The Synthesis and Reactions of Fluorine-Containing Organo-Silicon Compounds

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I. INTRODUCTION

The critical shortage of natural rubber during World War II was relieved by the development of synthetic materials. However, these materials did not meet all the demands set up by the military. For example, a rubber which was fuel resistant would lose its elasticity when subjected to cold temperatures. One which would retain its elastic properties at low temperatures would fail in other respects. The need for an elastomer which possesses good low-temperature properties, resists swelling when in contact with hydrocarbon fuels, and resists deterioration by oxidizing agents was foreseen several years ago. The arrival of the "Space Age" has greatly magnified this need. The Office of the Quartermaster General established and is currently sponsoring a long-range Arctic Rubber Program for the purpose of discovering and developing rubber-like products which have the desired properties.

One of the approaches which seemed promising was the modification of existing materials by the introduction of fluorine atoms. Fluorocarbons are known to possess thermal and chemical stability and are generally immiscible with hydrocarbons. The comparable sizes of fluorine and hydrogen also favored this approach since it was also known that the introduction of bulky groups or atoms on butadiene decreased the elastic properties of the resulting polymers.

Investigations into the synthesis of fluorine-containing dienes led to the discovery that haloalkanes containing fluorine would add to olefins in the presence of peroxides. The resulting addition compounds
could then be converted to the desired olefin by chemical methods. For example, the work of Lillyquist (11,17), Lovelace (16), and Gillman (5,16) has demonstrated that such compounds as 1,2-dibromo-2-chloro-1,1,2-trifluoroethane, CF<sub>2</sub>BrCFClBr, and dibromodifluoromethane, CF<sub>2</sub>Br<sub>2</sub>, in the presence of catalytic amounts of free radical initiators, would react with such olefins as ethene, fluoroethene and 2-fluoropropene to give one-to-one addition products.

\[
\begin{align*}
\text{CF}_2\text{BrCFClBr} + \text{CH}_2=\text{CH}_2 \xrightarrow{\text{peroxides}} & \quad \text{CF}_2\text{BrCFClCH}_2\text{CH}_2\text{Br} & \quad (1) \\
\text{CF}_2\text{Br}_2 + \text{CH}_2=\text{CFCH}_3 \xrightarrow{\text{peroxides}} & \quad \text{CF}_2\text{BrCH}_2\text{CFBrCH}_3 & \quad (11)
\end{align*}
\]

The product from reaction 1 can be dehydrohalogenated and dehalogenated to give 1,1,2-trifluorobutadiene.

\[
\begin{align*}
\text{CF}_2\text{BrCFClCH}_2\text{CH}_2\text{Br} \xrightarrow{\text{alcoholic base}} & \quad \text{CF}_2\text{BrCFClCH}=\text{CH}_2 \\
\text{CF}_2\text{BrCFClCH}=\text{CH}_2 \xrightarrow{\text{zinc}} & \quad \text{CF}_2=\text{CFCH}=\text{CH}_2 \\
\text{Likewise, the product from reaction 11 can be dehydrohalogenated with tri-n-butylamine to give 1,1,3-trifluorobutadiene.}
\end{align*}
\]

\[
\begin{align*}
\text{CF}_2\text{BrCH}_2\text{CFBrCH}_3 \xrightarrow{\text{R}_3\text{N}} & \quad \text{CF}_2=\text{CHCF}=\text{CH}_2
\end{align*}
\]

The results of the polymerization studies of these and other fluoroolefins showed that the basic assumptions were correct in that the desired change in properties of the elastomers was effected. However, it also became evident that the number of fluorine atoms introduced on the monomer played an important role in determining the properties of the elastomer. With just a few fluorine atoms, the change
was not appreciable while too many fluorine atoms caused the elastomer to become stiff and brittle.

The introduction of an atom or group of atoms on the monomer which would provide the necessary flexibility seemed to offer an approach to the solution of this problem. In considering the groups which could be introduced on the monomer unit for the desired flexibility, special interest was focused on silicon. The recent advances made in the field of organo-silicon elastomers were noted and consideration was given to the possible ways in which these units could be incorporated into one molecule. Furthermore, the tetravalency of silicon offered sites for additional reactions such as crosslinking and three-dimensional chain growth.

Silicone rubber is known for its exceptional thermal stability and excellent electrical properties. The rubber is not affected by ozone, and the elastomer itself has very low water absorption. However, some of the chief disadvantages are swelling caused by solvents and degradation by strong acids and bases. It has been found that the swelling could be reduced if strongly electronegative atoms or groups such as fluorine and nitrile were substituted on the polymer chain.

There are many methods used in the preparation of organo-silicon compounds. These methods may be combined into three major categories: direct methods, in which a silicon-carbon bond is formed; substitution methods, in which a functional group is introduced into an unsubstituted organo-silicon compound; and replacement methods, in which functional groups already present are replaced with other functional groups. These
basic types of reaction are illustrated below by means of equations.

**Direct Methods**

\[ \text{Direct Methods} \]

\[
\begin{align*}
\text{Cu} &\quad \text{heat} \\
\text{CH}_2=\text{CHCH}_2\text{Cl} + \text{Si} &\rightarrow (\text{CH}_2=\text{CHCH}_2)_2\text{SiCl}_2 \\
\text{SiCl}_4 + C_6\text{H}_5\text{MgBr} &\rightarrow C_6\text{H}_5\text{SiCl}_3 \\
\text{CICH}_2\text{CH}=\text{CH}_2 + \text{HSiCl}_3 &\rightarrow \text{CICH}_2\text{CH}_2\text{CH}_2\text{SiCl}_3
\end{align*}
\]

**Substitution Method**

\[
\begin{align*}
(\text{CH}_3)_2\text{SiCl}_2 + \text{Cl}_2 &\rightarrow (\text{CH}_3)(\text{CH}_3)\text{SiCl}_2 \\
(\text{CH}_3)_2\text{SiCH}=&\text{CH}_2 + \text{HSi(CH}_3)_2\text{COOH} &\rightarrow (\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{SCH}_2\text{COOH}
\end{align*}
\]

**Replacement Methods**

\[
\begin{align*}
(\text{CH}_3)_3\text{SiCH}=&\text{CH}_2 + \text{ClCOOC}_2\text{H}_5 &\rightarrow (\text{CH}_3)_3\text{SiCH}_2\text{COOC}_2\text{H}_5 \\
(\text{CH}_3)_3\text{SiCH}=&\text{CH}_2 + \text{HSiCl}_2\text{CH}_2\text{CH}_2\text{SiCl}_2 &\rightarrow (\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{SCH}_2\text{COOH}
\end{align*}
\]

Of these methods, the most promising for laboratory scale are the Grignard reactions and the addition reactions to alkenyl silicon compounds. The use of these two methods for the preparation of fluorine-containing alkenyl silicon compounds may be illustrated by the following equations:

**Grignard**

\[
\begin{align*}
\text{CF}_2\text{BrCFClCH}_2\text{CH}_2\text{MgBr} + (\text{CH}_3)_3\text{SiCl} &\rightarrow \text{CF}_2\text{BrCFClCH}_2\text{CH}_2\text{Si(Ch}_3)_3 \\
\text{CF}_2\text{BrCFClCH}_2\text{CH}_2\text{Si(Ch}_3)_3 &\rightarrow \text{CF}_2\text{BrCFClCH}_2\text{CH}_2\text{Si(Ch}_3)_3
\end{align*}
\]

**Addition**

\[
\begin{align*}
(\text{CH}_3)_3\text{SiCH}=&\text{CH}_2 + \text{CF}_2\text{BrCFClBr} &\rightarrow (\text{CH}_3)_3\text{SiCHBrCH}_2\text{CFClCF}_2\text{Br}
\end{align*}
\]
These reactions are general and a great many products could be expected by the use of the proper reagents. It should be noted that the product from the addition reaction can be converted to a conjugated diene which is highly desirable from a polymerization point of view.

\[
\begin{align*}
(CH_3)_3SiCHBrCH_2CFClCF_2Br & \xrightarrow{\text{alcoholic base}} (CH_3)_3SiCH=CHCFClCF_2Br \\
(CH_3)_3SiCH=CH_2CFClCF_2Br & \xrightarrow{\text{zinc alcohol}} (CH_3)_3SiCH=CHCF=CF_2
\end{align*}
\]

Furthermore, by varying the other groups attached to the silicon, and substituting more reactive chlorine for one or more of the methyl groups, the possibility exist of converting this material to siloxane linkages.

With these facts as a basis, it was concluded that the presence of silane and siloxane linkages in the monomer might supply the necessary flexibility in the elastomer backbone. It therefore appeared that a study of the addition of fluorine-containing haloalkanes to vinyl and allyl silanes would be in order. Consequently, the object of this research was to study methods of preparing unsaturated organo-silicon compounds containing fluorine for evaluation as possible low-temperature elastomers.
II. DISCUSSION

Free radical addition reactions to unsaturated systems have become useful and important tools for the synthetic organic chemist. A wide variety of compounds has been successfully added to olefins to give simple one-to-one addition products. Among such compounds are mercaptans (4), bromoesters (6), ketones (8), aldehydes (10) and haloalkanes (7). An important consequence of these free radical reactions was the discovery that fluorine-containing haloalkanes would add to olefins and fluoroolefins to form useful intermediates. These products could easily and conveniently be converted to dienes by chemical methods (16,17,18).

The generally accepted mechanism for these reactions is the one postulated by Kharasch (9) which involves a free radical, chain type mechanism as illustrated below:

\[
\begin{align*}
\text{II} & \quad \text{II} \\
\text{RC-0-O-CR} & \quad \longrightarrow & \quad \text{R}^* + \text{RCOO}^* + \text{CO}_2 & \quad \text{I} \\
\text{R}^* + \text{CX}_4^- & \quad \longrightarrow & \quad \text{RX} + \text{CX}_3^* & \quad \text{II} \\
\text{CX}_3^* + \text{CH}_2=\text{CHR}^- & \quad \longrightarrow & \quad \text{CX}_3\text{CH}_2\text{CHR}^* & \quad \text{III} \\
\text{CX}_4^- + \text{CX}_3\text{CH}_2\text{CHR}^- & \quad \longrightarrow & \quad \text{CX}_3\text{CH}_2\text{CHR}^- + \text{CX}_3^* & \quad \text{IV}
\end{align*}
\]

The peroxide decomposes into free radicals which abstract an X atom from \(\text{CX}_4^-\). X can be iodine, bromine, chlorine or hydrogen. The resulting free radical, \(\text{CX}_3^*\), will then combine with an olefin.
molecule to form the intermediate radical as shown in step III. This intermediate can now react in one of two ways: It can complete the addition as seen in step IV, or it can react with another molecule of olefin to form the two-to-one addition product.

\[
\text{CX}_3\text{CH}_2\text{CHR}^* + \text{R}^*\text{CH} = \text{CH}_2 \rightarrow \text{CX}_3\text{CH}_2\text{R}^*\text{HCCH}_2\text{CHR}^* \quad \text{V}
\]

Step V accounts for the higher boiling material found in these reactions.

Alkenyl silicon compounds are also known to undergo addition reactions. Burkhard (2) has shown that various thiols will add to vinyl and allyl silicon compounds to form the simple one-to-one addition product. Sommer (12) also found that butyraldehyde will add to vinyltrimethylsilane in the presence of peroxides. Tarrant and his co-workers (15) discovered that a convenient method of introducing fluorine into organo-silicon compounds involved the peroxide catalyzed addition of perhaloalkanes to vinyltrimethyl- and vinyltrichlorosilanes. Reagents such as CF$_3$I, CF$_2$CICFCII, CF$_2$BrCFCIBr and CCl$_3$Br gave good yields of the one-to-one addition products. Furthermore, for example, the product obtained from the reaction of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane with vinyltrimethylsilane was converted to the corresponding diene.

\[
\text{CF}_2\text{BrCFCIBr} + \text{CH}_2=\text{CHSi(CH}_3)_3 \rightarrow \text{CF}_2\text{BrCFCICH}_2\text{CHBrSi(CH}_3)_3 \quad \text{I}
\]

\[
\text{CF}_2\text{BrCFCICH}_2\text{CHBrSi(CH}_3)_3 \xrightarrow{\text{base}} \text{CF}_2\text{BrCFCICH}=\text{CHSi(CH}_3)_3 \quad \text{II}
\]

\[
\text{CF}_2\text{BrCFCICH}=\text{CHSi(CH}_3)_3 \xrightarrow{\text{zinc, alcohol}} \text{CF}_2=\text{CFCH}=\text{CHSi(CH}_3)_3 \quad \text{III}
\]
It is of interest to note that in step III, a product boiling much higher than the starting material was also encountered. Furthermore, on standing, the diene would convert to this higher boiling material which was identified as being the cyclic dimer

\[
\text{CF}_2\text{-CFCH}=\text{CHSi(CH}_3)_3
\]

\[
\text{I} \quad \text{I}
\]

\[
\text{CF}_2\text{-CFCH}=\text{CHSi(CH}_3)_3
\]

The availability of starting materials determined the starting point of the present research. It was found that several vinyl and allyl silanes were commercially available. Among these was vinylidimethylethoxysilane, which could be easily converted to divinyltetramethyldisiloxane by acid hydrolysis in benzene.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{I}
\end{array}
\xrightarrow{\text{H}^+} \begin{array}{c}
\text{CH}_3 \\
\text{I}
\end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{I}
\end{array}
\xrightarrow{\text{H}_2\text{O}} \begin{array}{c}
\text{CH}_3 \\
\text{I}
\end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{I}
\end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{I}
\end{array}
\]

This material offered an excellent starting point since one would expect two products to arise from the addition reaction. One product would result from the addition to one vinyl group and the other product would result from the addition to both.

Consideration was also given to the addendum. This material had to meet several requirements. The first was that it be easily obtainable in large quantities. Furthermore, it was desirable that this material be a liquid at room temperature with a boiling point around 100°C. This material had to be sufficiently reactive to
propagate the chain reaction and give only one reactive species.

A material which adequately met these requirements was 1,2,-
dibromo-2-chloro-1,1,2-trifluoroethane. Lillyquist (II) showed that
this material gave rise to only one reactive species which was
CF₂BrCFCl⁻. It should further be noted that the products from this
material could easily be converted to a diene structure having a
CF₂=CF⁻ grouping.

The addition of CF₂BrCFClBr to divinyltetramethyldisiloxane
gave rise to two products as predicted. These products were
identified as being

\[
\text{CF}_2\text{BrCFClCH}_2\text{CHBr-Si-O-Si-CH=CH}_2
\]

\[
\begin{array}{cccc}
\text{CH} & \text{CH}_3 \\
\text{CF}_2\text{BrCFClCH}_2\text{CHBr-Si-O-Si-CHBrCH}_2\text{CFClCF}_2\text{Br} \\
\text{CH}_3 & \text{CH}_3
\end{array}
\]

1-(1,4-dibromo-3-chloro-3,4,4-trifluorobutyl)-3-vinyl-1,1,3,3-
tetramethyldisiloxane, and

\[
\begin{array}{cccc}
\text{CH} & \text{CH}_3 \\
\text{CF}_2\text{BrCFClCH}_2\text{CHBr-Si-O-Si-CHBrCH}_2\text{CFClCF}_2\text{Br} \\
\text{CH}_3 & \text{CH}_3
\end{array}
\]

1,3-bis-(1,4-dibromo-3-chloro-3,4,4-trifluorobutyl)-1,1,3,3-
tetramethyldisiloxane.

It should be noted that the system used by Chemical Abstracts is
employed throughout in naming these products. The numbers preceding
the substituents indicate the silicon atom to which they are attached.
Furthermore, where there is no ambiguity as to the position of the substituents, the numbers will be omitted for ease of writing. For complex structures and names, a number will be assigned and further reference to this material will be made through number only.

Structures I and II were confirmed by elemental analyses, molecular weight determination and infra-red spectra. In each case, the analyses were in good agreement with the expected values. The spectra for the two were essentially the same except a band at 6.25 μ appeared for I which was absent in II. This was expected since this band was attributed to the silicon-vinyl group as observed in the spectrum of the initial starting material.

Several attempts were made to dehydrohalogenate I and II. Quinoline and alcoholic potassium hydroxide were used as the dehydrohalogenating agent. In the reactions of I and II with alcoholic base, a large quantity of salt precipitated which was identified as being a mixture of potassium chloride and potassium bromide. In each case, the organic material distilled over a very wide temperature range. One of the fractions was believed to be a product in which hydrogen chloride, rather than hydrogen bromide, split out. Later efforts to prepare more of this material for more conclusive data proved fruitless. The very wide temperature range of the distillates led to the conclusion that the reaction was not a simple one, and that alterations other than those expected occurred. A possible explanation for this occurrence is the instability of the silicon-oxygen bond. It is known that strong bases easily cleave a silicon-oxygen bond. It was further shown in this research that weak bases also effected this cleavage since such bases as quinoline and pyridine caused the reaction mixture to
distill over a wide temperature range. The disiloxane linkage reformed in all possible combinations when the reaction mixture was neutralized.

The possibility of dehalogenating the CF₂BrCFCl⁻ portion with powdered zinc and alcohol was then studied. A substantial reduction in boiling point and molecular weight would be expected from this reaction. Furthermore, the double bond would be expected to activate the dehydrohalogenation reaction so that the reaction could be carried out under less drastic conditions.

It was found that I reacted smoothly and easily with zinc in ethanol. Furthermore, two fractions were obtained from the reaction mixture. The infra-red spectra of these fractions were similar with just a few minor exceptions. Both showed strong absorptions at 5.5 μ which Lillyquist (II) assigned to an isolated CF₂=CF⁻ group. The lower boiling fraction gave a negative test for chlorine or bromine whereas the higher boiling fraction gave a quantitative test for bromine corresponding to the value expected for the dehalogenated product. The lower boiling fraction was believed to be

\[
\begin{align*}
\text{CH₃} & \quad \text{CH₃} \\
\text{CF₂=CFCH₂CH₂-Si-O-Si-CH=CH₂} & \\
\text{CH₃} & \quad \text{CH₃}
\end{align*}
\]  

I-(3,4,4-trifluoro-3-butenyl)-3-vinyl-1,1,3,3-tetramethyldisiloxane.

Elemental analyses for this material were in good agreement with the expected values. The other fraction was the expected

\[
\begin{align*}
\text{CH₃} & \quad \text{CH₃} \\
\text{CF₂=CFCH₂CHBr-Si-O-Si-CH=CH₂} & \\
\text{CH₃} & \quad \text{CH₃}
\end{align*}
\]  

(IV)
1-(1-bromo-3,4,4-trifluoro-3-butenyl)-3-vinyl-1,1,3,3-tetramethyldisiloxane.

In the reaction of II with zinc and ethanol, three fractions were isolated and identified as being

\[
\begin{align*}
\text{CH}_3 & \text{CH}_3 \\
\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Br}-\text{O}-\text{Si}-\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2 & \quad (V) \\
\text{CH}_3 & \text{CH}_3
\end{align*}
\]

1,3-bis-(3,4,4-trifluoro-3-butenyl)-1,1,3,3-tetramethyldisiloxane, in which dehalogenation and reduction occurred at both ends of the molecule,

\[
\begin{align*}
\text{CH}_3 & \text{CH}_3 \\
\text{CF}_2=\text{CFCH}_2\text{CHBr}-\text{O}-\text{Si}-\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2 & \quad (VI) \\
\text{CH}_3 & \text{CH}_3
\end{align*}
\]

1-(1-bromo-3,4,4-trifluoro-3-butenyl)-3-(3,4,4-trifluoro-3-butenyl)-

1,1,3,3-tetramethyldisiloxane, in which dehalogenation occurred at both ends but reduction occurred at only one end, and

\[
\begin{align*}
\text{CH}_3 & \text{CH}_3 \\
\text{CF}_2=\text{CFCH}_2\text{CHBr}-\text{O}-\text{Si}-\text{CHDrCH}_2\text{CF}=\text{CF}_2 & \quad (VII) \\
\text{CH}_3 & \text{CH}_3
\end{align*}
\]

1,3-bis-(1-bromo-3,4,4-trifluoro-3-butenyl)-1,1,3,3-tetramethyldisiloxane, in which only the expected dehalogenation occurred at both ends.

In order to further classify what appeared to be the replacement of a bromine atom by hydrogen, the known compound \( \text{CF}_2\text{BrCFClCH}_2\text{CHBrSi(CH}_3)_3 \), VIII, was treated in a similar manner. The results of this reaction were consistent with those observed for I and II, in that two products were isolated and identified as being

\[
\text{CF}_2=\text{CFCH}_2\text{CHBr}-\text{Si}-(\text{CH}_3)_3 \quad (IX)
\]

(1-bromo-3,4,4-trifluoro-3-butenyl) trimethylsillane, and
CF₂=CFCH₂CH₂-Si-(CH₃)₃

(3,4,4-trifluoro-3-butenyl) trimethylsilane. This evidence conclusively proves that reduction of the bromine does occur and probably proceeds through the formation of a complex with the excess zinc which subsequently reacts with the solvent, pulling off a hydrogen atom.

Reduction of the α-halogen was somewhat surprising in view of the ready formation of CF₂=CFCH₂CH₂Br from CF₂BrCFCICH₂CH₂Br without evidence of reduction. However, it will be noted that this is a general reaction for the α-bromo silanes prepared in this investigation since each one formed the reduced product, CF₂=CFCH₂CH₂SiX₃, to some extent.

Several attempts were made to convert IV to the corresponding triene. In every case, the products distilled over a wide temperature range which again was explained by the cleavage of the silicon-oxygen bond.

Another monomer which was readily available was vinylpentamethyl-disiloxane. The addition of CF₂BrCFCICBr to this material gave a 60% yield of the one-to-one addition product

\[
\begin{align*}
\text{CF₂BrCFCICCH₂CH₂Br-Si-O-Si-CH₃} & \quad \text{(XI)} \\
\text{CH₃} & \quad \text{CH₃} \\
\end{align*}
\]

\[
\begin{align*}
\text{l-(1,4-dibromo-3-chloro-3,4,4-trifluorobutyl)-1,1,3,3,3-pentamethyl-disiloxane with only a very slight amount of higher boiling materials.}
\end{align*}
\]

Several reactions were carried out with this material. Efforts to dehydrohalogenate failed. Reaction with zinc and ethanol resulted in the isolation of two products
CH₃  CH₃
\[ \text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Si-O-Si-CH}_3 \]  \hspace{1cm} (XII)
\[ \text{CH}_3 \text{ CH}_3 \]

1-(3,4,4-trifluoro-3-hutenyl)-1,1,3,3,3-pentamethyldisiloxane, and

\[ \text{CH}_3 \text{ CH}_3 \]
\[ \text{CF}_2=\text{CFCH}_2\text{CHBr-Si-O-Si-CH}_3 \]  \hspace{1cm} (XIII)
\[ \text{CH}_3 \text{ CH}_3 \]

1-(l-bromo-3,4,4-trifluoro-3-butenyl)-1,1,3,3,3-pentamethyldisiloxane.

The reaction of XIII with quinoline was also carried out. The products from this reaction distilled over a wide temperature range and could not be positively identified. However, a small amount of material came over at 100 °C which was believed to be hexamethyldisiloxane. XIII readily reacted with zinc and hydrochloric acid to give XII.

Another obtainable monomer was vinylidimethylchlorosilane. The addition of \( \text{CF}_2\text{BrCFClBr} \) to this material gave a 30% yield of the desired one-to-one addition product.

\[ \text{CH}_3 \]
\[ \text{CF}_2\text{BrCFClCH}_2\text{CHBr-Si-Cl} \]  \hspace{1cm} (XIV)
\[ \text{CH}_3 \]

(1,4-dibromo-3-chloro-3,4,4-trifluorobutyl)-dimethylchlorosilane, and a large quantity of higher boiling material. It was later discovered that this addition product was contaminated with benzoic acid (a by-product from the initiator) which caused the analysis to be in error. The benzoic acid and XIV formed a constant boiling azeotrope. Normal chemical methods for removing the benzoic acid could not be employed since the chlorosilane will react with water to form the disiloxane. Efforts to de-
hydrohalogenate XIV were unsuccessful; with quinoline and pyridine, a precipitate immediately formed and the reaction products could not be identified. Alcoholic base gave a mixture of products which distilled over a wide temperature range. Aqueous base gave the symmetrical disiloxane II as the principal product. It was from this reaction that the benzoic acid contamination was discovered since the boiling points of the disiloxane II and benzoic acid were sufficiently different to afford separation by distillation.

The addition of CF\textsubscript{2}BrCFCICBr to vinyldimethylethoxysilane, CH\textsubscript{2}=CHSi(CH\textsubscript{3})\textsubscript{2}OC\textsubscript{2}H\textsubscript{5}, was also studied. Several initiators were tried and α, α\textsuperscript{′}-azo-di-isobutyronitrile gave the largest conversion of olefin to addition products. A constant boiling fraction was isolated; however, the analyses of this material did not correspond to the values expected for the one-to-one addition product. Furthermore, the infra-red spectrum showed a band at 6.24 μ which indicated that a material containing a silicon-vinyl group was present. The reaction products were further reacted with zinc and ethanol in order to obtain the products in a form such that they could be separated and identified. Two fractions were isolated from this reaction and were identified as being III and V. Therefore it appeared that the addition mixture consisted of

\[
\begin{align*}
\text{CF}_2\text{BrCFCICICH}_2\text{CHBr-Si-O-Si-CH=CH}_2
\end{align*}
\]

(1)

and

\[
\begin{align*}
\text{CF}_2\text{BrCFCICICH}_2\text{CHBr-Si-O-OC}_2\text{H}_5
\end{align*}
\]

(XV)
(1,4-dibromo-3-chloro-3,4,4-trifluorobutyl) dimethylethoxysilane. The formation of I, although unexpected, can be readily explained by considering the ease of hydrolysis of the ethoxysilane to the disiloxane. It is therefore not unreasonable to believe that some of the vinylidimethyl-ethoxysilane hydrolyzed to the corresponding disiloxane and that addition then occurred to both reactants.

The precursor for V was postulated as being XV since the boiling points of I and XV are expected to be of the same order of magnitude. II cannot be the precursor because this material is known to boil at a temperature considerably higher than was found for the mixture. The explanation offered for the formation of V from XV was that the zinc halide, a Lewis acid, caused the conversion of the ethoxysilane to the disiloxane.

Another monomer which was readily obtainable was divinylidimethylsilane. Since it was found that the presence of silicon-oxygen bonds led to complicated mixtures in the reactions with base, divinylidimethylsilane offered the advantage of not having the siloxane linkage but still presenting two reactive sites. The addition reaction resulted in good conversion of monomer to products. Two fractions were isolated from this reaction mixture. The higher boiling fraction, when reacted with base, gave a material with the same properties as the lower boiling fraction. This factor seems to indicate that some thermal dehydrohalogenation occurred during distillation. The infra-red spectra of all these materials indicated that these fractions were contaminated with benzoic acid. Furthermore, the addition products were found to readily react with zinc and ethanol and a portion of the resulting
reaction products was identified as being

\[
\begin{align*}
\text{CH}_3 & \quad \text{CF}_2=\text{CFCH}_2\text{CH}_2\text{-Si-CH=CH}_2 \\
& \quad \text{CH}_3
\end{align*}
\]  

(XVI)

vinyl-3,4,4-trifluoro-3-butenyldimethylsilane. It therefore was concluded that the reaction mixture consisted of the desired addition product

\[
\begin{align*}
\text{CH}_3 & \quad \text{CF}_2\text{BrCFClCH}_2\text{CHBr-Si-CH=CH}_2 \\
& \quad \text{CH}_3
\end{align*}
\]  

(XVII)

vinyl-(1,4-dibromo-3-chloro-3,4,4-trifluorobutyl)-dimethylsilane, and the dehydrohalogenated product

\[
\begin{align*}
\text{CH}_3 & \quad \text{CF}_2\text{BrCFClCH=CH-Si-CH=CH}_2 \\
& \quad \text{CH}_3
\end{align*}
\]  

(XVIII)

vinyl-(4-bromo-3-chloro-3,4,4-trifluoro-1-butyl)-dimethylsilane.

The reason for the inability to isolate the conjugated system when the mixture was reacted with zinc was that the conjugated diene either polymerized or dimerized since some higher boiling material remained in the distillation flask.

An interesting phenomenon was observed in the addition of CF₂BrCFClBr to allyltrimethylsilane. It was found that cleavage of the carbon-silicon bond occurred and that the olefin CF₂BrCFClCH₂CH=CH₂, XIV, was formed. The position of the double bond was confirmed by the dehalogenation of this material to the corresponding diene. The infra-red spectrum of the diene was identical with that obtained by Gillman (5)
Sommer (14) has shown that allyltrimethylsilane reacted with electrophilic reagents such as bromine, hydrogen chloride and sulfuric acid to give propylene and the corresponding silicon residue. Furthermore, the addition of hydrogen bromide to allyltrimethylsilane did occur at low temperatures; however, propylene evolved as the material was heated and bromotrtrimethylsilane remained as the residue. The following mechanism was postulated by Sommer to account for these facts:

$$X^+Y^- + CH_2=CHCH_2Si(CH_3)_3 \rightarrow XCH_2CHCH_2Si(CH_3)_3 + Y^-$$

In considering a mechanism for the cleavage observed in this study, it must be remembered that free radical conditions existed and that the intermediate radical which formed from the initial attack could rearrange to account for the cleaved products.

$$CF_2BrCFCl \rightarrow CF_2BrCFClCH_2=CH_2Si(CH_3)_3 + III$$

As can be seen from the above series of equations, the intermediate can react in two ways: it could rearrange to form the olefin and more stable $Si(CH_3)_3$, step II; or it could complete the addition by abstracting a bromine from the addendum, step III. It is entirely possible that both
reactions occurred to some extent since a small amount of higher boiling material was formed. However, the rearrangement step predominated.

The reaction of CF<sub>2</sub>BrCFClBr with diallyldimethylsilane was also studied. It was found that this reaction gave a good conversion of olefin to products and that cleavage was not encountered. However, it was observed that hydrogen bromide split out during distillation. A fraction was identified as being the result of the addition to one allyl group in which hydrogen bromide split out

\[
\begin{align*}
\text{CH}_3 & \\
\text{CF}_2\text{BrCFClCH}_2\text{CH}=&\text{CH-} \text{Si-CH}_2\text{CH}=\text{CH}_2
\end{align*}
\]

(XX)

allyl-(5-bromo-4-chloro-4,5,5-trifluoro-1-pentenyl)-dimethylsilane. This fraction amounted to only ten percent of the higher boiling material. The remaining residue could not be separated into its various components.

Butler (1) has reported that 1-6 diene systems will undergo cyclic intra-intermolecular polymerization. Freidlander (3) showed that cyclization also occurred when diallyl ether was reacted with bromo-trichloromethane. Furthermore, the hetero-atom could be sulfur or nitrogen. However, the product obtained in this laboratory is believed to be linear since its infra-red spectrum showed two peaks at 6.02 and 6.15 μ. This indicates that there are two types of double bonds. If cyclization occurred, only one double bond would be expected. An attempt was made to quantitatively determine the double bond content of this material. However, the results were inconclusive since widely divergent values were observed.

The position of the double bond was determined by dehalogenating
XX to the corresponding triene. The resulting product could have either of the following structures

\[
\begin{align*}
\text{CH}_3 & \\
\text{CF}_2=\text{CFCH}_2\text{CH}=&\text{CH}-\text{Si}-\text{CH}_2\text{CH}=&\text{CH}_2 \\
\text{CH}_3 & \\
(XXI)
\end{align*}
\]

or

\[
\begin{align*}
\text{CH}_3 & \\
\text{CF}_2=\text{CFCH}=&\text{CHCH}_2-\text{Si}-\text{CH}_2\text{CH}=&\text{CH}_2 \\
\text{CH}_3 & \\
(XXII)
\end{align*}
\]

The infra-red spectrum of the reaction product was compared with those obtained by Gillman (5) for \(\text{CF}_2=\text{CFCH}=&\text{CHCH}_3\) (A) and \(\text{CF}_2=\text{CFCH}_2\text{CH}=&\text{CH}_2\) (B). The spectrum of the material in question was more nearly identical with (B) than with (A). Therefore it appears that the structure XXI is preferred. Furthermore, Lilyquist (11) pointed out that isolated \(\text{CF}_2=\text{CF}\) groups absorbed sharply at 5.5 \(\mu\) whereas when this group was conjugated with \(-\text{CH}=&\text{CH}\), a shift to 5.65 \(\mu\) was observed. These data also substantiate structure XXI.

Several other reactions were also studied. Sommer (13) has reported that concentrated sulfuric acid will selectively cleave a methyl group from substituted silanes and that the resulting sulfate ester would hydrolyze to the disiloxane. The possibility of converting \(\text{CF}_2\text{BrCFClCH}_2-\text{CHBrSi(CH}_3)\) to the disiloxane II was studied. It was found that this conversion was successful but in extremely low yields. Furthermore, it was felt that the reaction did not end with the cleavage of one methyl group since higher boiling materials were encountered. The formation of this material probably resulted from the reaction of two or possibly
all three methyl groups with sulfuric acid.

The effect of excess base on silanes was also studied. Prolonged treatment of $\text{CF}_3\text{BrCFCICCH} = \text{CHSi(CH}_3\text{)}_3$ with base produced cleavage to $\text{CF}_2\text{BrCFCICICH}_2$ and $(\text{CH}_3)\text{SiOSi(CH}_3\text{)}_3$. The boiling points of these two materials are identical so that the mixture was identified from its infra-red spectrum.
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<th>Cpd. No.</th>
<th>Compound</th>
<th>Yield</th>
<th>b.p. °C</th>
<th>P mm Hg.</th>
<th>t</th>
<th>n</th>
<th>d</th>
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<td>I</td>
<td>CF₂BrCFClCH₂CHBr(CH₃)₂SIO(Si(CH₃)₃)CH=CH₂</td>
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<td>85</td>
<td>0.5</td>
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<td>1.407</td>
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<td>[CF₂BrCFClCH₂CHBr(CH₃)₂Si]₂O⁻</td>
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<td>25</td>
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<td>1.795</td>
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<td>XIV</td>
<td>CF₂BrCFClCH₂CHBr(CH₃)₂SICl</td>
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<td>0.8</td>
<td>25</td>
<td>1.4721</td>
<td>1.663</td>
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<td>CF₂BrCFClCH₂CHBr(CH₃)₂SIO(Si(CH₃)₃)</td>
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<td>81-82</td>
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<td>$\delta_{PC}$</td>
<td>$P_{mm Hg}$</td>
<td>$t$</td>
<td>n</td>
<td>d</td>
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<tr>
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* Reported by Tarrant (15)
** Reported by Gillman (16)
TABLE 2

ANALYSES OF THE COMPOUNDS PREPARED

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<th>Cpd</th>
<th>$\text{M}_R$</th>
<th>$\text{H}$</th>
<th>$% \text{ Carbon}$</th>
<th>$% \text{ Hydrogen}$</th>
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<td>Calcd.</td>
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<td>37.40</td>
<td>118.8$^a$</td>
<td>118.9$^a$</td>
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</tbody>
</table>

$^a$ Ag eq., $^b$ % Br; $^c$ hydrol. % Cl (contaminated with benzoic acid)
In general, all reactions were carried out in a three necked, round bottomed flask equipped with stirrer, reflux condenser and, when needed, a dropping funnel.

The best procedure for the addition reactions was found to be the one in which all the reactants were heated and stirred together for six to ten hours at 90 to 100°C. Although this method is conducive to the formation of two-to-one and higher ratio products, it by far gave the best conversion of olefin to desired product. The method, in which the initiator is dissolved in the olefin and solvent, and added to the hot addendum over a period of time, resulted in the recovery of 50 to 70% of unreacted olefin. After the reaction was complete, the mixture was crudely distilled to remove the excess addendum. The residue washed with a solution of sodium bicarbonate to remove any benzoic acid, dried and then subjected to vacuum distillation.
GENERAL CONSIDERATIONS

All temperatures reported in this dissertation are on the centigrade scale and are uncorrected. Where possible, distillations were carried out using a 60 cm. electrically heated, jacketed column packed with 1/8 inch glass helices. For small amounts of material, a 22 cm. column of the above description was used. For extremely high boiling and viscous materials, a 30 cm. Vigereaux column was used. Pressures under 10 mm. were determined by a McLeod gauge.

Refractive indices were determined with an Abbe refractometer at the temperature indicated. Densities were determined using a one milliliter pycnometer calibrated with distilled water at 20° C. and corrected to 40 C. Molar refractions were calculated using the Lorenz-Lorentz equation. The values for the bond refractions were taken from Warrick's (19) application of Denbigh's bond refractions to organo-silicon chemistry.

Analyses for carbon-hydrogen content were carried out by Galbraith Laboratories, P. O. Box 4187, Knoxville, Tennessee. Halogen analyses were carried out by the author, using the Parr sodium peroxide fusion method for the decomposition of the sample and the Volhard method for determining the halogen content. Where possible, the analysis was reported as percentage halogen. In cases where both chlorine and bromine were present in the same molecule, the analysis was reported as silver equivalent. Molecular weights were determined using the freezing point depression method with benzene the solvent.

The infra-red spectra were obtained on a Perkin-Elmer Model 21
double beam, recording, infra-red spectrophotometer. All absorptions are reported in microns.

The following abbreviations were used to describe the relative intensities of the bands:

- *vw* — very weak
- *w* — weak
- *m* — medium
- *ms* — medium strong
- *s* — strong
- *vs* — very strong
- *brd* — broad
- *smear* — a band which covered a wide range
- *shld* — shoulder

Where possible, the reactants were purchased. Most of the vinyl- and allyl silanes were obtained from Peninsular Chem Research, Inc., Gainesville, Florida. Reactants not commercially available were prepared in the laboratory by procedures described in a later section of this dissertation.

A. Additions of 1,2-Dibromo-2-chloro-1,1,2-trifluoroethane to Alkenyl Silicon Compounds

1. Divinyltetramethyldisiloxane

A typical run is described as follows: A solution of divinyltetramethyldisiloxane (186 g., 1 mole), CF₂BrCFClBr (2200 g., 8 moles) and benzoyl peroxide (10 g.) was refluxed and stirred for ten hours. The excess CF₂BrCFClBr (henceforth called dibromide) was distilled off and the residue washed with a solution of sodium bicarbonate. The organic
material was dried over CaCl₂ and distilled under vacuum. Two fractions were obtained. The lower boiling fraction, b.p. 80-100 °/0.5 mm, 257 g., (56% yield), was identified as the one-to-one addition to one vinyl group, I. A center cut had the following properties: b.p. 85 °/0.5 mm; n²° 1.4524; d²° 1.407. Anal. Calcd. for C₁₀H₁₆Br₂ClF₃Si₂O: Mᵣd 87.26; Ag eq. 154.6; %C 25.89; %H 2.91; MW 464. Found: Mᵣd 88.70; Ag eq. 154.5; %C 26.21; %H 4.01; MW 462.

Infra-red absorptions: (in microns)

3.26(wv); 3.37(m); 6.24(w); 7.09(m); 7.96(s); 8.40(ms); 8.76(s); 9.50(brd s); 10.15(ms); 10.45(m); 11.30(m); 12.00(brd s); 12.65(brd s); 14.20(brd ms).

The other fraction, b.p. 160-160/0.5 mm, 114 g. (15% yield), was identified as the one-to-one addition to both vinyl groups, II. A center cut had the following properties: b.p. 163-165/1 mm; n²⁵ 1.4020; d²⁵ 1.795. Anal. Calcd. for C₁₀H₁₈Br₄Cl₂F₆Si₂O: Mᵣd 117.28; Ag eq. 123.2; %C 19.52; %H 2.46. Found: Mᵣd 117.80; Ag eq. 123.6; %C 19.70; %H 2.64.

Infra-red absorptions:

3.40(m); 7.06(m); 7.36(w); 7.96(s); 8.40(s); 8.80(s); 9.50(brd s); 10.15(s); 11.30(s); 11.95(brd s); 12.65(brd s); 13.55(w).

The only difference between the two spectra is the disappearance of the silicon-vinyl C=C stretch absorption at 6.24 μ. This is expected for the latter compound.

2. Vinylpentamethyldisiloxane

A solution of 100 g. of dibromide, vinylpentamethyldisiloxane
(80 g., 0.46 mole) and 10 g. of benzoyl peroxide was added to 450 g. of dibromide which had been previously heated to 92°. The solution was added in 25 ml. portions and then refluxed for an additional 4 hours. The excess dibromide was distilled through a Claisen head until the pot temperature reached 175°. The residue was washed with a solution of sodium bicarbonate, dried and distilled. A fraction, b.p. 84-89/1.6-2.0 mm., 124 g., 60% yield, was collected and identified to be the one-to-one addition product XI. A center cut had the following properties: b.p. 81-82/1.2 mm.; n° 1.4470; d° 1.455. Anal. Calcd. for C_{2}H_{14}Br_{2}ClF_{3}SiO: Mr d 83.06; Ag eq. 150.2. Found: Mr d 82.90; Ag eq. 150.3.

3. Vinylidimethylethoxysilane

A solution of vinylidimethylethoxysilane (100 g., 0.77 mole), dibromide (540 g., 2 moles) and C_{4}H_{10}-azo-dl-isobutyronitrile (5 g.) was heated to 90° for 10 hours. The reaction mixture was worked up in the usual manner. A fraction, 76 g., b.p. 72-90°/1 mm., was collected. A center cut had the following properties: b.p. 81-82/0.9 mm.; n° 1.4560; d° 1.5110. Anal. Calcd. for C_{9}H_{14}Br_{2}ClF_{3}SiO: Ag eq. 135. Found: Ag eq. 145.5. Infra-red absorptions:

3.40(ms); 5.69(m); 6.12(v); 6.24(w); 6.84(w); 6.95(w); 7.10(m); 7.35(w); 7.62(w); 7.75(m); 7.92(s); 8.20(m); 8.45(m); 9.50(brd s); 10.25(v); 11.25(brd s); 11.95(brd s); 12.50(brd s).

It appears that the product is contaminated with other materials. The bands at 5.68, 6.12 and 6.24 are not expected and the absorption at 6.24 is characteristic of silicon-vinyl. It appears that some of the ethoxysilane hydrolyzed to divinyltetramethyldisiloxane and that
addition occurred to both components.

4. Vinylidimethylchlorosilane

A solution of vinylidimethylchlorosilane (157 g., 1.3 mole),
benzoyl peroxide (10 g.) and dibromide (1450 g., 5.2 mole) was re-
fluxed for 10 hours. The reaction mixture was worked up in the usual
manner with care taken to exclude moisture. A 28% yield of the
one-to-one addition product XIV, 144 g., was obtained. A center cut
had the following properties: b.p. 67/0.8 mm.; n^25 1.4721; d^25
1.663. Anal. Calcd. for C_6H_9Br_2Cl_2F_3Si: Mr_d 65.78; hydrol Cl 8.95%.
Found Mr_d 67.39; hydrol. Cl 7.85%.

Infra-red absorptions:

3.40(m); 5.60(w); 5.85(m); 7.10(m); 7.95(s); 8.40(s); 8.78(s);
9.20(ms); 9.75(ms); 10.10(s); 11.25(s); 11.85(s); 12.40(brd s); 14.05(mw).
The bands at 5.60 and 5.85 indicate that the material may be con-
taminated with benzoic acid.

5. Divinylidimethylsilane

A solution of divinylidimethylsilane (100 g., 0.9 mole), dibromide
(1000 g., 3.5 mole) and benzoyl peroxide (10 g.) was refluxed for
4 hours. The reaction mixture was worked up in the usual manner and
110 g. of material boiling between 40-80°/1 mm. was collected. This
material was fractionated to give two cuts. The first had the following
properties: b.p. 51-55/2.2 mm.; n^20 1.426; d^20 1.337; yield 25 g.
This material was believed to be XVIII, the addition product to one
vinyl group in which hydrogen bromide split out. Anal. Calcd. for
C_{8}H_{11}BrClF_{3}Si: Ag eq. 153.7. Found: 161.8.
Infra-red absorptions:

3.40(m); 5.60(brd w); 6.20(shld w); 6.26(w); 6.85(w); 7.09(ms); 7.65(w); 7.93(s); 8.15(m); 8.32(s); 8.75(s); 9.60(brd s); 9.93(ms); 10.10(s); 10.50(brd s); 12.00(brd s); 14.00(brd s).

The band at 5.60 indicates that the material may still be contaminated with benzoic acid. This fact could account for the discrepancy in the analysis. Furthermore, the shoulder at 6.20 indicates that hydrogen bromide did split out.

The second fraction, 30 g., had the following properties:
b.p. 74/1.6 mm.; n\(^{20}\) 1.4762; d\(^{20}\) 1.566. Anal. Calcd. for C\(_9\)H\(_{12}\)Br\(_3\) Cl\(_3\)SI: Ag eq. 129.5. Found: Ag eq. 137.7.

Infra-red absorptions:

3.40(m); 5.60(w); 5.80(m); 6.26(w); 7.09(ms); 7.59(w); 7.97(s); 8.40(s); 8.75(s); 9.10(ms); 9.46(s); 9.93(ms); 9.46(s); 9.93(ms); 10.10(s); 10.42(ms); 11.30(s); 12.00(brd s); 12.85(brd s); 14.10(m).

This material is believed to be the one-to-one addition product XVII, which is still contaminated with benzoic acid. The infra-red spectrum has bands at 5.60 and 5.80 to support this assumption. It therefore appears that the one-to-one addition to one vinyl group does occur and that some of this material is dehydrohalogenated during distillation.

6. Allyltrimethylisilane

A solution of allyltrimethylisilane (50 g., 0.48 mole), benzoyl peroxide (5 g.) and dibromide (100 g.) was added dropwise to 700 g. of dibromide which had been heated to 90\(^\circ\). The excess dibromide was removed by distillation and as the pot temperature reached about 170\(^\circ\), hydrogen bromide began to evolve. A fraction, 35 g., 30% yield,
was collected and had the following properties: b.p. 121.5°; n° 1.4145; d° 1.588. Anal. Calcd. for C₅H₅BrClF₃: Mr endemic 37.42; Ag eq. 118.8. Found: Mr 37.40; Ag eq. 118.9. This material is CF₂BrCFClCH₂CH=CH₂ (XIX).

Infra-red absorptions:

5.37(vw); 6.04(w); 6.97(m); 7.97(m); 8.30(s); 8.75(s); 9.55(s); 10.20(s); 10.75(s); 11.25(s); 11.90(w); 12.10(w); 12.85(s); 13.80(m); 14.40(s).

Some higher boiling material was also formed in the reaction. However, this material could not be positively identified. It is felt that this material was the one-to-one addition product which would undergo cleavage during distillation.

7. Diallyldimethylsilane

A solution of diallyldimethylsilane (60 g., 0.43 mole), dibromide (276 g., 1 mole) and α,α'-azo-di-isobutyronitrile (3 g.) was heated to 70° for 3 hours and then to 95° for 2 hours. The excess dibromide was distilled off and the residue distilled under vacuum. Hydrogen bromide evolved throughout the distillation and the distillates appeared to be saturated with HBr. The distillates were combined, washed with a solution of sodium bicarbonate and redistilled. A fraction was identified as being the one-to-one addition product to one allyl group in which hydrogen bromide split out XX. A center cut had the following properties: b.p. 61°/0.5 mm., n° 1.4580; d° 1.350. Anal. Calcd. for C₁₀H₁₅BrClF₇Si: Mr endemic 69.73; Ag eq. 167.7. Found: Mr 68.40; Ag eq. 167.7.
Infra-red absorptions:
3.45 (m); 6.04 (ms); 6.17 (ms); 6.95 (m); 7.13 (m); 7.97 (s); 8.35 (s);
8.65 (s); 9.50 (brd s); 10.20 (s); 10.75 (brd m); 12.00 (brd s); 12.50 (brd s).

This material accounted for only 10% of the higher boiling residue. Attempts to separate and identify the other components failed.

Another run of the above reaction was tried in which a solution of allylisilane, dibromide and initiator was added dropwise to the remaining dibromide which had been heated to 70°C. About 65% of unreacted allylisilane was recovered with only a small amount of addition products.

B. Reactions of the Addition Products

1. CF₃BrCFCIC₂H₄CHBr(CH₃)₂SiOSi(CH₃)₂CH=CH₂

   a. With Base

   A solution of potassium hydroxide (56 g., 1 mole) dissolved in methanol (500 cc.) was added dropwise to a stirred solution of 1 (257 g., 0.56 mole) and 200 cc. methanol. The stirring was continued for 3 hours at room temperature, after which the precipitated salt was filtered off. The methanolic solution was washed with cold dilute HCl and the organic layer dried and distilled. The distillate was collected over a wide temperature range (85/500 mm to 80/0.7 mm.).

   All efforts to separate this mixture into its components failed and none of the fractions could be identified.

   b. With Zinc and Alcohol

   Eighty-eight grams, 0.19 mole, of 1 were added dropwise to a slurry of zinc (20 g., xs) and methanol (300 cc.). The mixture was heated for two hours after which time the excess zinc and zinc halide...
were filtered off. The methanolic solution was drowned with cold water. A gelatinous precipitate formed which dissolved when neutralized with dilute HCl. The organic layer was separated and the aqueous layer extracted with ether. The ether extracts were combined with the organic layer, dried, and distilled. Two fractions were obtained, the first having the following properties: b.p. 54-55°C/2.5 mm; n\(^20\) 1.3992; d\(^20\) 0.971. Anal. Calcd. for C\(_{10}\)H\(_9\)F\(_3\)S\(_4\): MR \(_d\) 66.63; % C 44.72; % H 7.14; MW 268. Found: MR \(_d\) 66.70; % C 44.69; % H 7.21; MW 297.

Infra-red absorptions:

\[
\begin{align*}
3.37(s); & 5.23(vw); 5.52(s); 5.74(m); 6.24(m); 6.93(m); 7.08(s); \\
7.75(s); & 7.95(s); 8.05(s); 8.42(s); 8.55(s); 9.50(brd vs); 9.80(s); \\
10.45(ms); & 11.10(ms); 11.90(brd s); 12.70(brd s); 14.20(s).
\end{align*}
\]

It appears that this fraction is the dehalogenated product in which the \(\alpha\) bromine was replaced by hydrogen, III.

The second fraction had the following properties: b.p. 83°C/2.5 mm; n\(^20\) 1.4296; d\(^20\) 1.198. This material is the dehalogenated product IV. Anal. Calcd. for C\(_{10}\)H\(_9\)BrF\(_3\)S\(_4\): MR \(_d\) 73.90; %Br 23.0; %C 34.60; %H 5.22. Found: MR \(_d\) 74.20; %Br 22.8; %C 35.01; %H 5.43.

Infra-red absorptions:

\[
\begin{align*}
3.37(s); & 5.23(vw); 5.52(s); 5.86(w); 6.24(m); 6.93(ms); 7.08(ms); \\
7.45(w); & 7.75(s); 7.95(s); 8.05(s); 8.42(s); 8.55(s); 9.50(brd s); \\
10.05(s); & 10.45(m); 11.10(s); 11.90(brd s); 12.70(brd s); 14.20(s).
\end{align*}
\]

c. CF\(_2\)=CFCH\(_2\)CHBr(CH\(_3\))\(_2\)SiOSi(CH\(_3\))\(_2\)CH=CH\(_2\)(IV) with Quinoline

The dehalogenated product (24 g.) was heated with 50 g. of
quinoline and the distillate collected as it formed. The crude distillate was redistilled several times in order to separate it into its various components. All efforts to identify these fractions were unsuccessful.

2. \[
[\text{CF}_2\text{BrCFCICH}_2\text{CHBr(CH}_3)_2\text{Si}]_2\text{O}
\]

a. With Alcoholic Base

A methanolic potassium hydroxide solution consisting of 20 g. of base in 500 cc. of methanol was added dropwise to 114 g. (0.15 moles) of II. The reaction was kept six hours at room temperature. The salt which precipitated was filtered off and analyzed to be a mixture of KCl and KBr. The filtrate was drowned with cold dilute hydrochloric acid and the organic layer separated, dried and distilled. This material distilled over a wide temperature range and none of the fractions could be identified positively.

b. With Zinc and Alcohol

To a solution of ethanol (200 ml.), dioxane (200 ml.), and zinc (33 g., 0.5 moles) was added 185 g. (0.25 moles) of II. The reaction was kept at room temperature for two hours. The mixture was filtered, the filtrate washed with dilute HCl, and the organic layer separated. The aqueous layer was extracted with ether. The ether extracts were combined with the organic layer, dried and distilled. Three fractions were obtained. The first, V, corresponded to dehalogenation and reduction on both ends of the molecule. This fraction, 10 g., 5% yield, had the following properties: b.p. 93-96\(^0\)/5 mm.; \(n_2^o\) 1.3975; \(d_2^o\) 1.085. Anal. for \(\text{C}_{12}\text{H}_{20}\text{F}_{6}\text{Si}_{2}\text{O}\): Calcd.
Infra-red absorptions:

3.45(m); 5.56(s); 6.95(m); 7.18(m); 7.75(s); 7.95(s); 8.06(s); 8.45(s); 8.56(s); 9.35(brd s); 10.05(ms); 11.20(ms); 11.95(brd s); 12.65(brd s); 14.25(brd w).

The second fraction, 10 g., 5% yield, was identified as the product in which dehalogenation occurred on both ends with the reduction of only one bromine, VI. This material had the following properties: b.p. 80°/0.8 mm.; n23 1.4238; d23 1.282. Anal. Calcd. for C12H9Br6Si2O: Mr 83.60; %Br 18.6; %C 33.60; %H 4.46; MW 429. Found: Mr 84.80; %Br 18.6; %C 33.16; %H 4.41; MW 422.

Infra-red absorptions:

3.39(m); 5.54(s); 5.90(vw); 6.95(mw); 7.07(m); 7.75(s); 7.95(s); 8.09(s); 8.44(m); 9.35(brd s); 10.00(m); 11.15(m); 11.95(brd s); 12.60(brd s); 14.15(brd w).

The third fraction, 30 g., 20% yield, had the following properties: b.p. 103-106/0.8 mm.; n23 1.4405; d23 1.426. This material was identified as the product in which dehalogenation alone occurred at both ends of the molecule, VII. Anal. Calcd. for C12H10Br2F6Si2O: Mr 91.28; %Br 31.4; %C 28.40; %H 3.57. Found: Mr 93.50; %Br 30.9; %C 29.06; %H 3.65.

Infra-red absorptions:

3.38(ms); 5.54(s); 5.90(vw); 7.08(m); 7.70(s); 7.95(s); 8.10(s); 8.46(s); 9.50(s smear); 11.20(m); 12.00(m); 12.50(smear); 14.25(smear).
3. $C_F^2 BrCFClCHBr(CH_3)_2 SiOSi(CH_3)_3$ (XI)

a. With Pyridine

A solution of pyridine (30 g.) and XI (40 g., 0.9 mole) was heated and stirred for 3 hours. The pyridine was washed out with water and the organic layer dried and distilled. The only fraction identified was unreacted XI.

b. With Zinc and Alcohol

XI (45 g., 0.1 mole) was added dropwise to a slurry of zinc (10 g.) and ethanol (250 ml.). The mixture was heated for an additional 4 hours and the reaction mixture worked up in the usual manner. Two products were isolated. The lower boiling had the following properties: b.p. 62-63°/15 mm.; n^20_0 1.3869; d^20_0 0.975. This material was XII, the dehalogenated reduced product. Anal. Calcd. for C_{9}H_{19}F_{3}Si_{2}O: MR_d 62.42; %C 42.60; %H 7.47. Found: MR_d 61.65; %C 42.40; %H 7.52.

Infra-red absorptions:

3.45(m); 5.54(s); 5.82(w); 6.95(w); 7.75(m); 7.97(s); 8.16(ms); 8.45(m); 8.56(m); 9.35(brd s); 10.06(w); 11.85(s); 12.30(smear).

The second fraction, 20 g., 61% yield, had the following properties: b.p. 92-93°/15 mm.; n^20_0 1.4186; d^20_0 1.206. This material was XIII, the dehalogenated product. Anal. Calcd. for C_{9}H_{18}BrF_{3}Si_{2}O: MR_d 70.10; %Br 23.8. Found: MR_d 70.38; %Br 23.8.

Infra-red absorptions:

3.45(m); 5.54(s); 5.82(w); 7.10(m); 7.65(s); 7.82(s); 7.95(s);
C. Reactions of \( \text{CF}_2=\text{CFCH}_2\text{CHBr(CH}_3\text{)}_2\text{SiOSi(CH}_3\text{)}_3 \) (XIII)

1. With Zinc and Hydrochloric Acid

XIII (15 g., 0.05 mole) was heated with an excess of zinc and \( \text{HCl} \), hydrochloric acid. The mixture was allowed to stand overnight and the organic layer separated, dried and distilled. The distillate had the following properties: b.p. 62-63 °C/15 mm.; \( n^\circ \) 1.3872; \( d^\circ \) 0.980. Yield 4.5 g. These physical constants are identical with those for XII.

II. With Quinoline

XIII (15 g., 0.05 mole) was heated with an excess of quinoline (13 g.) and the distillate collected as it formed. Redistillation of the crude material resulted in several fractions, none of which could be identified.

4. The Products obtained from the addition to Vinyl(dimethyl)ethoxysilane

This mixture (72 g.) was added dropwise to a slurry of zinc and ethanol. The reaction was exothermic. The mixture was heated for an additional 2 hours and then worked up in the usual manner. Two products were isolated from the reaction mixture. The lower boiling fraction, 15 g., had the following properties: b.p. 51-54 °C/14 mm., \( n^\circ \) 1.4010; \( d^\circ \) 0.9940. Anal. Found: No Cl⁻ or Br⁻, %C 45.56; %H 7.19; MW 275. These data along with the infra-red spectrum indicated that this material was XIII. Calcd. for \( \text{C}_{10}\text{H}_{19}\text{F}_{3}\text{Si}_{2} \): %C 44.72; %H 7.14; MW 268.
The second fraction, 25 g., had the following properties: b.p. 93-96 °/5mm.; n° 1.3975; d° 1.085. This material was identified as being V. Anal. Calcd. for C\textsubscript{12}H\textsubscript{20}F\textsubscript{6}Si\textsubscript{2}O: %H 5.75; %C 41.13; MW 350; Mr 75.94. Found: %H 5.94; %C 41.39; MW 360; Mr 77.70.

5. CF\textsubscript{2}BrCF\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}Cl (XIV)

a. With Pyridine

XIV (50 g.) and pyridine (40 g.) were combined in a 100 ml. distilling flask. A grey precipitate formed immediately. The filtrate was distilled at atmospheric pressure to remove the excess pyridine. The residue was distilled under vacuum. None of the resulting fractions could be identified as each came over a wide temperature range.

b. With Alcoholic Potassium Hydroxide

A solution of ethanol (200 ml.), potassium hydroxide (7 g.) and XIV (25 g.) was heated on a steam bath for 2 hours. The salt was filtered off and the filtrate worked up in the usual manner. Distillation of the crude organic layer resulted in several fractions, none of which could be identified.

c. With Aqueous Base

A solution consisting of 50 g. of XIV and an excess of aqueous potassium hydroxide was heated and stirred for 3 hours. The mixture was neutralized with dilute hydrochloric acid and the organic layer worked up in the usual manner. The forerun contained a material which crystallized in the distillation head. This material was heated with a flame and collected in the receiver. This solid was soluble
in hot water and was benzoic acid. The principal fraction, 15 g.,
came over at 165-170 \(^{\circ}\) C. The infra-red spectrum of this material
was identical with II.

It is evident from this reaction that the chlorosilane, XIV,
was contaminated with benzoic acid, a by-product of the initiator.

6. The Addition Products of Divinylidimethylsilane

a. With Alcoholic Base

The addition products were treated with an excess of alcoholic
base at room temperature. The salt was filtered and the filtrate
worked up in the usual manner. A material with the following physical
properties was isolated. b.p. 73.8-74 \(^{\circ}\) /8.5 mm.; \(\eta\) \(^{20}\) 1.4445; \(d\) \(^{20}\)
1.344. These constants were identical to those for the lower boiling
fraction of the addition reaction. Furthermore, the Ag eq. analysis
was also the same, 162. The infra-red spectrum of this material
indicated that hydrogen bromide did split out and that the product
was contaminated with some type of carbonyl compound, very likely
benzoic acid.

b. With Zinc and Alcohol

The addition mixture was reacted with an excess of zinc and
ethanol. The reaction mixture was worked up in the usual manner and
a material with the following properties isolated. b.p. 136-137 \(^{\circ}\);
\(\eta\) \(^{20}\) 1.4000; \(d\) \(^{20}\) 0.979. This material was identified as being XVI.

Anal. Calcd. for C\(_8\)H\(_{13}\)F\(_3\)SIO: \(M_r\) 47.92; \%C 49.46; \%H 6.74. Found:
\(M_r\) 48.15; \%C 49.78; \%H 6.97.

Infra-red absorptions:

3.45(m); 5.54(s); 6.26(w); 6.95(mw); 7.10(m); 7.75(s); 8.06(s);
8.45(s); 8.55(s); 9.35(s); 9.90(m); 10.05(m); 10.25(m); 11.15(ms);
12.00(brd s); 13.10(w smear); 14.50(w smear).

7. The Products obtained from the addition to Diallyldimethylsilane
   a. With Zinc and Ethanol

   These reaction products were treated with an excess of zinc and ethanol. The reaction mixture was worked up in the usual manner. A fraction, 5 g., with the following properties was isolated. B.p. 38-42°/3 mm.; n^20_2 1.4300; d^20_2 1.077. This material was believed to be XX. Anal. Calcd. for C_{10}H_{15}F_{3}SiO: MR_d 53.74; %C 54.60; %H 6.82. Found: MR_d 52.65; %C 54.10; %H 6.95.

   Infra-red absorptions:
   3.42(s); 5.56(s); 5.67(m); 6.10(vw shld); 6.16(ms); 6.91(m);
   7.05(m); 7.30(w); 7.75(s); 7.87(w); 7.94(s); 8.07(w); 8.45(m);
   9.25(s); 10.13(s); 11.95(s); 12.33(s); 12.75(s); 14.15(w).

8. CF_3BrCFCH_2CHBrSi(CH_3)_2 (VIII)
   a. With Zinc and Alcohol

   A solution of VIII (50 g., 0.13 mole), methanol (100 ml.) and excess zinc was stirred and refluxed for 3 hours. The reaction mixture was worked up in the usual manner and two products isolated. The lower boiling fraction, 5 g., was identified as being X and had the following properties: b.p. 114; n^23 1.3790; d^23 0.962. Anal. Calcd. for C_{6}H_{13}F_{3}Si: MR_d 43.77; %C 46.70; %H 7.11. Found: MR_d 43.60; %C 46.60; %H 7.25.

   Infra-red absorptions:
   3.38(s); 5.52(s); 6.94(ms); 7.05(m); 7.45(w); 7.70(s); 7.81(s);
7.90(s); 8.10(s); 8.45(s); 8.55(s); 9.35(s); 10.05(s); 11.15(s);
12.00(s smear); 12.65(m); 13.25(s); 13.50(s); 14.50(s).

The second fraction, 15 g., had the following properties: b.p. 
92°/60 mm.; n\textsuperscript{23} 1.4275; d\textsuperscript{23} 1.297. This material was IX. Anal.
Calcd. for C\textsubscript{6}H\textsubscript{12}BrF\textsubscript{3}Si: MR\textsubscript{d} 51.45; %Br 30.85. Found: MR\textsubscript{d} 51.50;
%Br 31.02.

Infra-red absorptions:
3.36(m); 5.52(s); 7.05(m); 7.40(s); 7.70(s); 7.81(s); 7.98(s);
8.10(s); 8.35(s); 8.62(w); 9.00(m); 9.18(s); 10.00(3); 11.18(m);
11.75(s brd); 13.35(m); 14.45(m).

C. MISCELLANEOUS REACTIONS

1. Reaction of CF\textsubscript{2}BrCFCH\textsubscript{2}CH\textsubscript{2}Si(CH\textsubscript{3})\textsubscript{3} with excess Base

A solution of the silane (29.5 g., 0.1 mole) and a large excess of ethanolic potassium hydroxide was heated on a steam bath for several hours. The mixture was worked up in the usual manner and a fraction b.p. 99-100° isolated. This material had the following properties:
n\textsuperscript{22} 1.3990; d\textsuperscript{22} 1.4470. A gas chromatogram showed two almost equal peaks. This material was undoubtedly a mixture of hexamethyldisiloxane and CF\textsubscript{2}BrCFCH\textsubscript{2}CH\textsubscript{2}Si since the boiling point reported for these compounds are both about 99°. The infra-red spectrum of the material in question showed peaks which were characteristic of both components.

2. Reaction of CF\textsubscript{2}BrCFCH\textsubscript{2}CHBrSi(CH\textsubscript{3})\textsubscript{3} with Concentrated
Sulfuric Acid

A mixture of 100 ml. of concentrated sulfuric acid and 25 g.
of VIII was heated at 105-120\(^\circ\) for 3 hours. This mixture was poured into crushed ice and the aqueous layer extracted with ether. The ether extracts were combined with the organic layer, dried and distilled. The principal fraction, 15 g., came over at 163-165\(^\circ\) \text{/ mm.}, and had the following properties: \(n^25 1.4320\); \(d^25 1.7950\). This material was the disiloxane II. \textbf{Anal.} Calcd. for II Ag eq. 123.2; found: 123.6.

The residue was extracted with hexane and treated with norlite. A clear viscous yellow oil remained. This material was probably the product of the reaction of two or possibly all three methyl groups with sulfuric acid.

3. Reaction of \(\text{CF}_2\text{BrCFClCH}_2\text{CH} = \text{CH}_2\) with Zinc and Alcohol

\textbf{(Proof of Structure)}

The olefin (25 g.) was dropped into a refluxing slurry of zinc and methanol. The resulting azeotrope was collected as formed. This mixture was washed with cold water and the organic material distilled. A fraction with the following properties was isolated. B.p. 42\(^\circ\); \(n^23 1.3420\); \(d^23 1.0350\). The infra-red spectrum of this material was identical to that reported for \(\text{CF}_2 = \text{CFCH}_2\text{CH} = \text{CH}_2\).

\textbf{D. PREPARATION OF STARTING MATERIALS}

1. Divinyltetramethyldisiloxane

A mixture of vinylidimethylethoxysilane (300 g.), benzene (700 ml.), water (100 ml.) and 0.5\(N\) hydrochloric acid (15 ml.) was heated and efficiently stirred for 12 hours. The benzene and water were azeotroped off and the residue distilled. The desired
product, b.p. 138-142°, was obtained in a 90% yield (196 g.).

2. **Vinyldimethylchlorosilane**

Vinyl magnesium bromide (8 moles), prepared by the addition of 10 moles of vinyl bromide to 10 moles of magnesium in 6 liters of tetrahydrofuran, was slowly added to 8 moles of dimethyldichlorosilane. The mixture was refluxed overnight and the salt filtered off. The filtrate was distilled to yield 200 g. of product b.p. 80-90°.

3. **Divinyldimethylsilane**

This material was prepared in the same manner as the vinyldimethylchlorosilane except that two moles of the Grignard reagent was used per mole of dimethyldichlorosilane.

4. **Diallyldimethylsilane**

Allyl magnesium chloride was prepared by the addition of allyl chloride to an excess of magnesium in tetrahydrofuran solvent. This reagent (2.4 mole) was added to 1 mole of dimethyldichlorosilane. The mixture was refluxed for 10 hours, filtered and the filtrate hydrolyzed with very dilute hydrochloric acid. A 60% yield of the desired product, b.p. 133-135°, 79 g., was obtained.

5. **Vinylpentamethyldisiloxane**

A solution of hexamethyldisiloxane (40 g., 0.25 mole), vinyldimethylethoxysilane (65 g., 0.5 mole), potassium hydroxide (14 g.) and 200 ml. of ethanol was refluxed for 2 hours. The mixture was neutralized with hydrochloric acid, dried and distilled. A 68% yield, (30 g., 30% conversion) of the desired product was obtained. B.p. 120°.
6. \( \text{CF}_2\text{BrCFClCH}_2\text{CHBrSi(CH}_3)_3 \) (VIII)

A solution of vinyltrimethylsilane (100 g.), dibromide (1500 g.) and benzoyl peroxide (10 g.) was refluxed for 10 hours. The excess dibromide was distilled off and the higher boiling residue distilled under vacuum. A 90% yield of the adduct was obtained. B.p. 620/1 mm.; \( n^23 \) 1.4630; \( d^{23} \) 1.610.
The addition of CF₂BrCFCIBr to a series of alkenyl silicon compounds was studied. These compounds were vinylidimethylethoxy-silane, vinylidimethylchlorosilane, divinylidimethylsilane, allyltrimethylsilane, diallyldimethylsilane, vinylpentamethyldisiloxane and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane. A mixture of products was obtained when two unsaturation sites were present as in 1,3-divinyl-1,1,3,3-tetramethyldisiloxane. This mixture consisted of the product of the addition to one vinyl group and the product of the addition to both vinyl groups.

An interesting phenomenon was observed in the addition of CF₂BrCFCIBr to allyltrimethylsilane. The olefin, CF₂BrCFCICH₂CH=CH₂ and bromotrimethylsilane were the products of this reaction. A mechanism involving the intermediate free radical was postulated to account for these products. It was further observed that the addition of the same haloalkane to diallyldimethylsilane did not result in the formation of the cleaved products. Only a small portion of the reaction mixture was identified. This material was the result of the addition to one allyl group in which hydrogen bromide split out.

All attempts to dehydrohalogenate the addition products of the disiloxanes resulted in cleavage of the disiloxane bond. It was felt that some dehydrohalogenation occurred since potassium bromide was present in the reaction mixture. However, when the mixture was neutralized, several different disiloxanes were undoubtedly reformed.
Unusual results were obtained when the addition products were treated with zinc and alcohol. Along with the expected dehalogenated product, a material was isolated in which replacement of the remaining α-bromine with hydrogen had occurred. This reduction was somewhat surprising in view of the ready formation of \( \text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Br} \) from \( \text{CF}_2\text{BrCFClCH}_2\text{CH}_2\text{Br} \) without evidence of reduction.

Concentrated sulfuric acid selectively cleaved a methyl group from \( \text{CF}_2\text{BrCFClCH}_2\text{CHBrSi(CH}_3)_3 \). The resulting sulfate ester readily hydrolyzed to the symmetrical disiloxane.
V. BIBLIOGRAPHY

Charles Tomasino was born on March 14, 1931, in Tampa, Florida where he attended local schools and was graduated from Thomas Jefferson High School in June, 1948.

He entered the University of Florida in July, 1948, and received his BS degree in chemistry in June, 1952. After graduation he immediately was called into military service where he spent two years as a Truck Officer in the U. S. Army Transportation Corp. The author was employed by Peninsular Chem Research, Inc. for one year as a research chemist before entering graduate school. He received his Master of Science degree in chemistry in January, 1957.

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The author is married, has one child and is a member of the American Chemical Society, Alpha Chi Sigma and Gamma Sigma Epsilon.
This dissertation was prepared under the direction of the Chairman of the candidate's Supervisory Committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

January 31, 1959

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Dean, College of Arts and Sciences

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