole, equivalent to 23.5% conversion], which were identified by infra-red spectroscopy, molecular weight and gas-liquid chromatography. Thus the gas recovered is equivalent to 98.2% reaction of the adduct and consists of 24% vinyl chloride and 76% vinyl fluoride (or ca. 3:1 $CH_2Cl.CHF.SiCl_3$ to $CH_2F.CHCl.SiCl_3$). Fluoride ions were detected in the aqueous residues.

The hydrolysis was repeated with distilled water to give vinyl fluoride (75%) as the only volatile product. Fluoride ions were not detected in the aqueous residues.

IRRADIATION OF THE STARTING MATERIALS

The Irradiation of Trimethylsilane

Trimethylsilane [0.592 g., 8.0 mmole] was irradiated with shaking in a silica tube at a distance of 10 cm. from a 500 watt "Hanovia" ultraviolet lamp for 100 hr. Fractionation in vacuo gave a non-condensable gas, assumed to be hydrogen (ca. 1%), and unreacted trimethylsilane [0.582 g., 7.85 mmole, equivalent to 98% recovery] which was identified by molecular weight and infra-red spectroscopy. No other component was present in the trimethylsilane on investigation by gas-liquid chromatography.

The Irradiation of Trimethylsilane in the Presence of Mercury

Trimethylsilane [0.148 g., 2.0 mmole] was irradiated as above in the presence of 1 ml. mercury. Fractionation in vacuo gave a non-condensable gas with no infra-red absorption spectrum which was assumed to be hydrogen (ca. 12%), unreacted trimethylsilane [0.1225 g., 1.65 mmole, equivalent to 82% recovery] identified by infra-red spectroscopy and molecular weight determination, and extremely small trace of an involatile oily material which remained on the surface of the mercury. A small unidentified peak was present in the infra-red spectrum of the trimethylsilane at 9.35 μ but investigation by gas-liquid chromatography indicated the presence of only one component.

The infra-red spectrum of the oil was essentially similar to

that of trimethylsilane and did not correspond to

hexamethyldisilane. The oil was not further investigated.

The Irradiation of Trichlorosilane

A silica tube was calibrated for volumes from 15-25 ml.

At room temperature one mole of trichlorosilane has a volume

of 100 ml. 22 ml. of trichlorosilane was introduced into a

silica tube and vigorously degassed several times, in vacuo

until the volume remaining was exactly 20 ml. Trichlorosilane

[27 g., 0.2 mole] was irradiated in vacuo for 90 hr. in a silica

tube before a 500 watt "Hanovia" ultraviolet lamp.

Fractionation in vacuo gave a non-condensable gas, [M = 4,],

having no infra-red absorption, which was assumed to be

hydrogen (ca. 1%), hydrogen chloride [0.265 g., 5.9 mmole,

equivalent to ca. 3% reaction of the trichlorosilane],

unreacted trichlorosilane [26.365 g., 0.194 mole, equivalent

to 97% recovery], and a high boiling yellow oil [0.15 g.].

Hydrogen chloride was identified by infra-red spectroscopy

and molecular weight determination; trichlorosilane was

identified by infra-red spectroscopy. The infra-red spectrum

of the yellow oil was essentially similar to that of

trichlorosilane and contained bands attributable to both

Si-H and Si-Cl stretching frequencies. The yellow oil was

not further investigated.

The Irradiation of Vinyl Fluoride

Vinyl fluoride $\left[0.00497 \text{ g.}, 0.108 \text{ mmole}\right]$ was irradiated

in vacuo for 113 hr. under standard conditions. Fractionation

in vacuo gave a gas$\left[0.106 \text{ mmole, equivalent to } 98\% \text{ recovery}\right]$

condensing at -196° which was shown to consist of vinyl fluoride

with ca. 10% of acetylene by infra-red spectroscopy. The

molecular weight of the gas was 44.5 $(CH_2:CHF = 46, CH:CH = 26)$,

indicating ca. 8% acetylene. No hydrogen fluoride or silicon-

fluorine absorption bands were detected in the infra-red

spectrum of the gas, but small peaks at 8.0 μ and 9.35 μ were

present which have not been identified. The small bands do

not correspond to 1,1-difluoroethane, and a spectrum of

1,2-difluoroethane was not available for comparison.

The Irradiation of 1-chloro-2-fluoroethylene

1-chloro-2-fluoroethylene $\left[1.61 \text{ g.}, 20.0 \text{ mmole}\right]$ was

irradiated in vacuo for 90 hr. under standard conditions.

Fractionation in vacuo gave unreacted 1-chloro-2-fluoroethylene

$\left[0.256 \text{ g.}, 3.2 \text{ mmole, equivalent to } 16\% \text{ recovery}\right]$, vinyl

fluoride [0.0160 g., 0.40 mmole, equivalent to 2% of the original olefin] identified by infra-red spectroscopy and gas-liquid chromatography, and a very viscous yellow liquid which was assumed to be polymeric 1-chloro-2-fluoroethylene from its infra-red spectrum and elemental analysis.

Found: C, 29.4; H, 2.2%; calc. for C_2H_2ClF, C, 29.8; H, 2.48%; . A thick intractable coating remained on the side of the tube nearest the lamp. Neither the liquid nor the tube coating was weighed as the viscosity of the liquid would have rendered this meaningless.

The Irradiation of Trifluoroethylene

Trifluoroethylene [0.00886 g., 0.108 mmole] was irradiated in vacuo for 113 hr. under standard conditions. Fractionation in vacuo gave unreacted trifluoroethylene [0.0074 g., 0.0885 mmole, equivalent to 83% recovery] as the only volatile product. A brown material was not investigated but was possibly polytrifluoroethylene.

PREPARATION OF COMPOUNDS REQUIRED AS STANDARDS

The Preparation of Ethyl Fluoride

Ethyl fluoride was prepared via the p-toluenesulphonate after the method of W.F. Edgell and L. Parts.[183] Pyridine [158 g., 2 mole] was added at a constant rate over two hours and with vigorous stirring to a mixture of ethanol [11.5 g., 0.25 mole] and p-toluenesulphonyl chloride [67 g., 0.55 mole] contained in a 500 ml. round bottomed flask and maintained at -40°. Stirring was continued for a further hour after which the reaction was quenched by pouring the reaction mixture into 300 ml. ice-water and shaking for 5 min. The suspension was extracted with 150 ml. ice cold diethyl ether, and was washed consecutively with ice cold dilute sulphuric acid (2N.), ice-water, ice cold dilute aqueous potassium hydroxide (2N.), and ice-water. The resulting solution was dried overnight over anhydrous sodium carbonate and the bright purple solution was separated by filtration. The ether was removed under vacuum at +10°. The product was a dark green solid (m.p.15-20°) which melted at room temperature to give a very dark green liquid. Anhydrous potassium fluoride [35 g., 0.6 mole] was added to the green solid along with 100 ml. β,β'- dihydroxyethyl

ether. The mixture was vigorously stirred with a magnetic stirrer, and heated to give an internal temperature of 150° over a period of two hours, under a pressure of 500 mm. Volatile products were collected in a trap at -196°. The pressure must be carefully maintained as frothing occurs readily in the early stages of the reaction. The volatile products were fractionated in vacuum through traps maintained at -96, -120, -130 and -196°. The product was found to have condensed in the trap at -130° and was identified as pure ethyl fluoride [5.45 g., 0.113 mole., equivalent to 45% yield based on ethyl alcohol] by molecular weight, infra-red spectroscopy and gas-liquid chromatography.

The Preparation of 1-chloro-2-fluoroethane

Using the method described for ethyl fluoride (above), pyridine [40.0 g., 0.63 mole] was added to ethylenechlorohydrin [20.0 g., 0.25 mole] and p-toluenesulphonylchloride [64.7 g., 0.3 mole] at 0°. Stirring was continued for two hours after the addition. The reaction was quenched, extracted, and washed, as above, to obtain the p-toluenesulphonate. To the product was added potassium fluoride [72.5 g., 1.25 mole] and β,β'- dihydroxyethyl ether (86 g.) and the mixture was stirred for five hours at 160° and 20-50 mm. pressure. The volatile

products were collected in a trap cooled to -196°.

The contents of the trap were fractionated under vacuum through traps cooled to -24, -56, -78 and -196°. The product condensed in the trap maintained at -78° and was shown to be pure 1-chloro-2-fluoroethylene [13 g., 0.16 mole, equivalent to 65% yield based on ethylenechlorohydrin] by infra-red spectroscopy, gas-liquid chromatography and refractive index.

Found: η_D^{20} 1.3760; bp. 53.0/760;

Literature[183] values, η_D^{20} 1.3752; bp. 53.2/760.

A trace of vinyl chloride was detected in the trap at -196°.

The Preparation of 1,1,2-trifluoroethane

1,2,2-trifluoroethyltrichlorosilane [3.016 g., 13.85 mmole] was introduced into a hydrolysis bulb and hydrolysed in vacuo with 1% aqueous sodium hydroxide solution. The volatile contents of the bulb were passed through a tube packed with phosphorus pentoxide and glass wool into the system. Fractionation in vacuo through traps at -96, -102, -120 and -196° was carried out. The -102° and -120° fractions were returned through the fractionation line for a second fractionation. The contents of the -96° and -102° traps were found to have identical infra-red spectra, and the -120° trap was empty.

The -196° fraction was found to contain 1,2-difluoroethylene [0.0015 g., 2.34 mmole, equivalent to 16.9% reaction] by molecular weight and infra-red spectroscopy. The combined -96° and -102° fractions were found to be 1,1,2-trifluoroethane [0.965 g., 11.5 mmole, equivalent to 83% reaction] by molecular weight and infra-red spectroscopy. The purity was checked by gas-liquid chromatography.

The Reaction of Aqueous Sodium Hydroxide Solution with the Fluoroethanes

a) Ethyl Fluoride

Ethyl fluoride [0.0432 g., 0.90 mmole] was condensed into a hydrolysis bulb and an excess of freshly prepared 10% aqueous sodium hydroxide solution was run in through the tap. The bulb was periodically shaken for 6 hr. at room temperature and allowed to stand overnight. Fractionation in vacuo gave ethyl fluoride [0.042 g., 0.875 mmole, equivalent to 97% recovery] which was identified by infra-red spectroscopy and molecular weight determination. Fluoride ions could not be detected in the aqueous residues.

b) 1-chloro-2-fluoroethane

1-chloro-2-fluoroethane [0.6667 g., 8.07 mmole] was condensed into a hydrolysis bulb and an excess of freshly

prepared 10% aqueous sodium hydroxide solution was added. The bulb was periodically shaken and allowed to stand overnight. Fractionation in vacuo gave unchanged 1-chloro-2-fluoroethane [0.6582 g., 8.0 mmole, equivalent to 99% recovery] which was identified by infra-red spectroscopy and boiling point determination, 53.0%(lit[183] 53.2°). Neither fluoride ions nor chloride ions could be detected in the aqueous residues.

    c)   1,1,2-trifluoroethane

       1,1,2-trifluroethane [0.5327 g., 6.35 mmole] was condensed into a hydrolysis bulb and an excess of freshly prepared 20% aqueous sodium hydroxide solution was added. The bulb was periodically shaken and allowed to stand overnight. Fractionation in vacuo gave unchanged 1,1,2-trifluoroethane [0.5280 g., 6.28 mmole, equivalent to 97.5% recovery] which was identified by infra-red spectroscopy and molecular weight determination.

Grignard Reactions: The Preparation of 1,2,2-trifluoroethyl-trimethylsilane

Preparation of the Grignard Reagent, Methyl Magnesium Iodide

    Magnesium turnings [2 g., 0.083 mole] were placed in a 250 ml. round-bottomed flask and 5 ml. dry di-n-butyl ether was added. The flask was fitted with a dropping funnel and

a reflux condenser. Methyl iodide [7.85 g., 35.2 mmole] was placed in the dropping funnel, and the flask fitted for magnetic stirring. A small crystal of iodine was introduced into the flask and ca. 1 ml. methyl iodide was added from the funnel. The mixture was stirred, and when the flask became warm 50 ml. dry di-n-butyl ether was added down the condenser. A further 50 ml. dry di-n-butyl ether was added to the methyl iodide remaining in the dropping funnel, and this solution was then added to the reaction mixture over a period of 90 min. Stirring was continued for a further hour after which the reagent was filtered into a three necked flask through a plug of glass wool.

Reaction with 1,2,2-trifluoroethyltrichlorosilane

The three-necked flask containing the Grignard reagent was fitted with a dropping funnel and a double surface condenser leading to two traps cooled to -78° and to a drying tube. The flask was fitted for magnetic stirring. 1,2,2-trifluoroethyltrichlorosilane [4.1 g., 19.0 mmole] in 10 ml. di-n-butyl ether was dropped slowly onto the stirred Grignard reagent at room temperature at such a rate of addition that the temperature was never discernibly above room

temperature. When the addition was complete the traps were cooled to -196° with the exit closed and the pressure was reduced to 40 cm. mercury. The flask was slowly warmed up and maintained at 80-100° for two hours. Fractionation of the cold trap in vacuo gave 1,1,2-trifluoroethyltrimethylsilane [0.8191 g., 5.25 mmole, equivalent to 25% conversion] which condensed at -78°, and was identified by infra-red spectroscopy, gas-liquid chromatography and elemental analysis.

Found: C, 38.3; H, 6.9%;

$C_5H_{11}F_3Si$ requires,   C, 38.5; H, 7.05%.

An unmeasured amount of 1,2-difluoroethylene was detected in high percentages by infra-red spectroscopy in the -196° fraction.

The Preparation of 1-fluoroethyltrimethylsilane

The Grignard reagent was prepared as above using methyl iodide [4.7 g., 33.1 mmole]. 1-fluoroethyltrichlorosilane [2.4 g., 13.2 mmole] in 10 ml. dry di-n-butyl ether was slowly added to the stirred reagent at -78°. The flask was allowed to come slowly to room temperature and was connected to the vacuum system via a trap cooled to -196°. The pressure was reduced to 250 mm. of mercury, and the flask

was gradually warmed to <u>ca.</u> 50° and maintained at that
temperature for 2 hr., while the volatile products were
collected in the trap at -196°. Fractionation of the
contents of the trap at -196° <u>in vacuo</u> gave a major
fraction condensing at -76° which was identified as
1-fluoroethyltrimethylsilane [1.45 g., 0.0121 mole,
equivalent to 91%] by infra-red spectroscopy, nuclear
magnetic resonance spectroscopy, and gas-liquid chromatography.
Infra-red band table for 1-fluoroethyltrimethylsilane,
$CH_3 \cdot CHF \cdot SiMe_3$
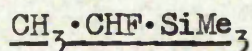
3.4	s	9.9	m
3.45	m	10.4	
3.55	w	10.5	w
6.3	vw	10.6	
6.4	vw	10.95	s
6.85	w	11.05	
7.1	w	11.55	vs
7.95	s	11.7	vs
9.1	m	11.9	broad
9.33	m	13.2	m

The Reaction of trimethylsilane with chlorotrifluoroethylene.

Trimethylsilane [44 g., 0.60 mole] and chlorotrifluoro-
ethylene [23.3 g., 0.20 mole] were irradiated with shaking
in a silica tube for 300 hr. Fractionation in vacuo gave
unreacted trimethylsilane [14.35 g., 0.194 mole],
trimethylchlorosilane [22 g., 0.20 mole, equivalent to 100%
reaction based on the olefin] and a reduced adduct of
trimethylsilane to chlorotrifluoroethylene [30.8 g., 0.198 mole,
equivalent to 99% reaction of the olefin]. Trimethylsilane and
trimethylchlorosilane were identified and estimated by
gas-liquid chromatography in conjunction with infra-red
spectroscopy. Fractionation at atmospheric pressure through
a vacuum jacketed packed column gave a reduced adduct of
trimethylsilane with chlorotrifluoroethylene [25.2 g., 0.162 mole,
equivalent to 81%] b.p. 90-92°. The reduced adduct was
recognised as 1,1,2-fluoroethyltrimethylsilane by elemental
analysis, infra-red and nuclear magnetic resonance
spectroscopy, and its purity was checked by gas-liquid
chromatography. Neither 2-chloro-1,1,2-
trifluoroethyltrimethylsilane ($CHClF \cdot CF_2 \cdot SiMe_3$) nor

1,2,2-trifluoroethyltrimethylsilane was detected.

Found:　　　　　　　　　C, 38.3; H, 7.0%;

$C_5H_{11}F_3Si$ requires,　　C, 38.5; H, 7.05%.

Infra-red band table for 1,1,2-trifluoroethyltrimethylsilane

$$(CH_2F.C F_2.SiMe_3)$$

3.43 m	8.66 w	11.06 s
3.5 w	8.90 m	11.85 vs
6.92 w	9.35 m shoulder	13.20 m
7.14 w	9.60 s doublet	14.45 w
7.30 vw	9.75 s	
8.02 s		

A P P E N D I X.

Nuclear Magnetic Resonance Spectroscopy.

Nuclear magnetic resonance spectroscopy has been used to determine the structures of the fluoroalkylsilicon compounds which have been prepared during this work.   The measurement and full interpretation of the spectra are extremely complex and come within the field of specialists in spectroscopy.   The spectra have been analysed and interpreted, in some cases with the aid of a computer programme, for which the author is indebted to Dr.J.Dyer of this Department.   It is possible in some cases to present a simple picture of the theoretical spectrum, and in such cases a non-specialist can predict the type of spectrum to be expected for a particular substituted ethyl group.   As spin-coupling from substituents at the silicon with nuclei of the ethyl group does not occur, the form of the spectrum (but not the position of absorption) is dependent only on the substituents on the ethyl group.   The spectra of some of the substituted ethyltrichlorosilanes have been reproduced to indicate the general pattern of absorption for such compounds, figs, 1-7.

An extremely simplified picture of nuclear magnetic resonance spectroscopy may make this approach clear. The nuclei of certain isotopes possess an intrinsic mechanical spin, i.e. they are associated with a particular angular momentum. Since nuclei are also associated with an electric charge, this spin gives rise to a magnetic field. In a uniform magnetic field the angular momentum of a nucleus with a spin number greater than zero $(I > 0)$ is quantised, taking up one of the possible $(2I + 1)$ orientations with respect to the field. Each orientation corresponds to a particular potential energy of the nucleus depending on the magnetic moment (μ) of the nucleus amongst other factors. Nuclear magnetic resonance spectroscopy is only concerned with nuclei of those elements in which both I and μ are not equal to zero. A transition of a nucleus from one orientation or spin state to an adjacent state may occur by either an absorption or emission of energy.

The proton is limited to two possible orientations in the applied field (i.e. $I = \frac{1}{2}$, $(2I + 1) = 2$), and these correspond to a low energy or parallel orientation with the field, and a high energy or anti-parallel orientation with the field. For nuclei with $I > \frac{1}{2}$ there are more possible orientations but selection rules only allow transitions between

adjacent levels. A collection of nuclei in which the spins are equally divided between the spin states would lead to failure to observe the nuclear transitions. Such a collection, however, takes up a Boltzmann distribution with a small but finite excess of spins in the lower states. A nett absorption of energy is then observable, but a necessary factor for maintaining the absorption condition is that energy should be lost from the upper state by so-called radiationless transitions. By this the nucleus returns to the lower state by relaxation phenomena in which the energy is dissipated into the rest of the molecule of which the resonating nucleus is part.

The frequency of the absorbed radiation is dependent on the strength of the field experienced by the nucleus. This is determined by the shielding of the nucleus by the extra-nuclear electrons. Thus factors affecting the electron distribution affect the frequency of the absorption. This is measured by the difference in the frequency for the observed nucleus and a reference compound. This difference or separation of the signals is called the chemical shift, and is measured differently for ^{1}H and ^{19}F resonances, e.g. for ^{1}H resonances the τ-value is usually quoted.

This is the chemical shift *relative* to tetramethylsilane (T.M.S.) at 10 ppm.

radio frequency = 60 mc/s.

H° |← separation c/s →|

signal   T.M.S. 10 ppm.
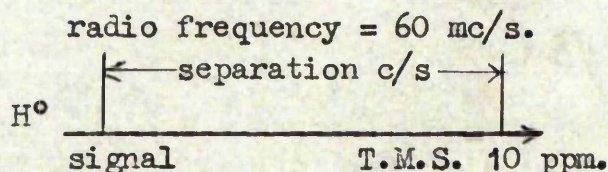
$$\text{chemical shift} = \frac{\text{separation}}{\text{radio frequency}} = \frac{\text{separation}}{60} = Y \text{ ppm.}$$

τ signal = 10-Y, conventionally positive to low field of T.M.S. e.g. for ^{19}F resonances the chemical shift δ, from trifluoro-acetic acid is usually quoted directly.

$$\delta^{19}F = \frac{\text{separation}}{\text{radio frequency}}, \quad \text{conventionally positive to high field of standard.}$$

The most important factor from the point of view of structural analysis is the phenomenon of spin coupling. If a nucleus experiences a particular field as the result of the applied field and the shielding effect, only a single absorption will be observed in the absence of adjacent magnetic nuclei (e.g. ^{1}H, ^{19}F). In the neighbourhood of such nuclei the absorption will be split by spin coupling from these nuclei, (i.e. the actual field now experienced by the resonating nucleus

has an additional term dependent on the spins of adjacent nuclei). The splitting will correspond to the number of orientations of these neighbouring nuclei. It is important to note that this is a spatial phenomenon, and not dependent on transfer via chemical bonds. Spin coupling is usually limited to groups in close proximity. The multiplicity of splitting by spin coupling can be obtained in simple cases by counting the orientations possible (Table 31).

This is applicable to simple cases of first order spectra where the spectra can be analysed by inspection, i.e. the chemical shifts are greater than the coupling constants. In molecules containing nuclei which are not equivalent by virtue of phenomena such as hindered rotation, the spectrum becomes perturbed and the chemical shifts may be of the same order of magnitude as the coupling constants. In this case analysis is by more detailed and complex methods and the use of computers is necessary. This approach is far beyond the scope of the present investigation.

Of the silicon compounds investigated only the compounds containing the 1,2,2-trifluoroethyl group needed analysis by the method for perturbed spectra.[184] The chemical shifts and coupling constants (J) are presented in Table and the spectra are reproduced in figures 1-7.

The correspondence between the predicted spectra
and the observed spectra is good. The spectrum of
2-fluoroethylmethyldichlorosilane was unusual in that the
intensities of the absorption first recorded were not in
the correct ratio nor of the correct form. The bands
observed were in the ratio 1:2:2:4:2:2:1. The expected ratio
for a $CH_2F \cdot CH_2-$ group is 1:2:1:2:4:2:1:2:1, or if overlap
occurs 1:2:3:4:3:2:1.

An attempt to detect the missing peak was made by
running the spectrum on an expanded scale. This peak was
detected close to but not overlapped by an adjacent peak but
it was also apparent that more fine structure was present in
the spectrum. Running the spectrum on a more expanded scale
successfully resolved each peak into a quartet structure with a
separation of ca. 0.9 c/s, (fig. 7). This is the correct
structure for coupling of the methyl hydrogens with the β -fluorine
atom. The complete spectrum is therefore a triplet of triplets
of quartets.

As the hydrogen atom and the fluorine atom involved
in this coupling are separated by five σ - bonds it is
tentatively suggested that this is the result of coupling
through space and that the methyl group and the fluorine atom

are relatively near together.   This type of observation is
new in silicon chemistry and more experimental evidence,
e.g. the temperature dependence of the coupling, is necessary
before conclusions about the configuration of the molecule
can be drawn.

The chemical shifts of fluorine atoms in different
environments have been compared in a series of fluoroethyl-
trichlorosilanes (Table 32).

TABLE 32

Chemical shifts for fluorine resonances in
fluoroethyltrichlorosilanes ($\delta^{19}F$).

Compound	δF_α	δF_β
$CH_3 \cdot CHF \cdot SiCl_3$	91.4	-
$CH_2F \cdot CH_2 \cdot SiCl_3$	-	131.6
$CH_3 \cdot CF_2 \cdot SiCl_3$	27.9	-
$CHF_2 \cdot CH_2 \cdot SiCl_3$	-	27.3
$CH_2F \cdot CF_2 \cdot SiCl_3$	44.3	157.6
$CHF_2 \cdot CHF \cdot SiCl_3$	154.1	45.9
$CHF_2 \cdot CF_2 \cdot SiCl_3$	49.0	54.0

It is clear from the table that no obvious correlation between the position of the fluorine atom relative to the silicon atom and the chemical shift exists.

From the limited number of compounds studied it does appear, however, that the chemical shift for a particular fluorine atom is related to the number of fluorine atoms on the adjacent carbon atom. The trend is an increase in chemical shift with an increase in the number of fluorine atoms attached to the adjacent carbon atom, e.g.

	δF_β		δF_α
CF_2H-CH_2-	27.3,	CH_3-CF_2-	27.9,
$CF_2H-CHF-$	45.9,	CH_2F-CF_2-	44.3,
CF_2H-CF_2-	54.0,	CHF_2-CF_2-	49.0,

If, however, chemical shifts are compared as the number of fluorine atoms attached to the same carbon atom is increased the trend is found to be reversed, i.e. an increasing number of fluorine atoms on the same carbon atom decreases the chemical shift, e.g.

e.g.,

	$\delta_{F\alpha}$		$\delta_{F\beta}$
CH_3-CHF-	91.4,	CH_2F-CH_2-	131.6
CH_3-CF_2-	27.9,	CHF_2-CH_2-	27.3
	$\delta_{F\alpha}$		$\delta_{F\beta}$
CHF_2-CHF-	154.1	CH_2F-CF_2-	157.6
CHF_2-CF_2-	49.0	CHF_2-CF_2-	54.0

These trends appear to be consistent in the compounds studied but the nature of the factors responsible for these effects is too complex to be discussed by the non-specialist.[184]
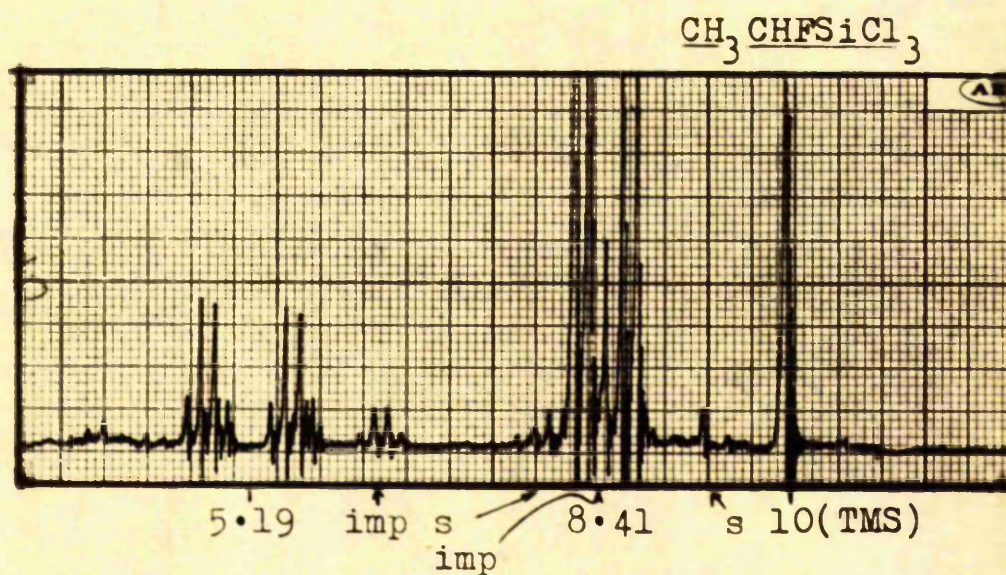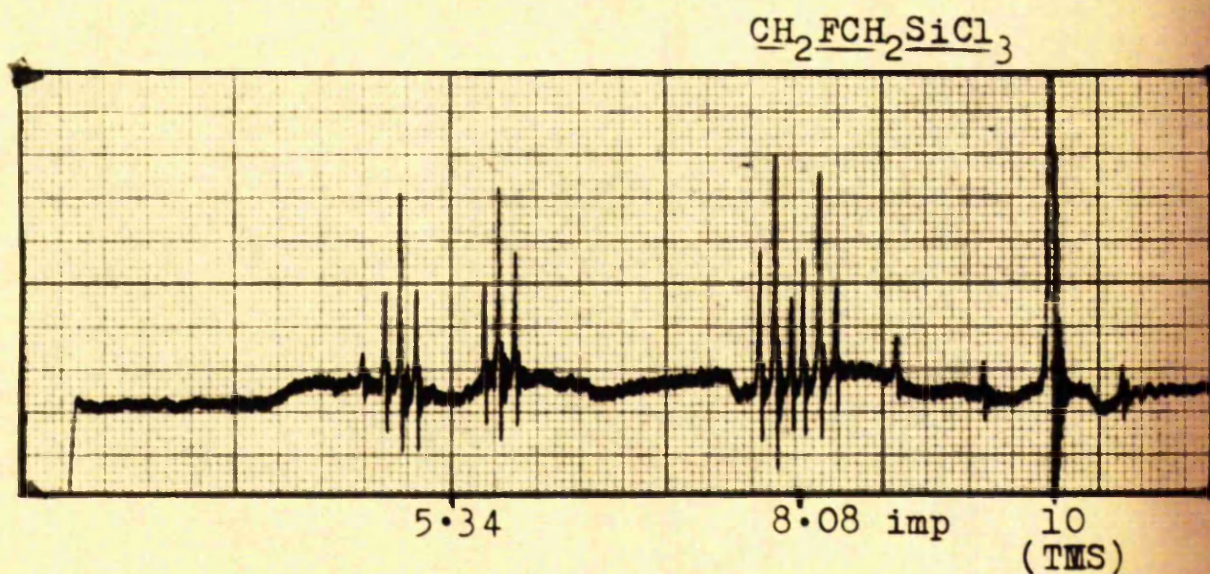
TABLE. 31 Theoretical splitting of C–X resonances by various α groups (first order splitting).

Nuclear Magnetic Resonance Spectra Fig1.

[1]H spectra of monofluoroethyltrichlorosilanes
at 60m/cs

$\underline{CH_2F CH_2 SiCl}_3$

5·34   8·08 imp   10
(TMS)

$\underline{CH_3 CHF SiCl}_3$

5·19   imp s   8·41   s 10(TMS)
              imp

imp – impurity

s – spinning side band

TMS – tetramethylsilane

Nuclear Magnetic Resonance Spectra Fig2.

^{19}F spectra of monofluoroethyltrichlorosilanes at 60m/cs.

$CF_3COOH(O)$ 131·6ppm $\underline{CH_2FCH_2SiCl}_3$

93c/s

91·4ppm $\underline{CH_3}\,\underline{CHFSiCl}_3$
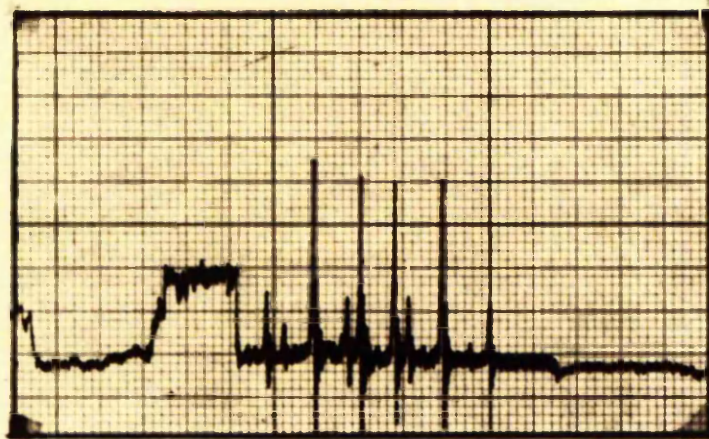
46c/s

Nuclear Magnetic Resonance Spectra Fig 3.

^{1}H spectra of trifluoroethyltrichlorosilanes at 60m/cs.

$\underline{CF_2}\underline{HCFHSiCl}_3$

3·94   5·30   imp /s 10 s
                                      (TMS)

$\underline{CH_2}\underline{FCF_2}\underline{SiCl}_3$

5·19   10
                                 (TMS)
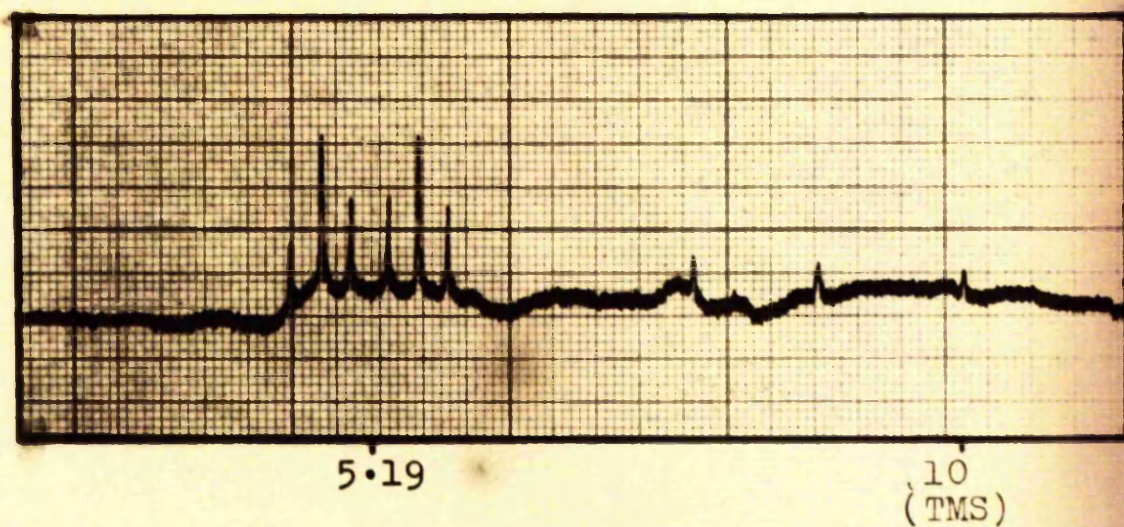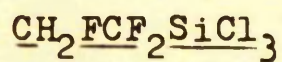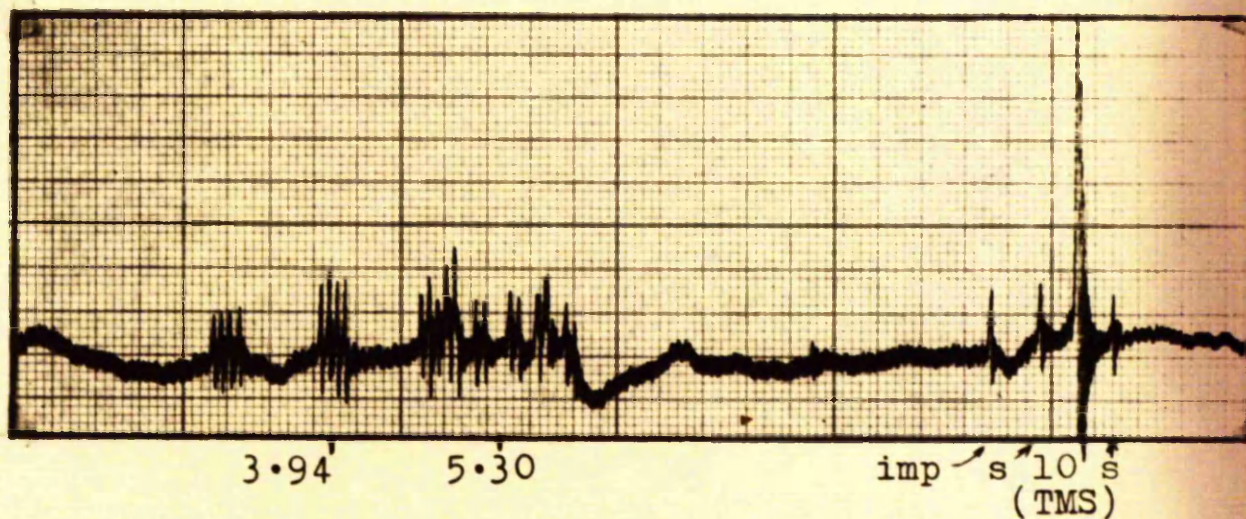
FIG. 4 ^{1}H SPECTRUM AT 60Mc/s OF $CF_2HCFHSiCl_3$

τ value   3.94   5.30

CF$_2$H   CFH
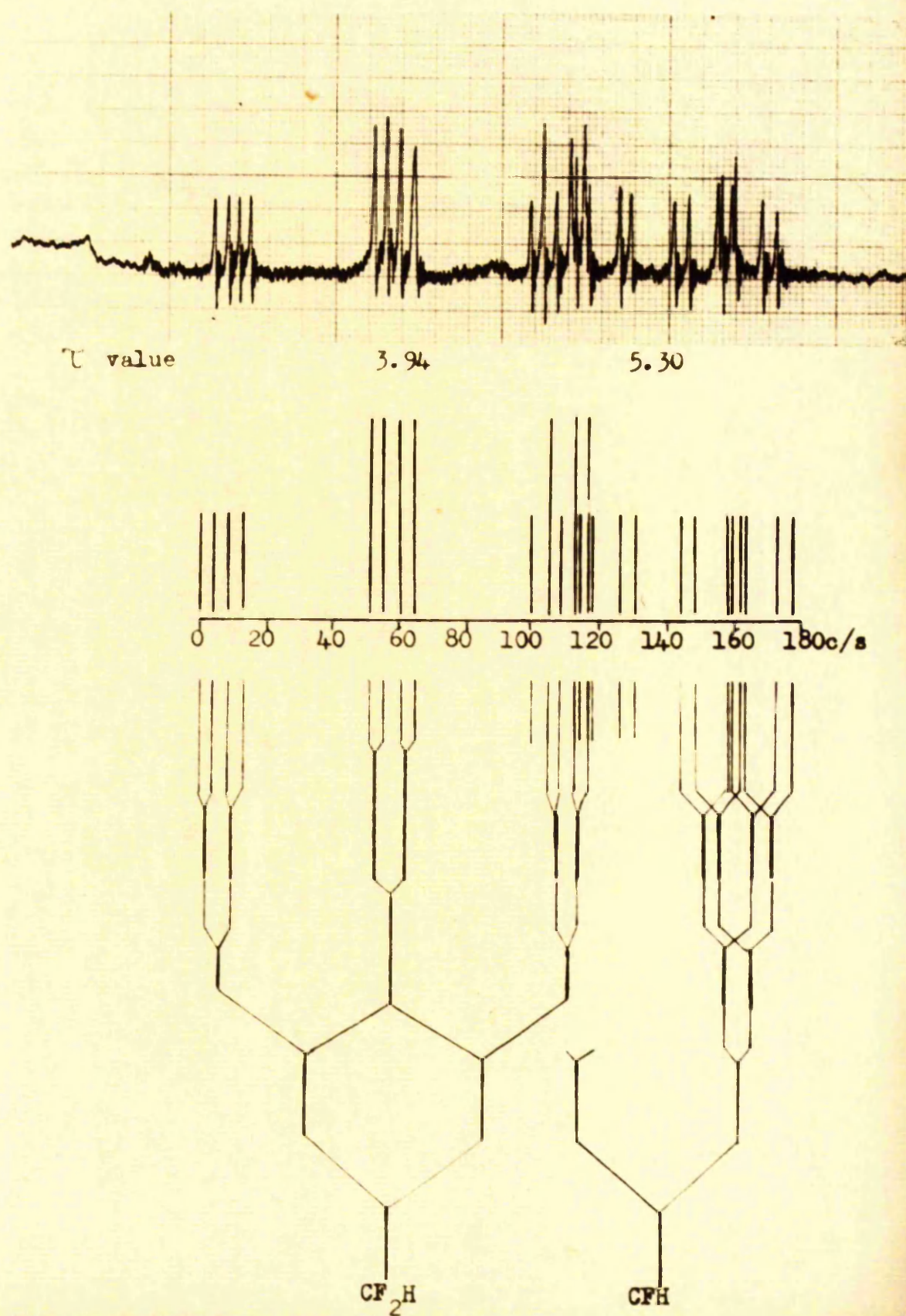
Nuclear Magnetic Resonance Spectra Fig 5.

^{19}F spectrum of 1,1,2-trifluoroethyltrichlorosilane

O(CF_3 COOH)   44·3   157·6   ppm

44·3
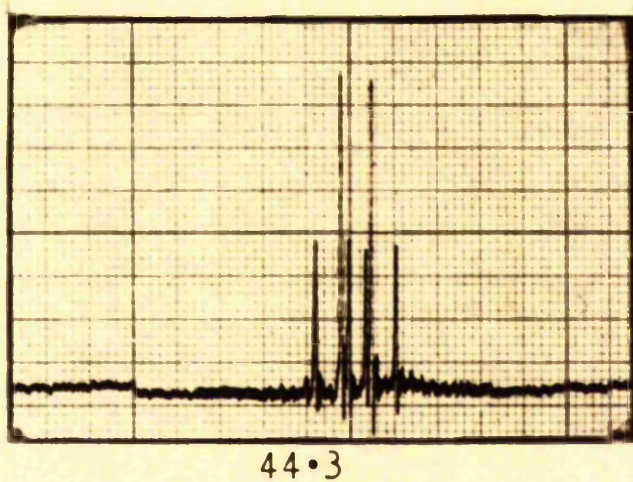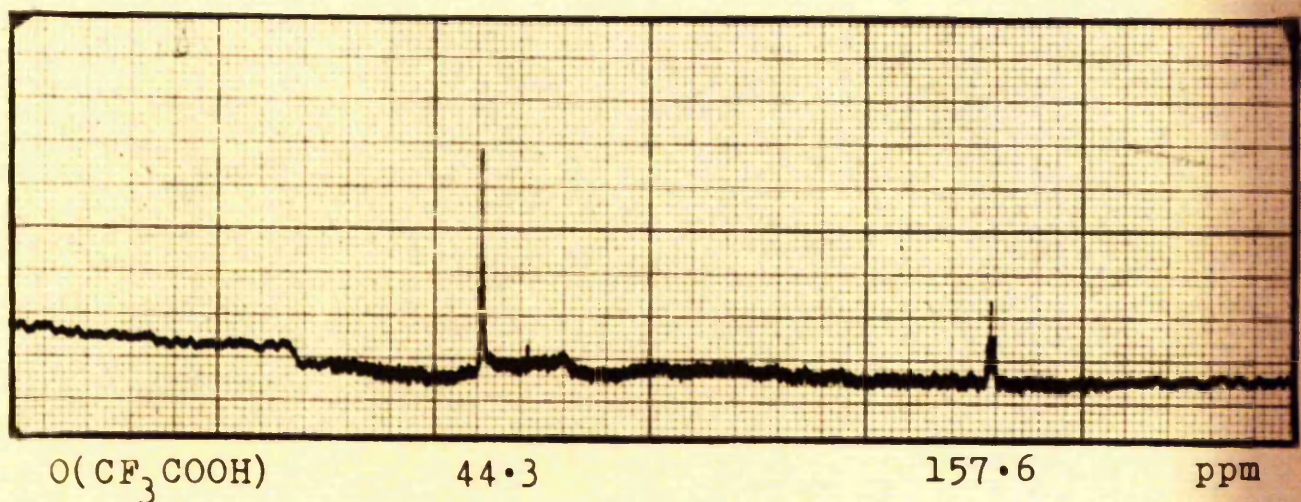
small peaks are
spinning side
bands

157·6
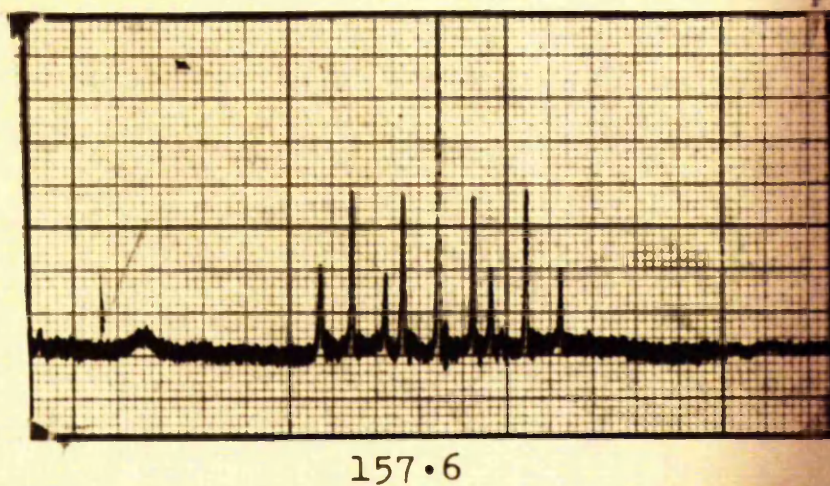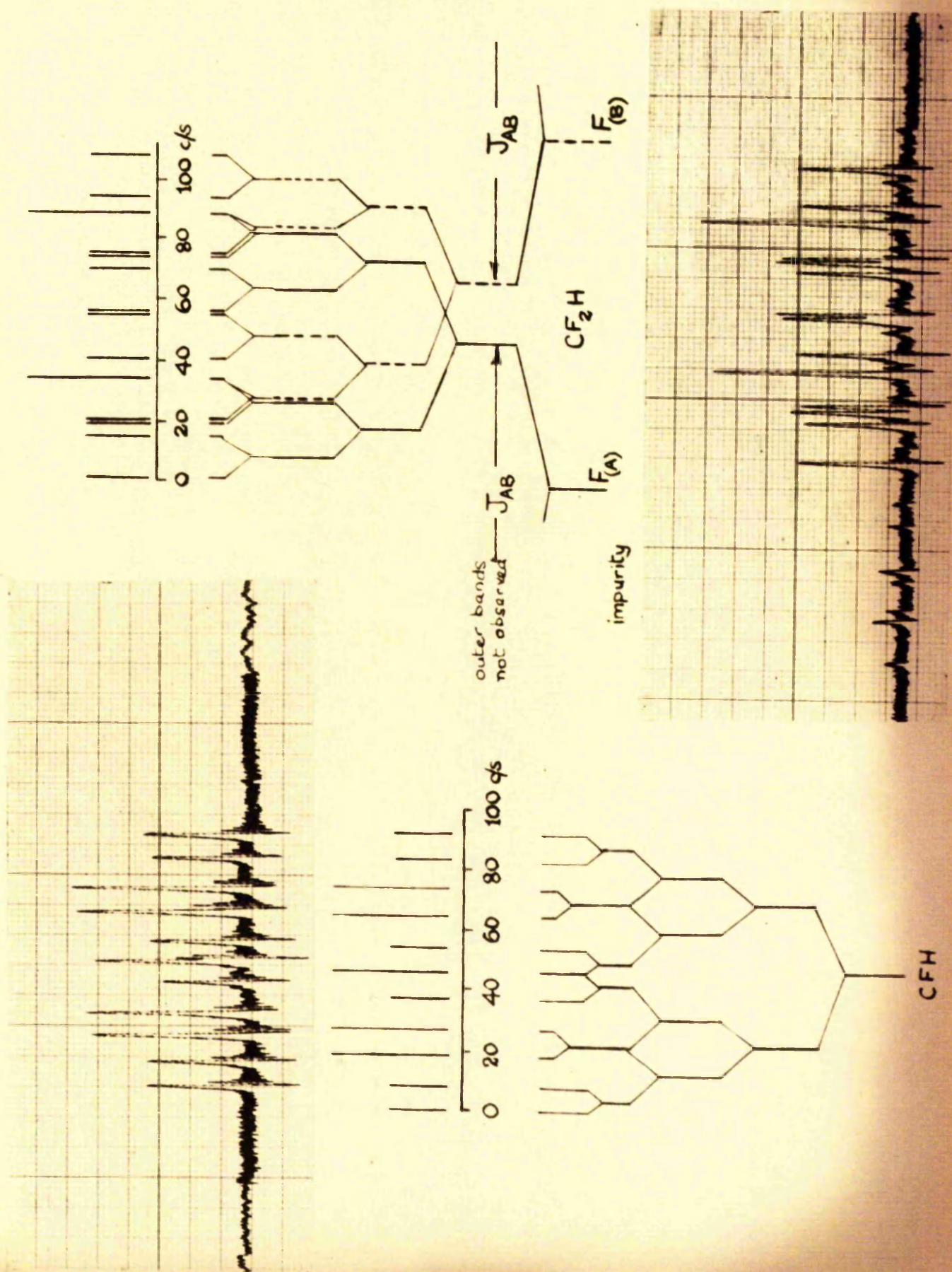
NUCLEAR MAGNETIC RESONANCE SPECTRA   Fig 7

^{19}F Spectrum of 1 fluoroethylmethyldichloro-
silane at 60 mc/s $CH_2F \cdot CH_2 \cdot SiCl_2Me$

0·9 c/s

49·7 c/s

23·5 c/s
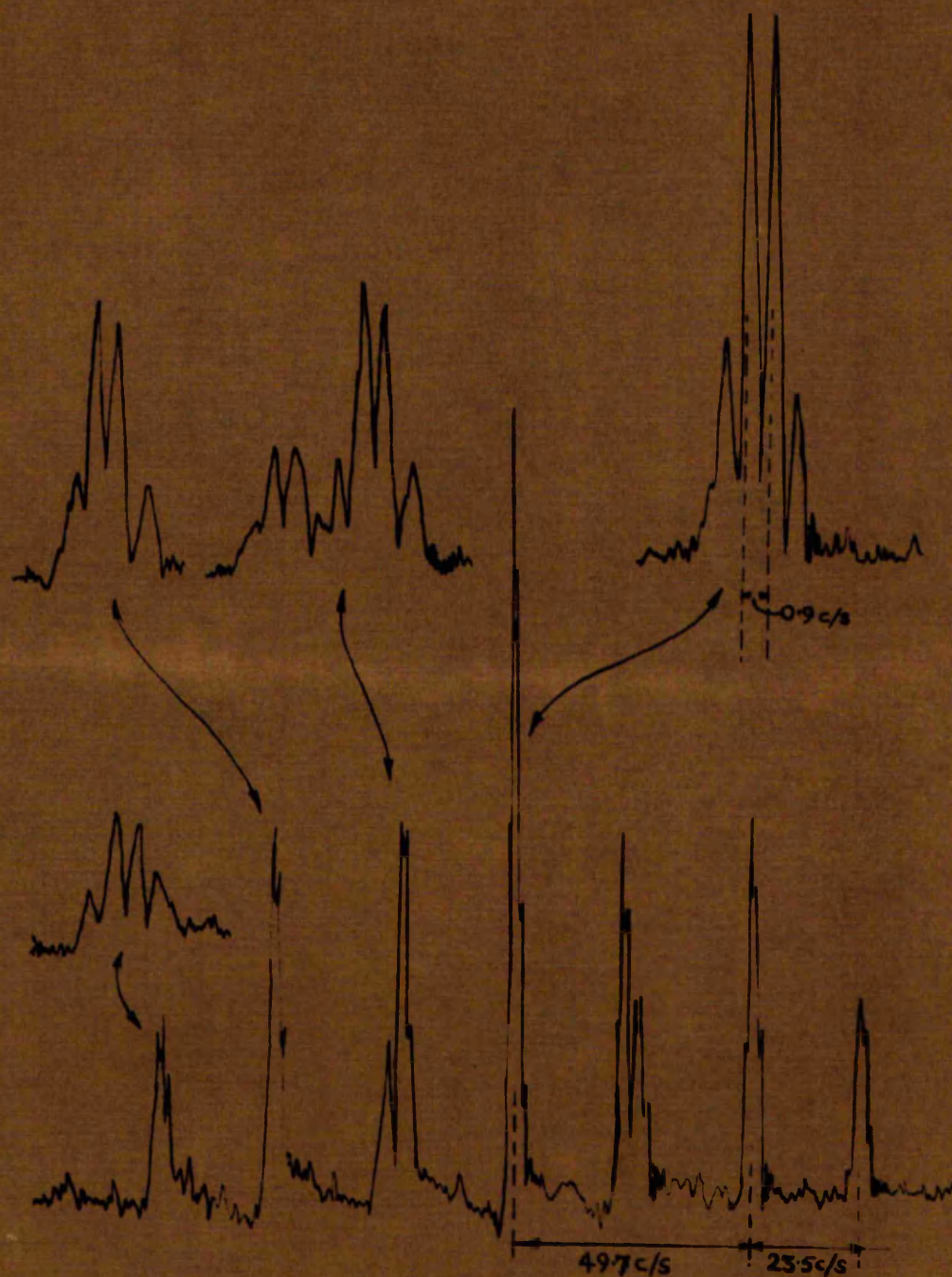
TABLE 33

Nuclear Magnetic Resonance Spectra:
Chemical shifts and coupling constants (J).

$CH_3 \cdot CHF \cdot SiCl_3$	τ		$\delta^{19}F$ (ppm.)	
	H_α	5.19	F_α	91.4
	H_β	8.41		
	$JH_\alpha F_\alpha$, 45.6; $JH_\alpha H_\beta$, 7.4; $JH_\alpha F_\beta$, 26.4 c/s.			
$CH_2F \cdot CH_2 \cdot SiCl_3$	τ		$\delta^{19}F$	
	H_α	8.08		
	H_β	5.34	F_β	131.6
	$JH_\alpha F_\beta$, 20.5; $JH_\alpha H_\beta$, 7.6; $JH_\beta F_\beta$, 47.6 c/s.			
$CH_2F \cdot CF_2 \cdot SiCl_3$	τ		$\delta^{19}F$	
	H_β	5.19	F_α	44.3
			F_β	157.6
	$JF_\alpha F_\beta$, 18.8; $JF_\alpha H_\beta$, 14.8; $JF_\beta H_\beta$, 46.5 c/s.			
$CF_2H \cdot CFH \cdot SiCl_3$	τ		$\delta^{19}F$	
Analysed as an ABGPX system, (perturbed spectrum).	H_α	5.30	F_α	154.1
	H_β	3.94	F_β	45.9 *
	$JH_\alpha F_\alpha$, 45.5; $JH_\alpha H_\beta$, 4.1; $JH_\alpha F_\beta'$, 16.3 c/s. $JH_\alpha F_\beta^2$, 11.9; $JF_\beta' H_\beta$, 45.5; $JF_\beta H_\beta$, 52.6 c/s. $JF_\beta' F_\alpha$, 16.9; $JF_\beta^2 F_\alpha$, 2.1 c/s.			
$CH_2F \cdot CH_2 SiCl_2 Me$	τ		$\delta^{19}F$	
	H_α	8.25		
	H_β	5.30	F_β	75.0
	$JH_\alpha F_\beta$, 23.5; $JF_\beta H_\beta$, 49.7; $JH_\alpha H_\beta$, 8.4 c/s. $JF_\beta H_{Me}$, 0.9 c/s (long range coupling).			
* Average position of $F_\beta 1$ and $F_\beta 2$				

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