8–9 g. of purified $S_3N_2O_2$ could be obtained from 200 g. of $SOCl_2$ in a 12-hr. run. These amounts correspond to about 10% yields calculated from the vaporized $SOCl_2$ on the basis of equation 6.

Using pure ammonium chloride pellets, a 3-hr. run was made using the apparatus shown in Figure 1. A mixture of 303 g. of S_2Cl_2 and 121 g. of $SOCl_2$ was used in the bubbler; during the run 34 g. of this mixture evaporated. Four g. of pure $S_3N_2O_2$ and one g. of crude $S_3N_2O_2$ were obtained from the red material deposited in the air condenser.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
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Vinyl Derivatives of Metals. XI. Reaction of Nucleophilic Reagents with Triethylperfluorovinylsilane[1,2]

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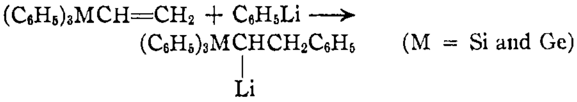
The reaction of organolithium reagents with triethylperfluorovinylsilane gave *trans*-$(C_2H_5)_3SiCF{=}CFR$ products (R = *n*-butyl, phenyl, vinyl, allyl, triphenylsilyl, triphenylgermyl, and diphenylphosphino), presumably by an addition–elimination sequence. The action of phenyllithium on α,β-difluoro-β-triethylsilylstyrene resulted in formation of triethylphenylsilane and diphenylacetylene. The possible mechanisms of this reaction are discussed. Treatment of triethylperfluorovinylsilane with sodium alkoxides and mercaptides also produced addition–elimination products, $(C_2H_5)_3SiCF{=}CFOR$ and $(C_2H_5)_3SiCF{=}CFSR$.

Previous studies concerned with the chemical reactivity of vinyl derivatives of Group IV metals have shown that a considerable difference exists between the reactions observed with vinylsilanes and vinylgermanes on the one hand, and vinyltin and vinyllead compounds on the other.[4] Thus, to cite an example of interest to the present study, triphenylvinylsilane and triphenylvinylgermane react with phenyllithium in the following manner[5,6]



$$(C_6H_5)_3MCH{=}CH_2 + C_6H_5Li \longrightarrow (C_6H_5)_3M\underset{\displaystyle Li}{\underset{|}{C}}HCH_2C_6H_5 \qquad (M = \text{Si and Ge})$$

while triphenylvinyltin and triphenylvinyllead undergo an exchange reaction with phenyllithium[6]

$$(C_6H_5)_3MCH{=}CH_2 + C_6H_5Li \longrightarrow (C_6H_5)_4M + CH_2{=}CHLi \qquad (M = \text{Sn and Pb})$$

Recent work in these Laboratories has shown that perfluorovinyltin compounds also undergo an exchange reaction with organolithium reagents to form the rather unstable perfluorovinyllithium.[1] It therefore was of interest to determine whether an exchange or an addition reaction would be observed on treating perfluorovinylsilanes with organolithium compounds. The results could not be predicted with certainty, since with olefinic silicon compounds both exchange and addition reactions are possible. Which reaction is observed seems to depend mainly on the nature of the unsaturated group. While the addition reaction is observed with vinylsilanes, the exchange reaction was found to occur with β-styryltriphenylsilane[7] and phenylethynyltriphenylsilane.[8] Thus an exchange reaction seemed not unlikely with silicon compounds containing the electronegative perfluorovinyl group.

Triethylperfluorovinylsilane[9] was chosen for this study because of the relative ease of its preparation. Treatment of this compound with a number of organolithium reagents did not result in an exchange reaction; instead, the products isolated were β-organo-α,β-difluorovinyltriethylsilanes

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(1) Preliminary communication: D. Seyferth, T. Wada, and G. Raab, *Tetrahedron Letters*, No. 22, 20 (1960).

(2) Part X: D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

(3) On leave from the Shin-Etsu Chemical Industry Co., Ltd., Tokyo, Japan.

(4) For a review see: D. Seyferth, "Vinyl Compounds of Metals" in "Progress in Inorganic Chemistry," Vol. III (F. A. Cotton, ed.), Interscience Publishers Inc., New York, N. Y., in press.

(5) L. F. Cason and H. G. Brooks, *J. Am. Chem. Soc.*, **74**, 4582 (1952); *J. Org. Chem.*, **19**, 1278 (1954).

(6) D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, in press.

(7) H. Gilman, T. C. Wu, and D. Wittenberg, *J. Org. Chem.*, **25**, 596 (1960).

(8) H. Gilman and H. Hartzfeld, *J. Am. Chem. Soc.*, **73**, 5878 (1951).

(9) D. Seyferth, K. A. Brändle, and G. Raab, *Angew. Chem.*. **72**, 77 (1960).

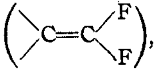
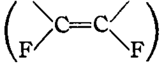
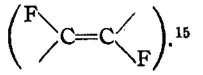
$$(C_2H_5)_3SiCF{=}CF_2 + RLi \xrightarrow{\text{Diethyl ether}} (C_2H_5)_3SiCF{=}CFR + LiF$$
$$(R = C_6H_5,\ CH_2{=}CH,\ CH_2{=}CHCH_2,\ n\text{-}C_4H_9)$$

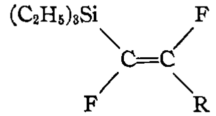
Such products could result either from a direct nucleophilic displacement of a β-fluorine atom by the organolithium reagent or from an addition-elimination sequence

$$(C_2H_5)_3SiCF{=}CF_2 + RLi \longrightarrow (C_2H_5)_3SiCFLiCF_2R \longrightarrow (C_2H_5)_3SiCF{=}CFR + LiF$$

Similar reactions of simple fluoroölefins, such as tetrafluoroethylene and chlorotrifluoroethylene, with organolithium reagents have been described previously.[10–13] Both the addition–elimination path[10,12] and the nucleophilic substitution mechanism[11] have been suggested for these reactions, but no conclusive proof for either possibility has been given. For reasons cited[10,12] we shall accept tentatively the former mechanism and discuss our results in these terms.

All $(C_2H_5)_3SiCF{=}CFR$ compounds were stable, distillable liquids. The vinyllithium product, 1,2-difluoro-1-triethylsilyl-1,3-butadiene, polymerized on standing. Similar addition–elimination reactions were observed with triphenylsilyllithium, triphenylgermyllithium, and diphenylphosphinolithium, and the compounds $(C_2H_5)_3SiCF{=}CFSi(C_6H_5)_3$, $(C_2H_5)_3SiCF{=}CFGe(C_6H_5)_3$ (both solids), and $(C_2H_5)_3SiCF{=}CFP(C_6H_5)_2$, a liquid, were isolated. Organomagnesium compounds of suitable structure also were found to undergo such reactions. Thus phenylmagnesium bromide in tetrahydrofuran reacted with triethylperfluorovinylsilane to give α,β-difluoro-β-triethylsilylstyrene in 64% yield. However, ethylmagnesium bromide did not appear to react with the perfluorovinylsilane in this manner under the same conditions. Similar observations concerning the relative reactivity of the phenyl and ethyl Grignard reagents toward 1,1-dichloro-2,2-difluoroethylene have been described by Tarrant and Warner.[14]

The question of the structure of these compounds was examined using F^{19} nuclear resonance spectroscopy. The nuclear resonance spectra of $(C_2H_5)_3SiCF{=}CFC_6H_5$, $(C_2H_5)_3SiCF{=}CFSi(C_6H_5)_3$, and $(C_2H_5)_3SiCF{=}CFGe(C_6H_5)_3$ consisted of a non-equivalence quartet in each case. The F–F spin coupling constants derived were 124, 132, and 144 c.p.s., respectively. In general, F–F spin coupling constants in fluoroölefins are in the range 27–87 c.p.s. for *gem*-fluorine atoms , 33–58 c.p.s. for *cis*-fluorine atoms , and 115–124 c.p.s. for *trans*-fluorine atoms .[15] It may be noted that attachment of the $CF_2{=}CF$ group to a silicon atom does not affect the validity of this generalization, which is based on the F^{19} nuclear resonance spectra of only a few compounds ($CF_2{=}CFX$, where X is H, Cl, Br, CN, and CF_3). The *gem, cis,* and *trans* F–F spin coupling constants in triethylperfluorovinylsilane are 71, 27, and 115 c.p.s., respectively.[16] The large values of the coupling constants observed in the present compounds indicate that the organic groups derived from the lithium reagents are on the carbon atom β to the silicon atom, and that the fluorine atoms are in the *trans* position



The F^{19} nuclear resonance spectrum of *trans*-1,2-difluoro-1-triethylsilyl-1-hexene was that expected for this structure, with an F–F coupling constant of 126 c.p.s. and further splitting of each line of the quartet into a triplet due to fluorine coupling with the protons of the CH_2 group attached to the β-carbon atom. A very similar situation obtained in the case of *trans*-1,2-difluoro-1-triethylsilyl-1,4-pentadiene.

It is known that tetrafluoroethylene can be converted to tetraphenylethylene by four successive addition–elimination steps when treated with an excess of phenyllithium.[10] It therefore was of interest to see whether α,β-difluoro-β-triethylsilylstyrene could be converted to more highly phenylated compounds in this manner. More specifically, the question arose as to which carbon atom of the olefinic system in *trans*-$(C_2H_5)_3SiCF{=}CFC_6H_5$ would be attacked by phenyllithium. Accordingly, this reaction was carried out with α,β-difluoro-β-triethylsilylstyrene and phenyllithium in 1:1 molar ratio. Neither $(C_2H_5)_3SiCF{=}$

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[10] S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).

[11] R. Meier and F. Böhler, *Chem. Ber.*, **90**, 2344 (1957).

[12] T. F. McGrath and R. Levine, *J. Am. Chem. Soc.*, **77**, 4168 (1955).

[13] G. Bier and H. Fritz, Ger. patent 1,006,852 (1957); *Chem. Abstr.*, **53**, 18862 (1959).

[14] P. Tarrant and D. A. Warner, *J. Am. Chem. Soc.*, **76**, 1624 (1954).

[15] H. M. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.*, **24**, 479 (1956).

[16] Unpublished work by Dr. G. E. Maciel in these Laboratories.

$C(C_6H_5)_2$ nor $(C_2H_5)_3SiC(C_6H_5){=}CFC_6H_5$ could be isolated; instead the only products obtained were starting silane (41%), diphenylacetylene (45%), and triethylphenylsilane (50%). When this reaction was carried out with phenyllithium and the silane in 2:1 molar ratio, only diphenylacetylene and triethylphenylsilane could be isolated. These results may be explained in terms of two possible mechanisms: (1) initial attack of phenyllithium on α,β-difluoro-β-triethylsilylstyrene may indeed give a diphenylated product. The phenyllithium added subsequently then has the possibility of reacting either with starting silane or with the diphenylated product. The reaction of the diphenylated product with phenyllithium would be one of lithium–silicon exchange, in which triethylphenylsilane and $(C_6H_5)_2C{=}CFLi$ or $C_6H_5CF{=}C(C_6H_5)Li$ are formed. These new lithium reagents would be expected to be unstable under these conditions (note perfluorovinyllithium[1]) and to undergo either α- or β-elimination of lithium fluoride, giving diphenylacetylene. The results obtained in the 1:1 reaction would be those expected if the transmetalation reaction of phenyllithium with diphenylated product occurs at a much faster rate than the reaction sequence which produces the diphenylated product. The proposed course of the reaction may be summarized by the equations

$$\begin{array}{l}\mathrm{(C_2H_5)_3SiCF{=}CFC_6H_5 + C_6H_5Li \longrightarrow} \\ \qquad\qquad \mathrm{LiF + (C_2H_5)_3SiCF{=}C(C_6H_5)_2} \\ \qquad\qquad\qquad \text{or } \mathrm{(C_2H_5)_3SiC(C_6H_5){=}CFC_6H_5}\end{array}$$

$$\left\{\begin{array}{l}\mathrm{(C_2H_5)_3SiCF{=}C(C_6H_5)_2 + C_6H_5Li \longrightarrow} \\ \qquad\qquad \mathrm{(C_2H_5)_3SiC_6H_5 + (C_6H_5)_2C{=}CFLi} \\ \text{or} \\ \mathrm{(C_2H_5)_3SiC(C_6H_5){=}CFC_6H_5 + C_6H_5Li \longrightarrow} \\ \qquad\qquad \mathrm{(C_2H_5)_3SiC_6H_5 + C_6H_5CF{=}C(C_6H_5)Li}\end{array}\right.$$

$$\left\{\begin{array}{l}\mathrm{(C_6H_5)_2C{=}CFLi \longrightarrow LiF + C_6H_5C{\equiv}CC_6H_5} \\ \text{or} \\ \mathrm{C_6H_5CF{=}C(C_6H_5)Li \longrightarrow LiF + C_6H_5C{\equiv}CC_6H_5}\end{array}\right.$$

All experiments carried out under milder conditions with the object of isolating a diphenylated product were unsuccessful. (2) In the other possible route to the observed products, the first step may be one of exchange, giving triethylphenylsilane and $C_6H_5CF{=}CFLi$. The latter would be expected to lose lithium fluoride readily, forming $C_6H_5C{\equiv}CF$, which could either couple directly with phenyllithium or undergo an addition–elimination sequence to produce diphenylacetylene. At present no experimental data are at hand which allow us to choose between these mechanisms. The equations for (2) are

$$\begin{array}{l}\mathrm{(C_2H_5)_3SiCF{=}CFC_6H_5 + C_6H_5Li \longrightarrow} \\ \qquad\qquad \mathrm{(C_2H_5)_3SiC_6H_5 + C_6H_5CF{=}CFLi} \\ \qquad \mathrm{C_6H_5CF{=}CFLi \longrightarrow C_6H_5C{\equiv}CF + LiF}\end{array}$$

$$\left\{\begin{array}{l}\mathrm{C_6H_5C{\equiv}CF + C_6H_5Li \longrightarrow C_6H_5C{\equiv}CC_6H_5 + LiF} \\ \text{or} \\ \mathrm{C_6H_5C{\equiv}CF + C_6H_5Li \longrightarrow} \\ \qquad \mathrm{(C_6H_5)_2C{=}CFLi}\ (\text{or } \mathrm{C_6H_5CF{=}C(C_6H_5)Li}) \\ \qquad\qquad \searrow\quad\swarrow \\ \qquad\quad \mathrm{C_6H_5C{\equiv}CC_6H_5 + LiF}\end{array}\right.$$

The reported[17] α-elimination of lithium bromide from $(C_6H_5)_2C{=}CBrLi$ to give diphenylacetylene provides an analogy which favors the β,β-diphenyl structure for our diphenylated intermediates in either mechanism. Work is in progress which may provide further insight into this reaction.

Not only organolithium reagents but also more conventional nucleophiles will undergo such reactions with triethylperfluorovinylsilane. Treatment of triethylperfluorovinylsilane with ethanolic sodium ethoxide gave, in addition to the cleavage product triethylethoxysilane, the addition–elimination product $(C_2H_5)_3SiCF{=}CFOC_2H_5$ in 28% yield. Usually saturated products result in such reactions of simple fluoroölefins when carried out in protonic solvents.[18] However, combustion analysis and the infrared and F^{19} nuclear resonance spectra of the product provided the structure given above. α,β-Difluoro-β-triethylsilylvinyl ethyl ether was obtained in 39% yield when triethylperfluorovinylsilane was added to a slurry of sodium ethoxide in tetrahydrofuran, and the action of sodium trimethylsilylmethoxide in this medium gave $(C_2H_5)_3SiCF{=}CFOCH_2Si(CH_3)_3$ in 66% yield. Similar reactions with sodium *n*-propylmercaptide and sodium thiophenolate in tetrahydrofuran suspension resulted in $(C_2H_5)_3SiCF{=}CFSC_3H_7$ and $(C_2H_5)_3SiCF{=}CFSC_6H_5$. Such olefinic products are to be expected in the absence of protonic solvents.[19] The F^{19} nuclear resonance spectra of both ethers and of the product derived from *n*-propyl mercaptan indicated that the alkoxy and the propylthio groups were on the carbon atom β to the silicon atom and that the fluorine atoms occupied *trans* positions. However, the F^{19} spectrum of analytically pure $(C_2H_5)_3SiCF{=}CFSC_6H_5$ showed the presence of two isomers. In addition to a

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(17) D. Y. Curtin and E. W. Flynn, *J. Am. Chem. Soc.*, **81**, 4714 (1959).

(18) Leading references are given by: D. C. England, L. R. Melby, M. A. Dietrich, and R. V. Lindsey, *ibid.*, **82**, 5116 (1960); and W. T. Miller, Jr., and A. H. Fainberg, *ibid.*, **79**, 4166 (1957).

(19) R. Meier and F. Böhler, *Chem. Ber.*, **90**, 2342 (1957).

quartet with an F–F spin coupling constant of 148 c.p.s. indicative of the *trans* isomer, there was another quartet at lower field with an F–F coupling constant of 20 c.p.s., probably due to the *cis* isomer. It may be noted in support of this assumption that the F–F coupling constant in *cis*-1,2-difluoroethylene has been reported to be 18.6 c.p.s.[20] The product was determined to contain *ca.* 74% of the *trans* isomer and *ca.* 26% of the *cis* compound by comparing the areas of the two quartets.

Substitution of a β-fluorine atom in triethylperfluorovinylsilane results in a lowering of the C=C stretching frequency characteristic for that compound (1709 cm.$^{-1}$). The C=C stretching frequencies in $(C_2H_5)_3SiCF{=}CFOC_2H_5$, $(C_2H_5)_3SiCF{=}CFOCH_2SiMe_3$, $(C_2H_5)_3SiCF{=}CFCH_2CH{=}CH_2$, and $(C_2H_5)_3SiCF{=}CFC_4H_9$ were 1688, 1680, 1672, and 1670 cm.$^{-1}$, respectively. Conjugation results in still further lowering, as shown by $\nu_{C=C}$ = 1637 cm.$^{-1}$ in $(C_2H_5)_3SiCF{=}CFC_6H_5$. The allyl adduct also showed a band at 1641 cm.$^{-1}$ attributable to the C=C stretching frequency of the terminal vinyl group. The spectrum of $(C_2H_5)_3SiCF{=}CFCH{=}CH_2$ showed weak absorption at 1642 cm.$^{-1}$ (shoulder at 1632 cm.$^{-1}$), in addition to strong absorption at 1595 cm.$^{-1}$.

Experimental[21]

Preparation of Triethylperfluorovinylsilane.—To 9.7 g. (0.4 g. atom) of magnesium turnings in a three-necked flask equipped with a stirrer, a reflux condenser topped with a nitrogen inlet tube, and a dropping funnel, was added 50 ml. of tetrahydrofuran (THF) and a few drops of 1,2-dibromoethane. The mixture was stirred, cooled to −10 to −15°, and another 100 ml. of THF was added. To this mixture was added, under nitrogen with stirring, a solution of 42 g. (0.28 mole) of triethylchlorosilane and 65 g. (0.4 mole) of bromotrifluoroethylene (Peninsular ChemResearch, Inc.) in 200 ml. THF. Stirring was continued for 4 hr. at −10 to −15° and for 8 hr. at 0 to −3°. The mixture then was hydrolyzed with 30 ml. of saturated ammonium chloride solution, and the separated organic layer was dried over anhydrous calcium chloride. The dry organic layer was distilled rapidly at low pressure into a receiver cooled to −78°. Fractional distillation of the distillate gave 23 g. (42% yield) of triethylperfluorovinylsilane, b.p. 30° (8.8 mm.) to 36° (9.5 mm.). A second distillation gave 22 g. of pure material, b.p. 35° (9.6 mm.), n^{25}D 1.4003.

Anal. Calcd. for $C_8H_{15}F_3Si$: C, 48.95; H, 7.70; F, 29.04. Found: C, 49.19; H, 7.95; F, 29.08.

Reaction of Triethylperfluorovinylsilane with Organolithium Reagents.—The reaction with phenyllithium is described as an example of the procedure used.

To 40 ml. of a 1.14 *M* solution of phenyllithium in ether under an atmosphere of nitrogen was added 8.0 g. (0.04 mole) of triethylperfluorovinylsilane. A white solid precipitated. The reaction mixture was stirred for 3 hr. at room temperature, cooled to 0°, carefully hydrolyzed with saturated ammonium chloride solution, and filtered. Distillation of the dried organic layer gave a colorless fraction boiling at 90–96° (0.75 mm.) and 1.0 g. of a viscous, yellow residue. A second fractional distillation resulted in 0.2 g. of liquid of b.p. 72–81° (0.3 mm.), n^{25}D 1.5091, and 7.9 g. (76%) of $(C_2H_5)_3SiCF{=}CCF_6H_5$, b.p. 81–84° (0.25 mm.), n^{25}D 1.5117 to 1.5113. Another distillation gave the pure compound, b.p. 91° (0.55 mm.), n^{25}D 1.5112.

Anal. Calcd. for $C_{14}H_{20}F_2Si$: C, 66.09; H, 7.92; F, 14.93. Found: C, 66.37; H, 7.92; F, 14.65.

The reaction of vinyllithium[2,22] with triethylperfluorovinylsilane gave $(C_2H_5)_3SiCF{=}CFCH{=}CH_2$ in 48% yield, b.p. 44.5° (1.1 mm.), n^{25}D 1.4556.

Anal. Calcd. for $C_{10}H_{18}F_2Si$: C, 58.79; H, 8.88; F, 18.59. Found: C, 58.88; H, 8.70; F, 18.58.

A similar reaction with allyllithium[23] gave $(C_2H_5)_3SiCF{=}CFCH_2CH{=}CH_2$ (55%), b.p. 51° (1.6 mm.), n^{25}D 1.4382.

Anal. Calcd. for $C_{11}H_{20}F_2Si$: C, 60.50; H, 9.23; F, 17.40. Found: C, 60.34; H, 9.33; F, 17.48.

$(C_2H_5)_3SiCF{=}CFC_4H_9$, b.p. 53° (0.4 mm.), n^{25}D 1.4309, was obtained in 79% yield by the action of *n*-butyllithium on triethylperfluorovinylsilane.

Anal. Calcd. for $C_{12}H_{24}F_2Si$: C, 61.49; H, 10.32; F, 16.21. Found: C, 61.72; H, 10.72; F, 15.96.

Reaction of Triethylperfluorovinylsilane with Triphenylsilyllithium and Triphenylgermyllithium.—A solution of triphenylsilyllithium[24] was prepared by cleavage of 10 g. (0.02 mole) of hexaphenyldisilane with 2 g. (0.29 g. atom) of finely cut lithium wire in 70 ml. THF. To 5.9 g. (0.03 mole) of triethylperfluorovinylsilane in a small volume of THF at 0° under nitrogen, 50 ml. of the triphenylsilyllithium solution was added dropwise with stirring. The resulting mixture was stirred for one hr. at room temperature. During this time the color of the lithium reagent was discharged, and a white precipitate formed. The reaction mixture was left at room temperature overnight hydrolyzed with saturated ammonium chloride solution, and filtered. The dried organic layer was evaporated. The residue crystallized on cooling to 0° for some time to give 9.5 g. of white crystalline solid. This solid dissolved in part in pentane; the insoluble portion was filtered. Evaporation of the pentane solution left 9.0 g. of white platelets, m.p. 70–73°, a yield of 67%. Recrystallization from methylene chloride gave pure $(C_2H_5)_3SiCF{=}CFSi(C_6H_5)_3$, m.p. 73.6–75°.

Anal. Calcd. for $C_{26}H_{30}F_2Si_2$: C, 71.51; H, 6.92; F, 8.70. Found: C, 71.68; H, 6.92; F, 8.62.

A similar procedure was followed in the reaction of tri-

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[20] T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.*, 743 (1961).

[21] All reactions were carried out in an atmosphere of prepurified nitrogen. Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[22] D. Seyferth and M. A. Weiner, *Chem. & Ind.* (London), 402 (1959).

[23] D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **24**, 1395 (1959).

[24] H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

phenylgermyllithium[25] with triethylperfluorovinylsilane in ethylene glycol dimethyl ether. The product, $(C_2H_5)_3SiCF{=}CFGe(C_6H_5)_3$, m.p. 64–66°, was obtained in 55% yield.

Anal. Calcd. for $C_{26}H_{30}F_2SiGe$: C, 66.27; H, 6.42; F, 8.06. Found: C, 66.01; H, 6.23; F, 7.83.

Reaction of Triethylperfluorovinylsilane with Diphenylphosphinolithium.—To 1.0 g. (0.14 g. atom) of lithium suspended in 20 ml. THF was added a solution of 8.0 g. of diphenylbromophosphine in 30 ml. THF. The reaction mixture was stirred and maintained at −25°. The initially pale yellow solution changed to bright red as the reaction proceeded. The reagent solution was stirred at −25° for 3 hr., and then was added dropwise to 5.9 g. (0.03 mole) of triethylperfluorovinylsilane in 20 ml. THF at 0°. The bright red color of the $(C_6H_5)_2PLi$ solution changed to dark brown. The reaction mixture was stirred at 0° for 2 hr. and then left to stand overnight at this temperature. Upon removal of solvent a dark brown, viscous liquid remained. Distillation gave 7.0 g. of colorless liquid, boiling range 70–162° (0.2 mm.). Fractional distillation of the latter resulted in 1.3 g., boiling range 57–153° (0.35 mm.) and 5.8 g. (53%) of colorless liquid, b.p. 153–155° (0.35 mm.), $n^{25}D$ 1.5619. This was identified as $(C_2H_5)_3SiCF{=}CFP(C_6H_5)_2$.

Anal. Calcd. for $C_{20}H_{25}F_2PSi$: C, 66.27; H, 6.95; F, 10.48; P, 8.55. Found: C, 66.38; H, 7.18; F, 10.60; P, 8.62.

Attempted quaternization of this product with methyl iodide resulted in partial cleavage of the $(C_2H_5)_3SiCF{=}CF$-group. To 1.8 g. (5 mmoles) of $(C_2H_5)_3SiCF{=}CFP(C_6H_5)_2$ in 20 ml. of ether was added 1.5 g. (11 mmoles) of methyl iodide. The mixture was refluxed for 30 min. Removal of volatiles left a viscous liquid which crystallized partially after several weeks. Recrystallization of the solid which had formed from acetone gave 0.6 g. (35%) of dimethyldiphenylphosphonium iodide, m.p. 240° (dec.).

Anal. Calcd. for $C_{14}H_{16}PI$: C, 49.14; H, 4.71; P, 9.05; I, 37.09. Found: C, 49.42; H, 5.09; P, 9.02; I, 37.13.

Reaction of Triethylperfluorovinylsilane with Phenylmagnesium Bromide.—The Grignard reagent was prepared from 5.5 g. (0.23 g. atom) of magnesium turnings and 31.5 g. (0.2 mole) of bromobenzene in 100 ml. THF. To 5.9 g. (0.03 mole) of triethylperfluorovinylsilane was added 20 ml. of the phenyl Grignard solution, and the resulting mixture was stirred at reflux for 24 hr. Hydrolysis with saturated ammonium chloride solution was followed by filtration and distillation of the organic layer. The product, $(C_2H_5)_3SiCF{=}CFC_6H_5$, b.p. 81–82° (0.2 mm.), $n^{25}D$ 1.5096, was isolated in 64% yield. The infrared spectrum of the product was identical with that of $(C_2H_5)_3SiCF{=}CFC_6H_5$ prepared *via* the phenyllithium–triethylperfluorovinylsilane reaction.

Anal. Calcd. for $C_{14}H_{20}F_2Si$: C, 66.09; H, 7.92; F, 14.93. Found: C, 66.39; H, 8.16; F, 14.70.

Reaction of α,β-Difluoro-β-triethylsilylstyrene with Phenyllithium. A. 1:1 Molar Ratio.—To 7.6 g. (0.03 mole) of $(C_2H_5)_3SiCF{=}CFC_6H_5$ in 80 ml. 1:1 ether–THF was added 35.3 ml. of 0.85 *M* phenyllithium (0.03 mole) in ether. The resulting mixture was refluxed for 4 hr., cooled to 0°, and hydrolyzed with saturated ammonium chloride solution until a neutral aqueous phase resulted. The organic layer was dried, and subsequently the solvent was distilled off. The residue was separated into two fractions by distillation: (1) 56–90° (0.25–0.3 mm.), 7.3 g., and (2) 90–110° (0.3 mm.), 1.4 g. Fraction 1 was analyzed using gas chromatography (Dow Corning 710 Silicone Fluid on firebrick; helium carrier gas at 14 p.s.i.; preheater at 300°; and jacket at 220°). It was found to consist of 41% triethylphenylsilane, 2% biphenyl, 37% $(C_2H_5)_3SiCF{=}CFC_6H_5$, and 19% diphenylacetylene (elution in that order). Triethylphenylsilane was isolated in macro amounts by preparative scale gas chromatography, $n^{25}D$ 1.5006 (lit.[26] $n^{25.1}D$ 1.5004). Its infrared spectrum was identical with that of an authentic sample prepared by the reaction of triethylchlorosilane with phenyllithium in ether. α,β-Difluoro-β-triethylsilylstyrene was identified by its infrared spectrum and its refractive index ($n^{25}D$ 1.5112). Fraction 2 solidified on standing at room temperature. It was dissolved in a minimum amount of xylene and analyzed by gas chromatography: 1% triethylphenylsilane, 27% $(C_2H_5)_3SiCF{=}CFC_6H_5$, and 72% diphenylacetylene. The latter was identified by isolation (m.p. 60–60.5°). No depression of m.p. occurred when the substance was mixed with authentic diphenylacetylene, and the infrared spectra of the product and of authentic diphenylacetylene are superimposable.

Anal. Calcd. for $C_{14}H_{10}$: C, 94.50; H, 5.63. Found: C, 94.50; H, 5.48. The gas chromatography data allowed approximate yields to be calculated (based on starting silane): triethylphenylsilane, 50%; starting silane, 41% recovery; diphenylacetylene, 45%.

B. 1:2 Molar Ratio.—The same procedure was used in the reaction of 10.2 g. (0.04 mole) of $(C_2H_5)_3SiCF{=}CFC_6H_5$ in 60 ml. THF with 80 ml. of 1.1 *M* phenyllithium (0.088 mole) in ether. The residue remaining after removal of solvent was separated into three fractions by distillation: (1) 54–59° (0.2–0.35 mm.), 7.4 g.; (2) 65–75° (0.3–0.25 mm.), 0.6 g.; (3) 90–100° (0.25–0.35 mm.), 3.5 g. Each fraction was analyzed by gas chromatography. Fraction 1: 96% triethylphenylsilane, 4% biphenyl; fraction 2: 71% triethylphenylsilane, 17% biphenyl, 12% diphenylacetylene; fraction 3 (as a 50% xylene solution): 6% triethylphenylsilane, 4% biphenyl, 90% diphenylacetylene. In addition, 2.1 g. of diphenylacetylene was isolated from the distillation apparatus after these fractions had been taken. These data gave the following yields: triethylphenylsilane, 97%; diphenylacetylene, 71% (based on starting silane). The distillation residue consisted of the diphenylacetylene mentioned above and black, apparently polymeric solid.

Reaction of Triethylperfluorovinylsilane with Sodium Ethoxide. A. In Ethanol Solution.—Sodium (0.5 g., 0.022 g. atom) was dissolved in 5 g. of anhydrous ethanol. The resulting solution was cooled to 0° and 5.9 g. (0.03 mole) of triethylperfluorovinylsilane was added. The mixture was stirred and allowed to warm to room temperature. A vigorous reaction commenced and continued for a few minutes. After the mixture had been stirred for 16 hr. at room temperature, it was diluted with 50 ml. of pentane. Dry carbon dioxide was bubbled in to precipitate sodium carbonate. The mixture was filtered and the filtrate frac-

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(25) H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **77**, 5509 (1955).

(26) A. Bygdén, *Z. physik. Chem.*, **90**, 243 (1915).

tionally distilled. Triethylethoxysilane, b.p. 30° (3.8 mm.) to 32° (4.0 mm.), $n^{25}\text{D}$ 1.4111, was obtained in 69% yield (2.9 g.). Another distillation gave pure material.

Anal. Calcd. for $C_8H_{20}OSi$: C, 59.92; H, 12.57. Found: C, 59.94; H, 12.79.

A higher fraction, b.p. 47.5–49° (0.9–1.1 mm.); redistilled, b.p. 36.5° (0.4 mm.), $n^{25}\text{D}$ 1.4252; was identified as $(C_2H_5)_3SiCF{=}CFOC_2H_5$. This product was isolated in 28% yield (1.8 g.).

Anal. Calcd. for $C_{10}H_{20}OF_2Si$: C, 54.02; H, 9.07; F, 17.09. Found: C, 54.49; H, 9.59; F, 17.10.

B. **In Tetrahydrofuran Solution.**—A suspension of 0.03 mole of dry sodium ethoxide in 19 ml. THF was added to 5.9 g. (0.03 mole) of triethylperfluorovinylsilane in 20 ml. THF at 0°. The mixture was stirred at room temperature for 2 hr. and subsequently quenched by bubbling in dry gaseous carbon dioxide. The precipitate was filtered and the filtrate distilled to give 2.3 g. of triethylethoxysilane (48%), b.p. 39° (8 mm.) and 2.6 g. of $(C_2H_5)_3SiCF{=}CFOC_2H_5$ (39%), b.p. 48.5° (0.95 mm.), $n^{25}\text{D}$ 1.4252.

Anal. Found: C, 54.05; H, 9.37.

Reaction of Triethylperfluorovinylsilane with Sodium Trimethylsilylmethoxide.—Sodium trimethylsilylmethoxide was prepared by dissolving 0.7 g. (0.03 g. atom) of sodium in a mixture of 3.2 g. (0.03 mole) of trimethylsilylmethanol[27] and 20 ml. diethyl ether. To the resulting turbid solution was added 5.9 g. of triethylperfluorovinylsilane in 15 ml. of ether at a rate sufficient to maintain a gentle reflux. The solution was stirred for 3 hr. at room temperature and left to stand overnight. Filtration was followed by fractional distillation to give 1.7 g. of colorless liquid, b.p. 48–51° (1.9 mm.), $n^{25}\text{D}$ 1.4238, and 5.6 g. (66%) of $(C_2H_5)_3SiCF{=}CFOCH_2Si(CH_3)_3$, b.p. 70° (0.65 mm.), $n^{25}\text{D}$ 1.4362.

Anal. Calcd. for $C_{12}H_{26}OF_2Si_2$: C, 51.38; H, 9.34; F, 13.55. Found: C, 51.55; H, 9.62; F, 13.47.

The lower boiling fraction is believed to be an azeotropic mixture of $(C_2H_5)_3SiOCH_2Si(CH_3)_3$ and $(C_2H_5)_3SiCF{=}CFOCH_2Si(CH_3)_3$, since its infrared spectrum showed strong absorption in the C=C region.

Reaction of Triethylperfluorovinylsilane with Sodium *n*-Propylmercaptide and Sodium Thiophenolate.—To 3.0 g. (0.03 mole) of sodium *n*-propylmercaptide (prepared by dissolving sodium in the calculated amount of *n*-propylmercaptan) suspended in 20 ml. THF was added 5.9 g. of triethylperfluorovinylsilane. The resulting mixture was heated at reflux for 18 hr. under nitrogen. Pentane (25 ml.) was added, and the mixture was filtered. The filtrate was distilled to give 1.3 g. (22% recovery) of triethylperfluorovinylsilane, b.p. 36.5–37.5° (11–13 mm.), and 4.5 g. (76% yield based on unrecovered silane) of $(C_2H_5)_3SiCF{=}CFSC_3H_7$, b.p. 65° (0.35 mm.), $n^{25}\text{D}$ 1.4640.

Anal. Calcd. for $C_{11}H_{22}F_2SSi$: C, 52.34; H, 8.79; F, 15.06; S, 12.68. Found: C, 52.54; H, 8.91; F, 14.99; S, 12.30.

A similar reaction carried out on the same scale with sodium thiophenolate in THF suspension resulted in isolation of 7.5 g. (87%) of $(C_2H_5)_3SiCF{=}CFSC_6H_5$, b.p. 101.5° (0.3 mm.), $n^{25}\text{D}$ 1.5217.

Anal. Calcd. for $C_{14}H_{20}F_2SSi$: C, 58.70; H, 7.04; F, 13.27; S, 11.19. Found: C, 58.83; H, 7.23; F, 12.98; S, 11.11.

Nuclear Resonance Spectra.—F^{19} Nuclear resonance spectra were measured by Mr. L. F. Herrick at Harvard University using a Varian V-4300B NMR Spectrometer equipped with a superstabilizer, a sample spinner, and a Sanborn 151 Recorder, and operating at 56.4 Mc. The solid compounds, $(C_2H_5)_3SiCF{=}CFM(C_6H_5)_3$ (M = Si and Ge), were measured as a solution in benzene; in all other cases pure liquid samples were used which contained CCl_3F as the internal reference. Chemical shifts are reported to be accurate to 1%. The lines observed are reported in p.p.m. relative to the CCl_3F standard.

$(C_2H_5)_3SiCF{=}CFC_6H_5$: 152.4, 154.6, 163.8, 166.0 p.p.m.; J_{FF} 124 c.p.s.

$(C_2H_5)_3SiCF{=}CFC_4H_9$: 145.7, 147.9 (each with secondary splitting of 23 c.p.s.), 172.9, 175.1 p.p.m. (each with secondary splitting of 5.8 c.p.s.); J_{FF} 126 c.p.s.

$(C_2H_5)_3SiCF{=}CFCH_2CH{=}CH_2$: 141.7, 143.9 (each with secondary splitting of 23 c.p.s.), 168.4, 170.6 p.p.m. (each with secondary splitting of 6 c.p.s.); J_{FF} 126 c.p.s.

$(C_2H_5)_3SiCF{=}CFSi(C_6H_5)_3$: 152.7, 155.0, 159.1, 161.5 p.p.m.; J_{FF} 132 c.p.s.

$(C_2H_5)_3SiCF{=}CFGe(C_6H_5)_3$: 153.2, 155.7, 157.2, 159.7 p.p.m.; J_{FF} 144 c.p.s.

$(C_2H_5)_3SiCF{=}CFSC_3H_7$: 128.2, 130.8, 148.1, 150.6 p.p.m.; J_{FF} 147 c.p.s.

$(C_2H_5)_3SiCF{=}CFSC_6H_5$: 96, 96.5, 120, 120.5 p.p.m.; J_{FF}(*cis*) 20 c.p.s.; 126.0, 128.6, 143.0, 145.6 p.p.m.; J_{FF}(*trans*) 148 c.p.s.

$(C_2H_5)_3SiCF{=}CFOC_2H_5$: 117.1, 119.3, 193.0, 195.2 p.p.m.; J_{FF} 122 c.p.s.

$(C_2H_5)_3SiCF{=}CFOCH_2Si(CH_3)_3$: 118.3, 120.4, 192.1, 194.3 p.p.m.; J_{FF} 122 c.p.s.

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[27] Prepared according to D. Seyferth, *J. Am. Chem. Soc.*, **81**, 1844 (1959).