

PREPARATION AND REACTIONS OF SOME  
FLUORINE CONTAINING SILANES

By

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## I. INTRODUCTION

The rapid advancement of technology during and since World War II has demanded the development of many materials that were not available twenty-five years ago. High performance aircraft and rockets require structural materials which are both light and strong; their engines require metals that will withstand extreme heat, as do their surfaces; they require fuels of very high energy content. Elastomeric materials are needed in many modern applications that maintain their properties over a wide temperature range, especially at low temperatures. In addition, very often they must be resistant to hydrocarbon solvents and harsh chemicals as well as different types of radiation.

It became evident soon after World War II that natural rubber could not be improved to meet the needs that further progress demanded. To meet the increasing need for new elastomers, the Office of the Quartermaster General established at the University of Florida and elsewhere in 1951 a long-range Arctic Rubber Program. Under this program, these laboratories, under the direction of Dr. Paul Tarrant, have been responsible for the synthesis of new monomers.

The discovery of Teflon, although not an elastomer, indicated the possible use of fluorine-substituted polymers. Its high thermal stability and resistance to chemical attack generated great interest. Subsequent work has proven quite fruitful, and the work in these laboratories has been centered predominately around synthesis of fluorine-containing monomers. Early interest centered around olefins and

dienes; thus Lovelace and Attaway (26) developed methods of preparing fluorine-substituted butadienes; Gray (4), Lutz (8), and Taylor (33) prepared fluorine-substituted isoprenes; Taylor (35) also prepared several isobutylenes; and Warner (34) prepared new fluoroolefins by the reaction of Grignard reagents with simple fluoroolefins.

Polymers containing a large percentage of fluorine tend to lack flexibility. Since heteroatoms in the backbone or side chain of polymers can add flexibility, methods of preparing the appropriate monomers were studied. O'Connor (31) and Pisacane (15) prepared fluorine-containing nitroso compounds; Stump (32) prepared fluorine-containing unsaturated ethers; and Tomasino (36) prepared several silanes and siloxanes containing fluoroolefin groups.

Polydimethylsilicone rubber is known for its exceptional thermal stability and resistance to ozone. It has excellent electrical properties and very low water absorption. However, it is degraded by strong acids and bases, and is particularly prone to swelling in hydrocarbon solvents.

The thermal stability and inertness of fluorocarbons to chemical attack and to solvents recommended their incorporation into silicone rubber to improve its properties. Studies showed that fluorine on a carbon either  $\alpha$  or  $\beta$  to the silicon atom decreased the stability of the molecule to both heat and strong base. Fluorine atoms three or more removed from the silicon atom, however, caused no decrease in stability.

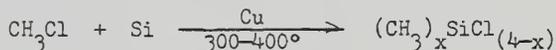
As part of a broad program to develop new polymers, the Materials Laboratory of the Wright Air Development Center (WADC) undertook research to develop fluoro-silicone elastomers. Under this program

McBee (9) prepared the first difunctional fluorine-containing silane,  $\text{CH}_3\text{Si}(\text{OCH}_3)_2\text{CH}_2\text{CH}_2\text{CF}_3$ , by the reaction of  $\text{CF}_3\text{CH}_2\text{CH}_2\text{MgBr}$  with  $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ . His attempts to polymerize this material and to copolymerize it with dimethyldichlorosilane yielded only viscous oils. However, at Dow-Corning (as part of the WADC project) an elastomeric polymer was achieved using  $\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}_2\text{CF}_3$ , a compound reported by Tarrant, et al. (27). This rubber, called Silastic LS-53, retained all of the exceptional high and low temperature properties of silicone rubber with the added feature of excellent fuel and oil resistance (16).

If an elastomer is to be produced in any quantity, it is necessary that the monomers be produced in good yield by an economical process. The more important general syntheses of silanes will be considered below:

### 1. The Direct Synthesis

The most important method of preparing organosilicon compounds is the direct reaction of an organic halide with elemental silicon. The reaction occurs when the halide vapors are passed over silicon at high temperatures in the presence of a metal catalyst. A mixture of products occurs.



but reaction conditions can be varied to favor a particular product. Copper is the preferred catalyst with alkyl halides, although several other metals can be used. Silver is the most effective catalyst with aryl halides.

### 2. The Organometallic Method

Grignard and organolithium reagents react with silicon halides, alkoxides, and hydrides to form compounds with new silicon-carbon bonds.



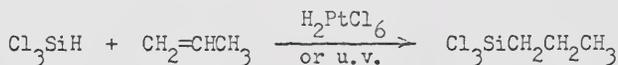
The chlorides are more easily replaced than the alkoxides or the hydrides:



Because of the availability of organosilicon chlorides, and the great variety of organometallic reagents, this is the most versatile method of preparing organosilicon compounds.

### 3. Addition of Olefins to Silicon Hydrides

Olefins (and alkynes) can be added to silicon hydrides in the presence of a catalyst such as peroxides, acids, metals, metal salts, ultraviolet light, or  $\gamma$ -rays. Chloroplatinic acid appears to be the most effective of these catalysts when u.v. light is not practical.



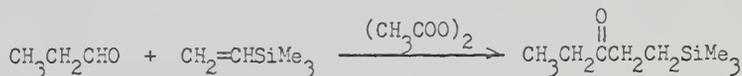
This reaction is general and is especially valuable in that a carbon-silicon bond can be formed without disturbing the

silicon-chlorine bond, as would be the case with organometallic reagents. This method has become a very important laboratory and industrial process.

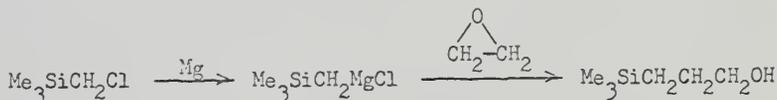
#### 4. Preparations from Carbon-Functional Organosilicon Compounds

Complex organosilicon compounds may be prepared by further reaction with a functional group already present in an organic substituent attached to a silicon atom. Many carbon-functional organosilicon compounds are readily prepared and are available commercially.

Silanes containing olefinic groups, such as vinyl and allyl groups, are perhaps the most important of these.



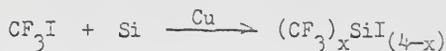
The halides are also useful:



These are very general examples. The reactions under this heading are very extensive, and with some notable exceptions, are the same as would be expected of the functional groups in hydrocarbon molecules.

All of the above methods have been used to prepare fluorine containing silanes. Haszeldine (5) was the first to report the successful

preparation by the direct method.



This method has been used with other perfluoroalkyl halides, but poor yields are generally obtained and thus the method is not of importance in monomer synthesis.

McBee's synthesis of the first difunctional fluorine-containing silane has already been referred to (9):

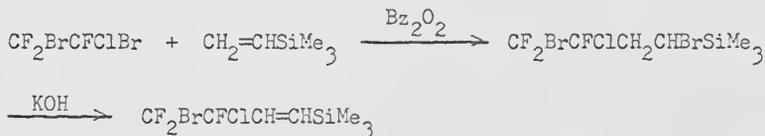


The organometallic method has been used very extensively to prepare fluorine-containing silicon monomers.

Tarrant and coworkers (27) were able to prepare a similar monomer to McBee's in a much more convenient reaction:



The free-radical addition of perhaloalkanes to olefins is an important step in preparing silanes containing fluoroolefin groups. Tarrant (23) reported the following reactions:



In these laboratories Tomasino studied the free-radical addition of  $\text{CF}_2\text{BrCFClBr}$  to a series of alkenyl silicon compounds. These compounds were vinyl dimethylethoxysilane, vinyl dimethylchlorosilane,

divinyldimethylsilane, allyltrimethylsilane, diallyldimethylsilane, vinylpentamethyldisiloxane, and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane. The addition products obtained were further dehalogenated and/or dehydrohalogenated to form new unsaturated compounds.

It was found that the normal addition products were obtained when  $\text{CF}_2\text{BrCFClBr}$  was reacted with the vinylsilanes. However, in the dehalogenation of these products with zinc and ethanol considerable reduction of the bromine on the carbon  $\alpha$  to the silicon took place. For instance, in the dehalogenation of  $\text{CF}_2\text{BrCFClCH}_2\text{CHBrSiMe}_3$ , a 43% yield of the expected  $\text{CF}_2=\text{CFCH}_2\text{CHBrSiMe}_3$  was obtained, as well as an additional 21% of the reduced product,  $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{SiMe}_3$ . This phenomenon was noted in each of the compounds containing a  $\alpha$  bromine atom.

Reaction of  $\text{CF}_2\text{BrCFClCH}_2\text{CHBrSiMe}_3$  with concentrated sulfuric acid gave  $[\text{CF}_2\text{BrCFClCH}_2\text{CHBrSiMe}_2]_2\text{O}$  in 16% yield. This compound was then dehalogenated to give a mixture of unsaturated disiloxanes, including  $[\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{SiMe}_2]_2\text{O}$  in a 5% yield.

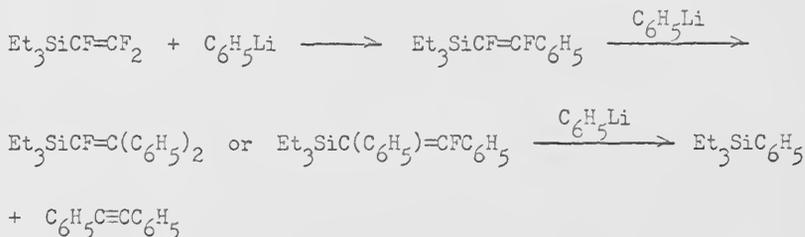
Reaction of  $\text{CF}_2\text{BrCFClBr}$  with allyltrimethylsilane did not give the expected  $\text{CF}_2\text{BrCFClCH}_2\text{CHBrCH}_2\text{SiMe}_3$ , but instead  $\text{CF}_2\text{BrCFClCH}_2\text{CH}=\text{CH}_2$  was obtained in a 30% yield. This was undoubtedly formed from the expected addition product, since it is known that silanes containing a halogen  $\beta$  to the silicon atom are quite unstable to heat and form terminal olefins (22). Diallyldimethylsilane, however, gave the desired mono-addition product,  $\text{CF}_2\text{BrCFClCH}_2\text{CHBrCH}_2\text{Si}(\text{Me}_2)\text{CH}_2\text{CH}=\text{CH}_2$ .

The first trifluorovinylsilane derivative was prepared by Knunyants (24). He reacted  $\text{CF}_2=\text{CFMgI}$  with  $\text{SiCl}_4$  and obtained  $\text{Si}(\text{CF}=\text{CF}_2)_4$  as the only product. It is interesting to note that no mixed products were obtained. Knunyants failed to obtain products when  $\text{CF}_2=\text{CFMgI}$  was

reacted with alkyl or phenyl substituted chlorosilanes.

Seyferth, however, was able to prepare  $\text{Et}_3\text{SiCF}=\text{CF}_2$  from the reaction of  $\text{Et}_3\text{SiCl}$  with  $\text{CF}_2=\text{CFMgBr}$  in THF (17) and  $\text{Me}_3\text{SiCF}=\text{CF}_2$  from the reaction of  $\text{Me}_3\text{SiCl}$  with  $\text{CF}_2=\text{CFLi}$  (21). He also prepared  $\text{Me}_3\text{SiCF}=\text{CF}_2$  from  $\text{CF}_2=\text{CFMgBr}$ , but the product boils very close to THF ( $67^\circ$ ) and had to be brominated before it could be recovered.

Knunyants (24) found that all the Si-C bonds in  $\text{Si}(\text{CF}=\text{CF}_2)_4$  were broken under the influence of aqueous base, yielding  $\text{CF}_2=\text{CFH}$  quantitatively. Seyferth (18) obtained, in reacting  $\text{Et}_3\text{SiCF}=\text{CF}_2$  with  $\text{EtONa}$ , a 69% yield of  $(\text{Et}_3\text{Si})_2\text{O}$  and only 28% of the expected  $\text{Et}_3\text{SiCF}=\text{CFC}_2\text{H}_5$ . He further found in reacting phenyllithium with  $\text{Et}_3\text{SiCF}=\text{CF}_2$  that the third mole of  $\text{C}_6\text{H}_5\text{Li}$  cleaved the Si-C bond:



These reactions indicate the instability of the Si-C bond in Si-CF=CFR to basic media. Further, considering the failure to get mixed products in reacting  $\text{CF}_2=\text{CFMgI}$  with  $\text{SiCl}_4$ , it is obvious that the presence of a fluorinated olefinic linkage  $\alpha$  to a silicon atom renders the silicon atom more susceptible to nucleophilic attack. This can be explained quite readily, realizing that there is p- $\pi$  d- $\pi$  overlap between the unsaturated carbon atom and the silicon atom. The electron withdrawing effect of the fluorine atoms is transmitted to the silicon



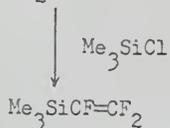
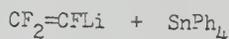
## II. DISCUSSION

In the course of this research, compounds of the type  $\text{RMe}_2\text{Si}(\text{CH}_2)_n\text{-CF=CF}_2$  have been prepared. R may represent a methyl group, chlorine, ethoxide, or the symmetrical disiloxane; and n may be 0, 1, 2, or 3. The compounds will be grouped for study according to the value of n, since each group required a different method of synthesis. The reactions will be considered separately.

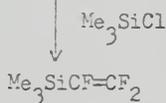
In addition, a new method of preparing fluorine-containing alkoxides of silicon will be discussed.

### Preparation of Compounds of the Type $\text{RMe}_2\text{SiCF=CF}_2$

The preparation of trifluorovinyl-Grignard (6,7,13) and -lithium (20,30) reagents made possible the incorporation of the trifluorovinyl group into many organic and organometallic compounds. However, at the beginning of this research, the only trifluorovinylsilanes reported were tetra-(trifluorovinyl)silane (24), trifluorovinyltriethylsilane (17), and trifluorovinyltriethoxysilane (19). These were prepared via the Grignard reagent. Later, Seyferth (21) reported the preparation of trifluorovinyltrimethylsilane from trifluorovinyl lithium. He prepared the lithium reagent by the metal exchange reaction between trifluorovinyltin compounds and phenyllithium, a process involving several steps and giving rise to low over-all yields.



Tarrant, et al., had meanwhile discovered a facile method of preparing trifluorovinyl lithium via the halogen exchange reaction between bromo-trifluoroethylene and alkyllithium compounds at  $-78^\circ$ . By this method, trifluorovinyltrimethylsilane [I] was prepared during this research in yields of 65% without the separation of intermediates.



[I]

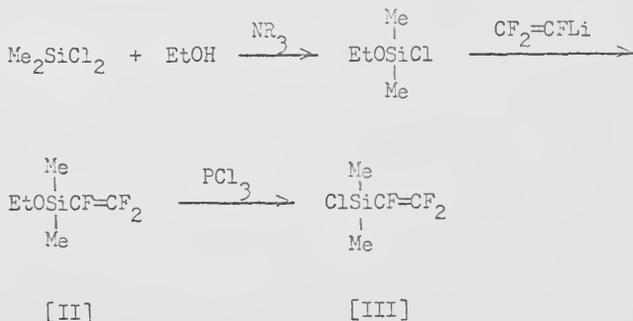
The physical properties of this compound were consistent with those reported by Seyferth. It should be noted that the trifluorovinyl group in this compound shows absorption in the infrared at 5.83 microns, while the same group attached to carbon, hydrogen, bromine, or chlorine absorbs between 5.5 and 5.6 microns. Triphenyltrifluorovinyltin (prepared in this laboratory) absorbs at 5.88 microns, while tris-trifluorovinylboron absorbs at 5.95 microns (2). All of the metal compounds mentioned have empty p- or d-orbitals on the metal atom which are undoubtedly responsible for the large shift from the usual absorption frequency. As a matter of fact, the authors in the above reference use this shift as evidence for carbon-boron  $\pi$ -bonding.

It was anticipated that other compounds of this series could be prepared with R being a functional group, such as chlorine or the ethoxide. As mentioned in the Introduction, Knunyants (24) found that only the tetra-substituted product was obtained when  $\text{CF}_2=\text{CFMgI}$  was reacted with  $\text{SiCl}_4$ . It was hoped that  $\text{ClMe}_2\text{SiCF}=\text{CF}_2$  could be prepared by reacting  $\text{CF}_2=\text{CFLi}$  with  $\text{Me}_2\text{SiCl}_2$  in a 1:1 ratio. However, only the di-substituted product was obtained:



Elemental analysis,  $\text{Mr}_D$  data, and infrared data were consistent with this structure.

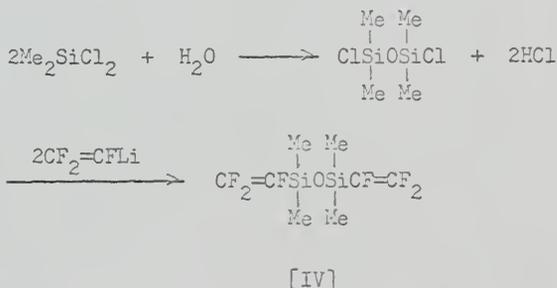
The alkoxy-silanes undergo approximately the same reactions as the chlorosilanes. Both, for instance, can be displaced by a Grignard or lithium reagent. However, the chlorosilanes are somewhat more reactive toward these reagents than the alkoxy-silanes. Thus,  $\text{ClSiMe}_2\text{OC}_2\text{H}_5$  was prepared from  $\text{Me}_2\text{SiCl}_2$  and  $\text{C}_2\text{H}_5\text{OH}$  in triethylamine. This compound then reacted with  $\text{CF}_2=\text{CFLi}$  to form  $\text{C}_2\text{H}_5\text{OSiMe}_2\text{CF}=\text{CF}_2$ , and the chlorosilane was then prepared by reaction with  $\text{PCl}_3$ .



The compounds were identified by elemental analysis,  $\text{Mr}_D$  data, and their infrared spectra.

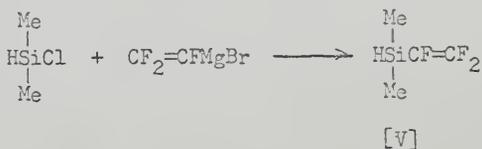
Compounds such as II and III might be of interest as crosslinking agents in polymers or intermediates in preparing other trifluorovinyl-silicon derivatives.

The symmetrical disiloxane is another di-functional compound in the series under consideration. The compound  $\text{CF}_2=\text{CFSiMe}_2\text{OSiMe}_2\text{CF}=\text{CF}_2$  could undoubtedly have been prepared readily from either II or III, but was actually prepared by another method before II and III were synthesized. The compound  $\text{ClSiMe}_2\text{OSiMe}_2\text{Cl}$  was prepared by the method of Patnode and Wilcox (14). This dichlorodisiloxane was then reacted with  $\text{CF}_2=\text{CFLi}$  to prepare IV:



Elemental analysis, i.r. spectra, and  $M_r$  data were consistent with the assigned structure.

Another interesting compound of this series was prepared where R represents hydrogen. The reactivity of the silicon-hydrogen bond was discussed in the Introduction. Trifluorovinyl-dimethylsilane was prepared by the reaction of dimethylchlorosilane with trifluorovinylmagnesium bromide:



Elemental analysis and  $M_r$  data were consistent with this structure. In addition to infrared absorption at 5.83 microns for the  $CF_2=CF$  group, a strong absorption at 4.65 microns was present which indicates the Si-H bond. Two later attempts to prepare this compound using  $CF_2=CFLi$  failed. A brown tar was obtained in each reaction.

Preparation of  $Me_3SiCH_2CF=CF_2$

Tarrant and Warner (34) discovered that Grignard reagents would substitute organic groups for fluorine in fluoroolefins. Dixon (3) discovered that lithium reagents would likewise substitute, and that they gave somewhat greater yields of the new olefins than the Grignard reagents:

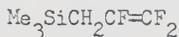


With tetrafluoroethylene, Grignard reagents give, in general, mono-substituted products. Lithium compounds, aryllithium compounds in particular, tend to give di-substituted products:



mostly

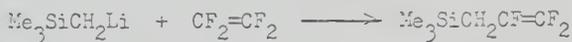
It was hoped that 2,3,3-trifluoroallyltrimethylsilane could be prepared from the Grignard reagent of chloromethyltrimethylsilane:



This reaction was run both by allowing a cold solution of Grignard reagent and  $\text{CF}_2=\text{CF}_2$  to warm to room temperature and by shaking the mixture in a sealed tube for several days. In neither case was any reaction observed.

The lithium reagent was prepared by reacting lithium with bromomethyltrimethylsilane. A cold solution of the lithium compound and  $\text{CF}_2=\text{CF}_2$  was allowed to warm to room temperature. An exothermic reaction took place and most of the material was lost. Recovered material gave a product boiling about  $100^\circ$  which showed no infrared absorption that would indicate a fluoroolefin. The tetrafluoroethylene was probably lost when the reaction heated.

The reaction was repeated in a sealed tube. The  $\text{CF}_2=\text{CF}_2$  was condensed into the tube at liquid nitrogen temperature, and the tube placed in an ice bath. After two days, the tube was opened and the desired compound was obtained.



[VIII]

Elemental analysis, infrared spectra, and  $M_r$  data all support the structure as shown. It should be noted that the i.r. absorption due to the double bond is at 5.83 microns. There is no shift observed due to the silicon atom in the allylic position.

Other compounds of this series were not prepared. It is not likely that a lithium reagent of the type  $\text{RMe}_2\text{SiCH}_2\text{Li}$  could be prepared where R is a functional group of interest in this series. The chemistry of VIII was not investigated at length.

Preparations of Compounds of the Type  $\text{RMe}_2\text{SiCH}_2\text{CH}_2\text{CF}=\text{CF}_2$

Tomasino (36), in his studies of some fluorine-containing organo-silicon compounds, prepared the first compound of this series. He added  $\text{CF}_2\text{BrCFClBr}$  to  $\text{CH}_2=\text{C}(\text{SiMe}_3)_2$ , and then dehalogenated the product with zinc to obtain the olefin. He found that a considerable amount of the bromine on the carbon atom adjacent to the silicon atom was reduced:



43%



21%

Thus it is obvious that the  $\alpha$ -bromine atom is readily reduced. Since this reduced product was desired in this research, it was anticipated that the yield could be increased by the addition of concentrated hydrochloric acid to the reaction mixture, containing excess zinc, when the dehalogenation was complete:



65%

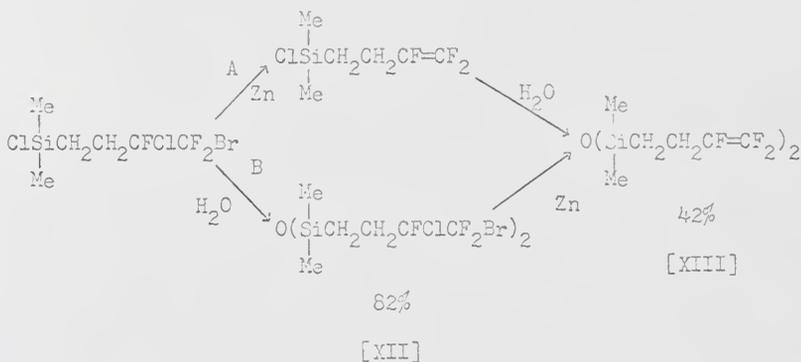
[IX]

This compound had the same properties as reported by Tomasino. It should be noted that the yield is almost exactly the same as Tomasino's total for the two compounds, indicating that reduction of the bromide is quantitative.



Elemental analysis and  $M_r$  data support this structure. This reaction gave the desired product in an acceptable yield. Other products were obtained, but dimethyldichlorosilane was the only one identified. Another product, which appeared to have no hydrogen but considerable carbon and fluorine, was obtained, but could not be separated from the reaction mixture in sufficient purity to be identified.

Compound X could then give the desired disiloxane by two possible pathways:



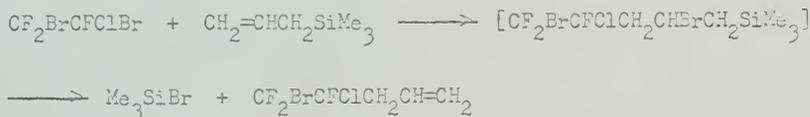
Pathway A was attempted, using THF as a solvent. The dehalogenation appeared to proceed normally. Since the chlorosilane was desired at this step, hydrolysis to remove the zinc halides could not be used. Upon distillation a reaction took place in the distilling flask and a two phase product was obtained, which proved to be a complex mixture that could not be separated. The contents of the distilling flask became very black.

Pathway B, however, went with no difficulty. The yield in the dehalogenation step can probably be improved considerably, since no attempt was made to find optimum conditions. The properties of XIII agree with those reported by Tomasino.

An attempt to prepare  $\text{ClMe}_2\text{SiCH}_2\text{CH}_2\text{CF}=\text{CF}_2$  directly by adding dimethylchlorosilane to 1,1,2-trifluoro-1,3-butadiene in a sealed tube with  $\text{H}_2\text{PtCl}_6$  at  $70^\circ$  resulted in an explosion. Irradiation of dimethylchlorosilane and 1,1,2-trifluoro-1,2-butadiene in a sealed tube in sunlight gave a white polymer characteristic of the polymer obtained by irradiation of the butadiene alone.

Preparation of Compounds of the Type  $\text{R}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$

The preparation of a silane of the type  $\text{R}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$  required some special considerations. Tomasino had attempted to prepare an analogous compound by the addition of  $\text{CF}_2\text{BrCFClBr}$  to  $\text{CH}_2=\text{CHCH}_2\text{SiMe}_3$ . He obtained, however, cleavage products of his desired intermediate:



It could not be determined if the addition product actually formed, or whether the intermediate radical form cleaved:



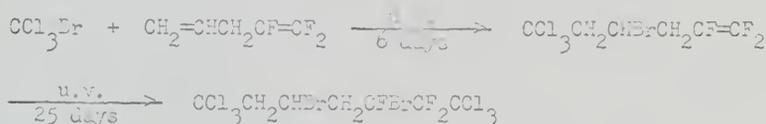
If the addition product were formed, it would not be expected to be stable at the reaction temperature, because  $\beta$ -halo silanes cleave at around  $80-90^\circ$  to form alkenes and the halo silane (22):



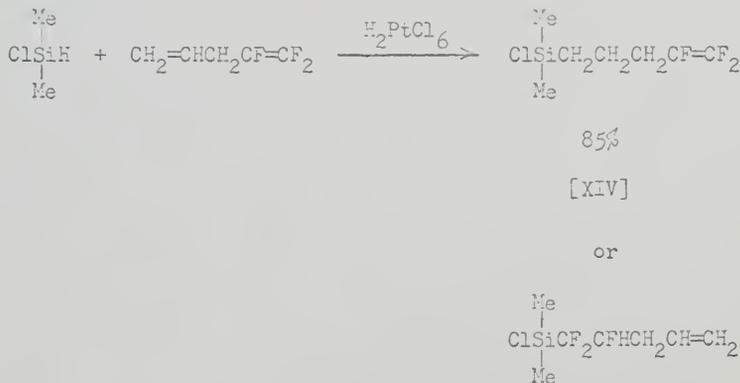
Tomasino was successful in obtaining an addition product with diallyldimethylsilane, but  $\text{HBr}$  was lost during distillation:



fluoroolefins and hydrocarbon olefins in such reactions had been made. Concurrently with this research, in these laboratories Muramatsu and Tarrant (11) studied the relative reactivity of this pentaene toward the free-radical addition of  $\text{CCl}_3\text{Br}$ . They found that after 6 days irradiation, attack on the hydrocarbon vinyl group was predominant. After 11 days a mixture of the two products was obtained. After 25 days, addition to both double bonds of the fluoroolefin was complete.



Thus, it is obvious that a free radical attack would take place preferentially at the hydrocarbon vinyl group. While the Si-H group can be readily added across an olefin by free radical initiation, addition by means of metal chloride catalysis is generally considered to be an ionic process (23). It was decided to run the reaction using  $\text{H}_2\text{PtCl}_6$  as a catalyst:



The reaction was carried out in a sealed glass tube due to the low

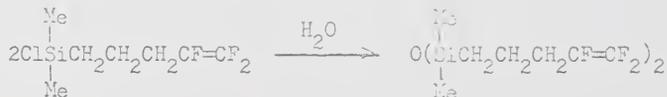
boiling point of the alkene (38°). The solution was heated at about 75° overnight and conversion was essentially quantitative. The distilled product showed only one infrared absorption which could be attributed to a carbon-carbon double bond. This was at 5.52  $\mu$ , which indicated a trifluorovinyl group. Thus addition was to the hydrocarbon vinyl group to give XIV. Elemental analysis and  $M_r_D$  data also support this structure.

The preparation of the trimethyl derivative was accomplished by reacting XIV with the methyl Grignard reagent. While the fluoroolefin might also be expected to react with the Grignard reagent, the much greater reactivity of the silicon-chlorine bond led to the desired product in good yield:



Structural proof was by elemental analysis, infrared spectra, and  $M_r_D$  data.

The disiloxane was readily prepared by reacting XIV with water:

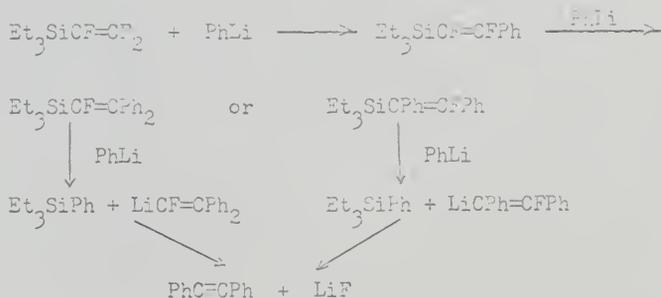


#### Reactions of $\text{Me}_3\text{SiCF}=\text{CF}_2$

Seyferth, in his studies of the vinyl derivatives of metals, has investigated the addition reactions of trifluorovinyltriethylsilane (19)

and the reaction of nucleophilic reagents with trifluorovinyltriethylsilane (18). The reactions of trifluoro-trimethylsilane would be expected to be similar to those of the trialkyl compound, and for this reason the addition reactions were not studied.

In his studies of nucleophilic reactions the trifluorovinyl group underwent, in general, the normal reactions of fluorosilanes. An exception was the reaction of the silane with sodium ethoxide in ethanol, where the major product was triethylthoxysilane, and in a lesser yield the displacement (or addition-elimination) product,  $\text{Et}_3\text{SiCF}=\text{CFOEt}$ . This is consistent with the instability of the trifluorovinyl-silicon bond in base. He found, however, that organometallic compounds, and metal alkoxides in nonprotic solvents, gave good yields of the displacement products. Thus, reaction with various Grignard and lithium reagents, as well as sodium alkoxides, cyanides, and mercaptides gave products of the type  $\text{Et}_3\text{SiCF}=\text{CPh}$ . He also studied the reaction of the silane with excess phenyllithium, and found that the third mole of phenyllithium broke the carbon-silicon bond:



The instability of  $(\text{CF}_2=\text{CF})_L\text{Si}$  to base, already discussed, and the instability of Seyferth's compound to a third mole of phenyllithium,

prompted a further study of the nucleophilic reactions of  $\text{Me}_3\text{SiCF}=\text{CR}$ . As anticipated, it was found that lithium reagents would react readily to form compounds of the type  $\text{Li-O-Si-CR}_2$ , if no other lithium reagents were used. Of the lithium reagents used, only  $\text{LiAlH}_4$  and  $\text{LiC}_2\text{H}_5$  and lithium failed to give adducts. In all other cases it is very successful and the desired lithium compound was usually formed.

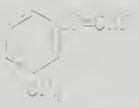
Adducts were formed where R represents methyl, n-butyl, phenyl, n-trifluoromethylphenyl, 1-naphthyl, 2-thiophenyl, allyl, and vinyl. The yields in the cases of the methyl, allyl, and vinyl products were poor.

It is obvious that, if the silicon-carbon bond is as subject to basic hydrolysis in compounds of the type  $\text{SiCF}=\text{CR}$  as in the trifluoro-vinylsilanes, this would represent a general method of preparing 1,3-difluoroolefins.

Each of the  $\text{Me}_3\text{SiCF}=\text{CR}$  adducts was reacted in alcoholic KOH solution. Good yields of the desired olefins,  $\text{CHF}=\text{CR}$ , was obtained in the cases of the n-butyl, phenyl, n-trifluoromethylphenyl, and 1-naphthyl adducts. In the cases of the methyl, allyl, and vinyl adducts, insufficient starting material ( $\text{Me}_3\text{SiCF}=\text{CR}$ ) was available. In each case a small amount of olefin was obtained, but not enough for positive identification. In the case of the 2-thiophenyl compound, the product obtained decomposed into a black tar in about 48 hours. While the infrared spectra was consistent for  $\text{SC}_4\text{H}_3\text{CF}=\text{CHF}$ , the elemental analysis was somewhat off from the calculated values. Since the compound had appeared pure by vapor phase chromatography, the compound had probably decomposed too much by the time the elemental analysis was run.

The olefins prepared by this method and the intermediates are listed in Table 1.

TABLE I  
Olefins Prepared from  $\text{Me}_3\text{SiOCF}=\text{CFCH}_2$  and Lithium Reagents

Lithium Reagent	Method of Preparation	Intermediate Compound	Final Olefin
$\text{CH}_3\text{Li}$	a	$\text{Me}_3\text{SiOCF}=\text{CFCH}_3$	d
$n\text{-C}_4\text{H}_9\text{Li}$	a	$\text{Me}_3\text{SiOCF}=\text{CFCH}_2\text{C}_4\text{H}_9$	$\text{C}_4\text{H}_9\text{OCF}_2\text{H}$
$\text{C}_6\text{H}_5\text{Li}$	a	$\text{Me}_3\text{SiOCF}=\text{CFCH}_2\text{C}_6\text{H}_5$	
	b	$\text{Me}_3\text{SiOCF}=\text{C}(\text{C}_6\text{H}_4\text{CH}_3)$	
	b	$\text{Me}_3\text{SiOCF}=\text{C}(\text{C}_{10}\text{H}_7)$	
	b	$\text{Me}_3\text{SiOCF}=\text{C}(\text{C}_4\text{H}_3\text{S})$	d
$\text{CH}_2=\text{CHCH}_2\text{Li}$	c	$\text{Me}_3\text{SiOCF}=\text{CFCH}_2\text{CH}=\text{CH}_2$	d
$\text{CH}_2=\text{CHLi}$	c	$\text{Me}_3\text{SiOCF}=\text{CFCH}=\text{CH}_2$	d

- a. Prepared directly:  $\text{R}_2\text{R} + \text{RLi} \longrightarrow \text{RLi} + \text{LiR}$   
 b. Prepared by halogen-lithium exchange:  $\text{RBr} + \text{BuLi} \longrightarrow \text{RLi} + \text{BuBr}$   
 c. Prepared by tin-lithium exchange:  $\text{R}_4\text{Sn} + 4\text{PhLi} \longrightarrow \text{RLi} + \text{Ph}_3\text{Sn}$   
 d. The desired olefin was not positively identified.

Another common reaction of fluoroolefins is the thermal dimerization reaction to give cyclobutanes. Trifluorovinyltrimethylsilane was heated for two days at 200° in a sealed tube to give a very small yield of a product tentatively identified as the dimer:

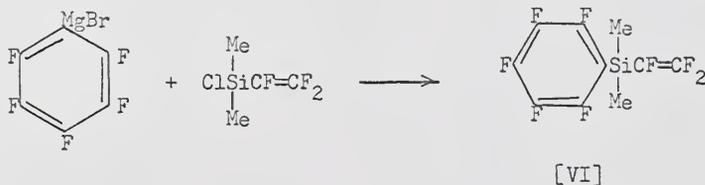


While the amount obtained was insufficient for complete analysis, the elemental analysis and infrared analysis was consistent for the dimer. The remaining black, viscous liquid indicated that much decomposition had taken place.

An attempt to prepare either the Diels-Alder product or the vinylcyclobutane with 1,3-butadiene failed. Only a hard, black solid product and a thick oil were formed. No volatile products were obtained.

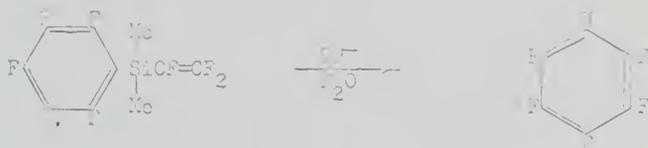
Reaction of  $\text{ClMe}_2\text{SiCF}=\text{CF}_2$  with Pentafluorophenylmagnesium Bromide

As an example of the use of  $\text{ClMe}_2\text{SiCF}=\text{CF}_2$  [III] as an intermediate in the synthesis of other silanes, III was reacted with pentafluorophenylmagnesium bromide:



Having noted the instability of the silicon-carbon bond to base in the fluoroolefin derivatives previously discussed, it was desired to find if the pentafluorophenyl group would be stable under similar

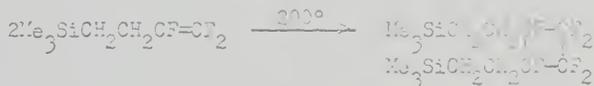
conditions. The same compound (VII) was reacted by Lemstra's VIII. A gas, presumably  $\text{CH}_2=\text{CF}_2$ , was evolved. If the cyclo-siloxane were stable to base, one would expect to find 1,7-difluoro-1,3,5,7-tetraethylsiloxane about the pressure after several weeks. If the bond were not stable to base, polymer formation would be expected. Examination of the products showed a small amount of the disiloxane, but pentafluorobenzene (identified by comparison of infrared spectra and v.p.c. retention time with those of an authentic sample) was present.



+  $\text{CF}_2=\text{CHF}$  + cyclic siloxanes

### Reaction of $(\text{C}_6\text{H}_5)_2\text{SiCF}_2$

Treatment of  $(\text{C}_6\text{H}_5)_2\text{SiCH}_2\text{CH}_2\text{CF}=\text{CF}_2$  [VIII] for two days at  $200^\circ$  in a sealed tube gave the dimer in 33% yield:



[XIX]

Infrared and n.m.r. spectra, and  $M_p$  data are consistent with this structure. Unreacted starting material was recovered, which indicates the stability of both the olefin and the product at this temperature. Some discoloration was apparent.

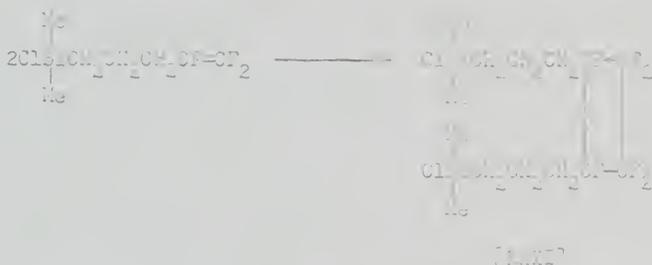




Elemental analysis and infrared spectra agree with this structure.

#### Thermal Decomposition of XIII

The only reaction observed with the pentacyclic derivatives was thermal decomposition of XIII:



Elemental analysis is consistent with this formula. The compound, a solid, was obtained in 42% yield. It is interesting to note the possibility of forming a polymer which would contain the cyclopentyl group in the backbone of the chain.

No further reactions were attempted with the  $\text{C}_2\text{Cl}_5\text{C}(\text{CH}_2)_2\text{C}(\text{CH}_2)_2\text{C}(\text{OCF}_2)_2$  compounds. There is no reason to expect them to differ from the reactions of the next lower members of the homologous series.

#### Preparation of Fluorocyclohexanones

Calas and Duffant (1) found that trichlorosilane and triphenylsilane added to aliphatic ketones to form the corresponding alkoxides when irradiated with ultra violet light. Having two fluorinated acetones ( $\text{CF}_3\overset{\text{O}}{\text{C}}\text{CF}_3$  and  $\text{CF}_2\overset{\text{O}}{\text{C}}\text{ClCF}_2\text{Cl}$ ) available, it was decided to attempt















TABLE 2 (Continued)

Compound No.	Compound	% Yield	b. p. °C/mm	$n_D^{20}$	$d_4^{20}$
XXVIII	CF=CHF 	83	69/1	1.5975	1.224
XXIX	$(CH_3)_3SiCH_2CH_2CF_2CF_2$ $(CH_3)_3SiCH_2CH_2CF_2CF_2$	33	70/0.8	1.4059	1.069
XXX	$(CH_3)_3SiCH_2CH_2CF_2CF_2$ 	69	90/2	1.4990	1.007
XXXI	$Cl(CH_3)_2SiCH_2CH_2CH_2CF_2CF_2$ $Cl(CH_3)_2SiCH_2CH_2CH_2CF_2CF_2$	42	145/5 (m. p. 53-56)		
XXXII	$Cl$ $ $ $Cl$ $CF_3$ $ $ $ClSiOCH$ $ $ $CH_3CF_3$	63	94	1.3333	1.439



### III. EXPERIMENTAL

#### General

All temperatures reported are uncorrected and are given in degrees Centigrade. Molar refraction ( $M_{r_D}$ ) data were calculated from bond refraction values reported by Warrick (38). It was found that the experimental  $M_{r_D}$  values were always somewhat higher than the calculated values when a fluorine atom was on an aromatic ring or on an olefin conjugated with an aromatic ring. The experimental value was also high in the butadiene,  $\text{Me}_3\text{SiCF}=\text{CFCH}=\text{CH}_2$ . No general correction could be calculated, so these values are not reported.

Refractive indices were determined with an Abbe refractometer at 20 degrees Centigrade, densities were determined at 20 degrees Centigrade using either a 5 milliliter or 1 milliliter pycnometer.

Infrared spectra were obtained using a Perkin-Elmer Infracord. Only absorption peaks indicative of the structure are reported.

Analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

#### Preparation of Trifluorovinylsilanes

The trifluorovinylsilanes, with the exception of dimethyltrifluorovinylsilane, were prepared by adding the appropriate chlorosilane to a solution of trifluorovinylolithium at  $-78^\circ$ . The trifluorovinylolithium was generally prepared as follows:







Preparation of 2,3,3-Trifluoroallyltrimethylsilane [VIII]

Bromomethyltrimethylsilane (8.4 g., 0.05 mole) was reacted with an excess of dispersed lithium in 50 ml. ether. The lithium reagent formed was filtered to remove the remaining lithium and added to a 100 ml. thick-walled glass tube. Tetrafluoroethylene (6 g., 0.06 mole) was condensed into the tube at liquid nitrogen temperature. The tube was evacuated and sealed and left in an ice bath overnight, and at room temperature for 12 hours. The tube was opened and all volatile materials were transferred into a cold trap via an aspirator to separate them from the solid residue. Distillation of the ether solution gave 3.6 g. (42%) VIII, b.p. 89°,  $n_D^{20}$  1.3745,  $d^{20}$  0.949,  $M_r$  calcd. 39.2, found 40.4.

Anal. Calcd. for  $C_6H_{11}F_3Si$ : C, 42.84; H, 6.59; F, 33.89. Found: C, 43.16; H, 6.61; F, 33.49.

Preparation of (3,4,4-Trifluoro-3-butenyl)silanes

(3,4,4-Trifluoro-3-butenyl)trimethylsilane [IX]

A 500 ml. 3-necked flask was fitted with a stirrer, condenser, and dropping funnel. A stirred mixture of isopropyl alcohol (200 ml.) and zinc dust (130 g., 2 moles) was heated to reflux. (1,4-Dibromo-3-chloro-3,4,4-trifluorobutyl)trimethylsilane (188 g., 0.50 mole) was added at a rate to maintain reflux without added heat. After the last of the silane was added the mixture was refluxed for an additional hour. The heat was then removed and 100 ml. of 38% HCl was slowly added. Upon completion of the reaction, the mixture was filtered to remove the zinc. The two liquid phases were added to a 1 l. separatory funnel and water and ether added. The water layer was discarded; the ether layer was

washed twice more with water and dried over  $\text{CaCl}_2$ . Distillation yielded 68.5 g. (75%) [IX], b.p. 112-114°,  $n_D^{20}$  1.3808. Tomasino reported b.p. 114°,  $n_D^{23}$  1.3790.

(3,4,4-Trifluoro-3-chloro-4-bromobutyl)dimethylchlorosilane [X]

A solution of dimethylchlorosilane (25 g., 0.37 mole), 3,4,4-trifluoro-3-chloro-4-bromo-1-butene (57 g., 0.26 mole) and 1/2 ml. 1 M solution of  $\text{H}_2\text{PtCl}_6$  in isopropyl alcohol was refluxed in a 200 ml. flask for 24 hours. Distillation of the products gave 11 g. dimethyldichlorosilane and 35.8 g. X (44%), b.p. 205°,  $n_D^{20}$  1.4400,  $d^{20}$  1.513,  $M_r$  calcd. 56.4, found, 56.0.

Anal. Calcd. for  $\text{C}_6\text{H}_{10}\text{BrCl}_2\text{F}_3\text{Si}$ : C, 22.65; H, 3.16; F, 17.91.

Found: C, 22.69; H, 3.57; F, 18.97.

(3,4,4-Trifluoro-3-chloro-4-bromobutyl)methyldichlorosilane [XI]

A solution of methyldichlorosilane (23 g., 0.020 mole), 3,4,4-trifluoro-3-chloro-4-bromo-1-butene (40 g., 0.18 mole), and 1/2 ml. 1 M  $\text{H}_2\text{PtCl}_6$  solution in isopropyl alcohol was refluxed 24 hours. Distillation gave 45 g. (71%) XI, b.p. 220°,  $n_D^{20}$  1.4451,  $d^{20}$  1.6076,  $M_r$  calcd. 56.1, found 56.0.

Anal. Calcd. for  $\text{C}_5\text{H}_7\text{BrCl}_2\text{F}_3\text{Si}$ : C, 17.74; H, 2.08; F, 16.84.

Found: C, 17.92; H, 2.23; F, 17.07.

Attempted Dehalogenation of X

X (7 g., 0.03 mole) was slowly added to a refluxing mixture of zinc (5 g.) and THF. The reaction appeared to proceed smoothly with evolution of heat. The mixture was then distilled without further treatment, due to the reactivity of the silicon chloride. As the THF was removed and the flask temperature increased, the residue quickly

turned black and a two-phase mixture was distilled. The products were not separated and identified, but no olefinic group showed in the i.r. spectra.

1,3-Bis(3,4,4-trifluoro-3-chloro-4-bromobutyl)-1,1,3,3-tetramethyldi-siloxane [XII]

(3,3,4-Trifluoro-3-chloro-4-bromobutyl)dimethylchlorosilane (36 g., 0.11 mole) was heated with stirring overnight in 25 ml. water. The organic layer was separated and dried over  $\text{CaCl}_2$ . Distillation yielded 23 g. (82%) XII, b.p.  $125^\circ/\text{mm}$ ,  $n_D^{20}$  1.4345,  $d^{20}$  1.4712,  $M_{rD}$  calcd. 101.9, found 102.7.

Anal. Calcd. for  $\text{C}_{12}\text{H}_{20}\text{Br}_2\text{Cl}_2\text{F}_6\text{OSi}_2$ : C, 24.78; H, 3.47; F, 19.62. Found: C, 24.93; H, 3.52; F, 19.74.

1,3-Bis(3,4,4-trifluoro-3-trifluoro-3-butenyl)-1,1,3,3-tetramethyldi-siloxane XIII]

XII (22 g., 0.045 mole) slowly added to a refluxing mixture of 10 g. zinc in isopropyl alcohol. Water was added and the product extracted with ether. The ether layer was washed twice and dried over  $\text{CaCl}_2$ . Distillation yielded 6.8 g. (42%) XIII, b.p.  $95^\circ/6\text{mm}$ ,  $n_D^{20}$  1.3932. Tomasino (34) reported b.p.  $95^\circ/6\text{mm}$ ,  $n_D^{20}$  1.3975.

Preparation of (4,5,5-Trifluoro-4-pentenyl)silanes

(4,5,5-Trifluoro-4-pentenyl)dimethylchlorosilane [XIV]

1,1,2-Trifluoro-1,4-pentadiene (50 g., 0.41 mole), prepared by the method of Tarrant and Gilman (26), was sealed in a thick-walled glass tube with dimethylchlorosilane (40 g., 0.42 mole) and 1/2 ml. 1 M  $\text{H}_2\text{PtCl}_6$  solution in isopropyl alcohol. The tube was heated overnight at  $75^\circ$ . Distillation of products yielded 75 g. (85%) XIV, b.p.  $163^\circ$ ,  $n_D^{20}$  1.4046,  $d^{20}$  1.116,  $M_{rD}$  calcd. 48.0, found 47.6.



hexamethyldisiloxane (60%), b.p. 97-99°,  $n_D^{20}$  1.3777 (Lit. b.p. 100.4,  $n_D^{20}$  1.3772).

#### Attempted Dimerization of I

I (7.0 g., 0.45 mole) was sealed in a glass tube and heated at 200° for two days. Distillation gave some starting material and 0.25 g. (3.8%) of material boiling 96°/24mm. Considerable decomposition was evident.

Anal. Calcd. for  $C_{10}H_{18}F_4Si_2$ : C, 38.94; H, 5.88; F, 36.96.

Found: C, 39.19; H, 6.07; F, 37.22.

i.r. Data, while not conclusive, are in agreement with that expected of the dimer.

#### Attempted Reaction of 1,3-Butadiene with I

I (6.7 g., 0.044 mole) and butadiene (4.75 g., 0.090 mole) was sealed under  $N_2$  in a glass tube and heated at 200° for 24 hours. A black solid was obtained, but no volatile products were present.

#### Reaction of Lithium Reagents with I

In general, the lithium reagent was prepared either directly or by the halogen exchange reaction with butyllithium. The lithium reagent was then slowly added to an ether solution of I in a 3-necked flask equipped with a stirrer and reflux condenser. The reaction mixture was then hydrolyzed, the ether layer separated and dried, and the product obtained by distillation.

Reaction of methyllithium with I. Methyllithium (0.05 mole) was added to I (7.7 g., 0.05 mole) in ether. A gas was evolved. A sample was collected, and the i.r. spectra indicated that it was probably  $CH_3CF=CHF$ . The reaction mixture was worked up as described and

distillate = 1.4 g. (19%) 1-trimethylsilyl-1,2-difluoro-1-hexene  
[XVII], b.p. 80°,  $n_D^{20}$  1.3921,  $d^{20}$  0.917,  $M_{rD}$  calcd. 39.1, found 39.1.

Anal. Calcd. for  $C_6H_{12}F_2Si$ : C, 47.97; H, 9.06; F, 25.30. Found:  
C, 47.78; H, 9.07; F, 25.14.

Reaction of butyllithium with I. Butyllithium (0.10 mole) was  
slowly added to I (15.4 g., 0.1 mole) in ether. Work-up of the reaction  
mixture gave 13.4 g. (70%) 1-trimethylsilyl-1,2-difluoro-1-hexene  
[XVIII], b.p. 76°/40mm,  $n_D^{20}$  1.4112,  $d^{20}$  0.887,  $M_{rD}$  calcd. 53.0, found  
53.9.

Anal. Calcd. for  $C_9H_{18}F_2Si$ : C, 56.21; H, 9.44; F, 19.76. Found:  
C, 56.39; H, 9.48; F, 19.53.

Reaction of phenyllithium with I. Phenyllithium (0.10 mole) was  
slowly added to I (15.4 g., 0.10 mole) in ether. Work-up of the reac-  
tion mixture gave 15.1 g. (72%)  $\beta$ -trimethylsilyl- $\alpha,\beta$ -difluorostyrene  
[XIX], b.p. 70-74°/2mm,  $n_D^{20}$  1.5062,  $d^{20}$  1.0304.

Anal. Calcd. for  $C_{11}H_{14}F_2Si$ : C, 62.22; H, 6.64; F, 17.90. Found:  
C, 62.51; H, 6.53; F, 17.75.

Reaction of m-trifluoromethylphenyllithium with I. m-Bromobenzoc-  
trifluoride (22.5 g., 0.10 mole) was reacted with butyllithium (0.10  
mole). The reagent was then slowly added to I (15.4 g., 0.10 mole)  
in ether. Work-up of the reaction mixture gave 14.0 g. (50%) of  
m-trifluoromethyl- $\beta$ -trimethylsilyl- $\alpha,\beta$ -difluorostyrene [XX], b.p.  
101-104°/6mm,  $n_D^{20}$  1.4640,  $d^{20}$  1.181.

Anal. Calcd. for  $C_{12}H_{13}F_5Si$ : C, 51.42; H, 4.68; F, 33.89. Found:  
C, 52.31; H, 4.57; F, 33.22.

Reaction of 1-naphthyllithium with I. 1-Bromonaphthalene (20.7 g.,  
0.10 mole) was reacted with butyllithium (0.10 mole). (It was later

found that less than 0.10 mole of BuLi was used, but the correct amount is unknown.) The 1-naphthyllithium was slowly added to I (15.4 g., 0.10 mole) in ether. Work-up of the mixture gave 10 g. (54%) of 1-(1,2-difluoro-2-trimethylsilylvinyl)naphthalene [XXI], b.p. 100°/2mm,  $n_D^{20}$  1.5588,  $d^{20}$  1.116.

Anal. Calcd. for  $C_{15}H_{16}F_2Si$ : C, 68.69; H, 6.15. Found: C, 68.69; H, 6.35.

Reaction of 2-thiophenyllithium with I. 2-Bromothiophene (13.0 g., 0.09 mole) was reacted with butyllithium (0.09 mole). The 2-thiophenyllithium was slowly added to I (14 g., 0.09 mole) in ether. Work-up gave 10 g. (50%) 2-(1,2-difluoro-2-trimethylsilylvinyl)-thiophene [XXII], b.p. 60°/2mm,  $n_D^{20}$  1.5201,  $d^{20}$  1.135.

Anal. Calcd. for  $C_9H_{12}F_2SSi$ : C, 49.50; H, 5.54; F, 17.35. Found: C, 49.62; H, 5.52; F, 17.17.

Reaction of allyllithium with I. Tetraallyltin (7.1 g., 0.025 mole) was slowly added to an ether solution containing phenyllithium (0.10 mole). A precipitate of tetraphenyltin was formed. I (15.4 g., 0.10 mole) was added slowly to this mixture. The mixture was stirred for two hours and filtered. Distillation of the filtrate yielded 3.5 g. (20%) of 1-trimethylsilyl-1,2-difluoro-1,4-pentadiene [XXIII], b.p. 50°/30mm,  $n_D^{20}$  1.4180,  $d^{20}$  0.924,  $M_r$  calcd. 47.9, found 48.0.

Anal. Calcd. for  $C_8H_{14}F_2Si$ : C, 54.32; H, 7.97; F, 21.58. Found: C, 54.33; H, 7.81; F, 21.76.

Reaction of vinylithium with I. Tetravinyltin (5.7 g., 0.025 mole) was slowly added to an ether solution containing phenyllithium (0.10 mole). A precipitate of tetraphenyltin was formed. I (15.4 g., 0.10 mole) was slowly added to this mixture. The mixture was stirred

for two hours and steam distilled to remove the product from the 1,1,1-trimethylsilyl-1,2-difluoro-1,3-butadiene. The ether layer was separated, dried, and distilled. The product was found to polymerize when heated, but 2.3 g. (10%) of 1,1,1-trimethylsilyl-1,2-difluoro-1,3-butadiene [XXIV] was obtained, b.p. 45°/40mm,  $n_D^{20}$  1.4400,  $d_4^{20}$  0.944.

Anal. Calcd. for  $C_7H_{12}F_2Si$ : C, 51.74; H, 7.45; F, 29.41. Found: C, 52.14; H, 7.30; F, 21.36.

Preparation of 1,2-Difluoroalkenes from the Products of the Organosilicon Reaction

In general, the compound formed in the reaction of the 1,1,1-trimethylsilyl reagents on I was refluxed for about two hours in a KOH-ethanol solution. Excess water was then added and the products extracted in ether. The ether layer was then dried and the product obtained by distillation.

Preparation of 1,2-Difluoro-1-hexene [XXV]

1-Trimethylsilyl-1,2-difluoro-1-hexene [XVIII] (13 g., 0.047 mole) was reacted as above with 20 ml. KOH-ethanol solution. Work-up yielded 5 g. (62%) XXV, b.p. 73°,  $n_D^{20}$  1.3680,  $d_4^{20}$  0.885,  $M_D$  calcd. 29.5, found 30.4.

Anal. Calcd. for  $C_6H_{10}F_2$ : C, 60.00; H, 8.34; F, 31.61. Found: C, 59.89; H, 8.21; F, 31.30.

Preparation of  $\alpha,\beta$ -Difluorostyrene [XXVI]

$\beta$ -Trimethylsilyl- $\alpha,\beta$ -difluorostyrene [XIX] (11.8 g., 0.056 mole) was reacted as above with 20 ml. KOH-ethanol solution. Work-up yielded 5.5 g. (61%) XXVI, b.p. 84/60,  $n_D^{20}$  1.5056,  $d_4^{20}$  1.155. Mad (12) reports b.p. 88-90°/60mm,  $n_D^{20}$  1.5060.

Preparation of *n*-Trifluoromethyl- $\alpha,\beta$ -difluorostyrene [XXVII]

1-(1,2-Difluoro-2-trimethylsilylvinyl)-naphthalene [XXI] (3 g., 0.047 mole) was reacted as above with 20 ml. KOH-ethanol solution. Work-up yielded 7.3 g. (75%) XXVII, b.p. 75°/40mm,  $n_D^{20}$  1.4467,  $d_4^{20}$  1.353.

Anal. Calcd. for  $C_{12}H_{15}F_2$ : C, 51.94; H, 2.42; F, 45.64. Found: C, 51.79; H, 2.50; F, 45.28.

This compound formed a clear glass with a H.M. of 68,500 when heated at 90° overnight with benzoyl peroxide.

Preparation of 1-(1,2-Difluorovinyl)naphthalene [XXVIII]

1-(1,2-Difluoro-2-trimethylsilylvinyl)naphthalene [XXI] (9.3 g., 0.09 mole) was reacted as above with 20 ml. KOH-ethanol solution. Work-up yielded 5.5 g. (83%) XXVIII, b.p. 70°/1mm,  $n_D^{20}$  1.5975,  $d_4^{20}$  1.224.

Anal. Calcd. for  $C_{12}H_8F_2$ : C, 75.77; H, 4.24; F, 19.97. Found: C, 75.23; H, 4.10; F, 19.14.

Attempted Preparation of 2-(1,2-Difluorovinyl)thiophene

2-(1,2-Difluoro-2-trimethylsilylvinyl)-thiophene [XXIV] (3 g., 0.04 mole) was reacted as above with KOH-ethanol solution. Work-up yielded 5.5 g. product, b.p. 65°/40mm,  $n_D^{20}$  1.5272. The compound quickly discolored, and the next day was a black tar.

Anal. Calcd. for  $C_8H_4F_2Si$ : C, 49.30; H, 2.76; F, 25.98. Found: C, 48.41; H, 2.89; F, 27.43.

Attempted Preparation of 1,2-Difluoro-1,4-pentadiene

1-Trimethylsilyl-1,2-difluoro-1,4-pentadiene [XXIII] (3 g., 0.017 mole) was reacted as above with KOH-ethanol solution. Work-up yielded a small amount of low boiling product, but not pure enough for analysis.

Attempted Preparation of 1,2-Difluoro-3-butene

The steam distillate from the preparation of 1,2-difluoro-3-butene was stripped of ether by repeated washings. The concentrated solution was then slowly added to a 50% sodium acetate solution. The gases evolved were caught in a Dry Ice-acetone trap. Separation by v.p.c. gave three fractions. One was identified by I.R. and M.W. as  $CF_2=CFH$ . Another was probably 1,2-difluorobutadiene, but there was not enough for elemental analysis. i.r. Data were consistent. The third component (highest boiling) was not identified.

Reactions of (3,4,4-Trifluoro-3-butenyl)trimethylsilane [IX]

Thermal Dimerization of IX

IX (25 g., 0.14 mole) was sealed in a thick-walled glass tube containing a pinch of hydroquinone. The tube was heated at 210°C for 48 hours. Distillation of the reaction mixture yielded 3 g. dimer [XII] (33%), b.p. 70°/0.8,  $n_D^{20}$  1.4059,  $d^{20}$  1.069,  $M_D$  calcd. 84.3, found 83.7.

Anal. Calcd. for  $C_{14}H_{20}F_6Si$ : C, 46.12; H, 7.19; F, 31.26. Found: C, 46.31; H, 7.19; F, 31.52.

Reaction of Phenyllithium with IX

IX (9.1 g., 0.05 mole) was slowly added to a solution containing phenyllithium (0.05 mole) in ether. The mixture was stirred for two hours, hydrolyzed and the organic layer dried. Distillation gave 6.3 g. (69%) (4-phenyl-3,4-difluoro-4-butenyl)trimethylsilane [XXX], b.p. 90°/2mm,  $n_D^{20}$  1.4990,  $d^{20}$  1.007.

Anal. Calcd. for  $C_{13}H_{18}F_2Si$ : C, 64.93; H, 7.56; F, 15.81. Found: C, 65.01; H, 7.67; F, 15.82.

XXV (27 g., 0.12 mole) was heated in a sealed tube at 200° for 18 hours. Distillation yielded 10 g. (37%) XXI, b.p. 145°,  $n_D^{20}$  1.439.

Anal. Calcd. for  $C_4H_4Cl_2F_2OSi_2$ : C, 35.71; H, 5.51; F, 24.35.

Found: C, 39.65; H, 5.53; F, 27.07.

Preparation of Methyl 2,3-Dichloroacetate

Preparation of (1,1,1,3,3,3-hexafluoro-2-propoxy)trimethylsilane [XXXII]

Hexafluoroacetone (16.6 g., 0.10 mole) and methylchlorosilane (15.0 g., 0.10 mole) were sealed in a thick-walled glass tube and irradiated in sunlight for about two weeks. Distillation gave 30 g. (80%) XXXII, b.p. 94°,  $n_D^{20}$  1.3555,  $d_4^{20}$  1.439,  $M_r$  calcd. 38.9, found 40.1.

Anal. Calcd. for  $C_4H_4Cl_2F_6OSi_2$ : C, 17.09; H, 1.43; F, 45.55.

Found: C, 17.15; H, 1.45; F, 40.31.

Preparation of (1,1,1,3,3,3-hexafluoro-2-propoxy)trimethylsilane [XXXIII]

1,1,3,3-Tetrafluoro-2,3-dichloroacetone (80 g., 0.40 mole) and methylchlorosilane (46 g., 0.40 mole) were sealed in a thick-walled glass tube and irradiated for about two weeks. Distillation yielded 89 g. (79%) XXXIII, b.p. 153°,  $n_D^{20}$  1.3930,  $d_4^{20}$  1.524,  $M_r$  calcd. 49.4, found 49.3.

Anal. Calcd. for  $C_4H_4Cl_4F_4OSi_2$ : C, 15.28; H, 1.29; F, 24.20.

Found: C, 15.85; H, 1.33; F, 24.35.

Preparation of (1,1,1,3,3,3-hexafluoroisopropoxy)trimethylsilane [XXXIV]

XXXII (17 g., 0.06 mole) was reacted with  $CH_3MgBr$  (0.12 mole) in ether. The mixture was hydrolyzed and the organic layer dried. Distillation gave 5 g. (35%) XXXIV, b.p. 80°,  $n_D^{20}$  1.3196,  $d_4^{20}$  1.177,  $M_r$  calcd. 40.5, found 40.3.

Reaction of IX with 1,3-Butadiene

IX (8.2 g., 0.045 mole) and 1,3-butadiene (4.8 g., 0.09 mole) were sealed in a thick-walled glass tube and heated at 200° for 24 hours. Distillation of the liquid residue gave 3.6 g. (33.6%) of a compound tentatively identified as either



Infrared analysis showed a vinyl group to be present.

Anal. Calcd. for  $\text{C}_{11}\text{H}_{19}\text{F}_3\text{Si}$ : C, 55.88; H, 8.11. Found: C, 56.87; H, 8.11.

Reaction of IX with NOCl

A 3-necked, 300 ml. round-bottomed flask was fitted with a stirrer, reflux condenser, and inlet tube. DMF (160 ml.),  $\text{AlCl}_3$  (11 g., 0.082 mole), and IX (11 g., 0.06 mole) was added to the flask. NOCl was bubbled in until no further reaction was obvious. (The reaction was quite exothermic.) The solution was extracted with pentane, and the pentane layer, containing the blue product, was passed through an alumina (acid) column. The blue material was collected and the pentane evaporated under vacuum. A deep blue product, tentatively identified as  $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CF}(\text{NO})\text{CFCl}$  was obtained. n.m.r. Spectrum indicated the structure was possible, although not definite.

Anal. Calcd. for  $\text{C}_7\text{H}_{13}\text{ClF}_3\text{NO}$ : C, 33.89; H, 5.29. Found: C, 33.76; F, 5.43.

Thermal Dimerization of  
(4,5,5-Trifluoro-4-pentenyl)dimethylchlorosilane [XIV]

XXXII. Calcd. for  $C_{10}H_{16}Cl_2F_2OSi$ : C, 27.4; H, 4.23; F, 17.4; Si, 10.0; O, 30.10; Cl, 4.13; S, 47.66.

Preparation of 11,1,2,2-tetrafluoro-1,2-dichloro-3-isopropoxypropane (XXXII)

XXXIII (51 g., 0.1 mole) was reacted with  $Cl_2$  (50 g., 0.2 mole) in ether. The mixture was hydrolyzed, and the organic layer distilled. Distillation yielded 15 g. (30%) XXXV, b.p.  $156^\circ$ ,  $n_D^{20}$  1.3965,  $d_4^{20}$  1.245,  $M_p$  calcd. 50.1, found 50.1.

Anal. Calcd. for  $C_8H_{10}Cl_2F_2OSi$ : C, 26.34; H, 3.69; F, 17.45; Si, 10.0; O, 30.10. Found: C, 26.39; H, 3.81; F, 27.93.

#### Polymerization of XXXII and XXXIII

Twenty gram samples of XXXII and XXXIII were rapidly added to separate beakers containing 50 ml. water. The mixtures were stirred rapidly. Each formed an elastomeric gum in about 10 to 15 minutes. The gums were resilient but not strong. The gums were put on watch-glasses to dry overnight. They hardened overnight to form brittle polymers. Elemental analysis of the polymer from XXXII showed only 4.41% fluorine; analysis of the polymer from XXXIII showed only 7.69% chlorine. (Calcd.: 50.4% and 27.4% respectively, if no hydrolysis of the isopropoxy groups took place.)

## 17. SUMMARY

A series of silanes of the general form  $R_nSi(CH_2CF=CF_2)_{3-n}$  have been prepared, where n is 0, 1, 2, or 3. R can be hydrogen, methyl, or some functional group.

The first of the series,  $Me_2SiCF=CF_2$ , was prepared by the reaction of  $CF_2=CFLi$  with the appropriate silane, where R is  $CH_3$ , and  $OSiMe_2CF=CF_2$ . Where R is  $CF_2=CF$ , the starting silane was  $CF_2=CF_2$  and where R is H,  $CF_2=CFH$  was reacted with  $ClMgSiH_3$ .

The compound  $Me_3SiCH_2CF=CF_2$  was prepared by the reaction of  $Me_3SiCH_2Li$  with  $CF_2=CF_2$ .

The compound  $Me_3SiCH_2CH_2CF=CF_2$  was prepared by the base-catalyzed addition of  $CF_2BrCFClBr$  to  $CH_2=CHSiMe_3$  and subsequent acidic oxidation and reduction of the addition product. Other derivatives were obtained from the addition product of  $CF_2BrCFClCH=CH_2$  and  $ClMg_2SiH_3$ .

Derivatives of  $RMe_2SiCH_2CH_2CF=CF_2$  were obtained from the addition product of  $ClMg_2SiH_3$  and  $CH_2=CHCH_2CF=CF_2$ . The chlorine, trimethyl, and disiloxane derivatives were prepared.

$Me_3SiCF=CF_2$  was found to give substitution products with several lithium compounds:



Lithium compounds used were methyl, n-butyl, phenyl, n-trifluoromethylphenyl, 1-naphthyl, 2-thiophenyl, allyl, and vinyl. These substitution

products did not further react in alcohol to give the corresponding  
 chlorides with the n-butyl, phenyl, n-octyl, dodecyl, and 2-  
 naphthyl alcohols.

The compound  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CF}=\text{CF}_2$  did not react with the alkyl  
 alkoxides, but reacted with phenyllithium to give  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{Ph}$ .  
 $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CF}=\text{CF}_2$  also formed the cyclobutyl dimer upon polymeriza-  
 tion, as did  $\text{ClMe}_2\text{SiCH}_2\text{CH}_2\text{CF}=\text{CF}_2$ .

Two ketones,  $\text{CF}_3\text{COCF}_3$  and  $\text{CF}_2\text{ClCOCF}_2\text{Cl}$ , were found to react with  
 methyltrichlorosilane to give the isopropoxides,



Both of these polymerized by reaction in water. Much of the chlorine  
 was lost, giving hard, brittle polymers instead of the desired di-  
 tomers. The trimethyl derivatives were also prepared from the two  
 alkoxides.

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Ward M. Oliver was born April 20, 1930, in Tallapoosa, Alabama. He attended public schools in Baldwin County, Alabama, and graduated from Baldwin County High School in May, 1948.

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This dissertation was prepared under the direction of \_\_\_\_\_ of the candidate's supervisory committee and has been approved by \_\_\_\_\_ members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved for partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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