which are linearly related refer to pure solvents. From this it may be inferred that Y values (and correspondingly the Z and E_T values) as determined in binary solvent mixtures do not relate simply to any intrinsic property of the gross solvent mixture but must be influenced by the microscopic behavior of the two-component solvent mixture in the vicinity of the solute molecules resulting from localized heterogeneities, solvent sorting, and selective hydrogen bonding.

The Preparation and Reactions of Some Silanes Containing the Trifluorovinyl Group

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A series of silanes of the type $CF_2=CF(CH_2)_nSiX_3$ where $n = 0, 1, 2,$ and 3 and X = alkyl, pentafluorophenyl, hydrogen, or negative groups has been prepared. Some of their chemical properties have been determined.

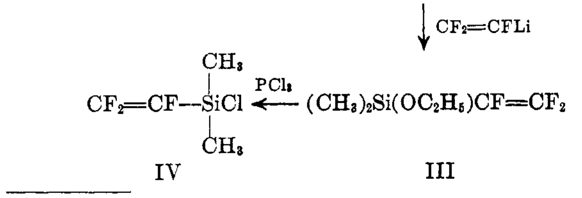
For a number of years interest in this laboratory has been focused on the preparation and reactions of fluoro olefins. As part of this continuing program it seemed desirable to synthesize and study the reactions of silanes containing the trifluorovinyl group separated from the silicon atom by varying numbers of methylene units.

The first trifluorovinylsilane was prepared by Knunyants,[1] who obtained $(CF_2=CF)_4Si$ as the reaction product of trifluorovinylmagnesium iodide and silicon tetrachloride. Seyferth[2,3] prepared $CF_2=CFSi(C_2H_5)_3$ by the Grignard method and $CF_2=CFSi(CH_3)_3$ by the reaction of trimethylchlorosilane with trifluorovinyllithium, which was prepared by treating trifluorovinyltin compounds with phenyllithium.

In our laboratory trifluorovinyltrimethylsilane (I) was prepared in 65% yield by a two-step reaction in which bromotrifluoroethylene reacted with methyllithium to give trifluorovinyllithium, which was allowed to react with trimethylchlorosilane.

An attempt was made to prepare trifluorovinyldimethylchlorosilane from the reaction of trifluorovinyllithium and dimethyldichlorosilane in a 1:1 molar ratio, but only bis(trifluorovinyl)dimethylsilane (II) was obtained. This experiment confirms the results of Knunyants in indicating the increased reactivity of the silicon–chlorine bond in silanes containing both this group and a trifluorovinyl group attached to silicon.

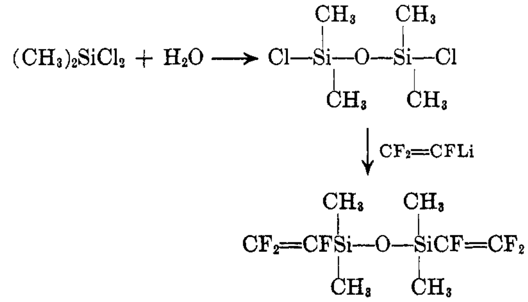
Alkoxysilanes undergo approximately the same reactions as chlorosilanes although they are somewhat less reactive; therefore, a synthetic procedure was devised which led to the formation of trifluorovinyldimethylchlorosilane by the scheme shown in eq 1. The compounds were identified by elemental analysis, MRD, and infrared spectra.



$$(CH_3)_2SiCl_2 + C_2H_5OH \xrightarrow{(C_5H_{11})_3N} (CH_3)_2SiCl(OC_2H_5) \xrightarrow{CF_2=CFLi} \underset{\text{III}}{(CH_3)_2Si(OC_2H_5)CF=CF_2} \xrightarrow{PCl_5} \underset{\text{IV}}{CF_2=CF-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}Cl} \quad (1)$$

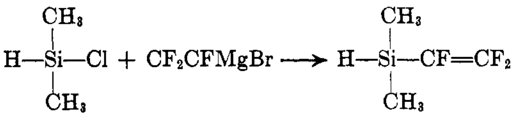
IV III

The *sym*-tetramethylbis(trifluorovinyl)disiloxane was prepared by the route shown in eq 2. Another compound of the series was prepared by allowing dimethylchlorosilane to react with trifluorovinylmagnesium bromide to give trifluorovinyldimethylsilane (eq 3).



$$(CH_3)_2SiCl_2 + H_2O \longrightarrow Cl-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-Cl \xrightarrow{CF_2=CFLi} CF_2=CF\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}CF=CF_2 \quad (2)$$

V



$$H-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-Cl + CF_2CFMgBr \longrightarrow H-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-CF=CF_2 \quad (3)$$

VI

Elemental analysis and infrared data were consistent with this structure. When trifluorovinyllithium was used instead of the Grignard reagent, a brown tar was obtained.

Pentafluorophenylmagnesium bromide was prepared and allowed to react with $CF_2=CFSi(CH_3)_2Cl$ to give the trifluorovinylpentafluorophenyldimethylsilane (VII). It was of some interest to determine whether one or both fluorine-containing groups would be cleaved by reaction with base. Consequently, a sample of the product was treated with alcoholic potassium hydroxide and a gas, presumably $CHF=CF_2$, was obtained. Examination of the liquid products showed that pentafluorobenzene had also been formed, thus indicating the cleavage of both groups.

A different approach was used to prepare $(CH_3)_3SiCH_2CF=CF_2$ (VIII). Earlier Tarrant and Warner[4] had shown that Grignard reagents reacted with fluoro olefins to give alkylated or arylated fluoro olefins while Dixon[5] reported that lithium reagents behaved in the same manner. With tetrafluoroethylene, lithium rea-

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[1] R. N. Sterlin, I. L. Knunyants, L. N. Pinkince, and R. D. Yatsenko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1492 (1959).

[2] D. Seyferth, K. A. Brandle, and G. Raab, *Angew. Chem.*, **72**, 77 (1960).

[3] D. Seyferth, D. E. Welch, and G. Raab, *J. Am. Chem. Soc.*, **84**, 4266 (1962).

[4] P. Tarrant and D. A. Warner, *ibid.*, **76**, 1624 (1954).

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

$$RMgX + CF_2{=}CX_2 \longrightarrow RCF{=}CX_2 + MgFX$$

$$RLi + CF_2{=}CX_2 \longrightarrow RCF{=}CX_2 + LiF$$

gents often give disubstituted products such as $RCF{=}CFR$. A Grignard reagent was prepared from trimethylchloromethylsilane and was treated with tetrafluoroethylene under a variety of conditions, but no 2,3,3-trifluoroallyltrimethylsilane was obtained. However, the desired compound was made by treating the corresponding lithium reagent with tetrafluoroethylene

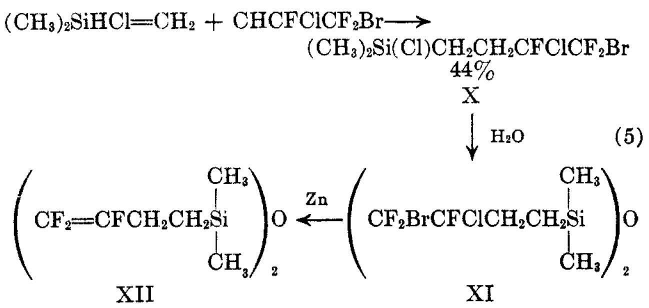
$$(CH_3)_3SiCH_2Li + CF_2{=}CF_2 \longrightarrow (CH_3)_3SiCH_2CF{=}CF_2$$

in a sealed tube at 0°. Elemental analysis and infrared data support the structure shown.

The preparation of the next member of the series, $(CH_3)_3SiCH_2CH_2CF{=}CF_2$ (IX), was adapted from a synthetic route used by Tarrant and Tomasino.[6] It is shown in eq 4. By carrying out a combined dehalogenation with zinc and reduction using zinc and hydrochloric acid, a 65% yield of the desired olefin was realized.

$$CF_2BrCFClBr + CH_2{=}CHSi(CH_3)_3 \longrightarrow CF_2BrCFClCH_2CHBrSi(CH_3)_3 \xrightarrow{C_2H_5OH-HCl-Zn} \underset{\text{IX}}{CF_2{=}CFCH_2CH_2Si(CH_3)_3} \quad (4)$$

The reaction of dimethylchlorosilane and $CH_2{=}CHCFClCF_2Br$ gave the corresponding adduct which was used to make the disiloxane as shown in eq 5.



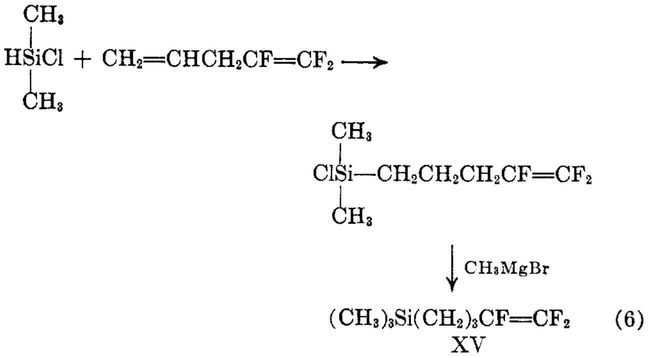
$$(CH_3)_2SiHCl{=}CH_2 + CHCFClCF_2Br \longrightarrow \underset{\text{X}}{\underset{44\%}{(CH_3)_2Si(Cl)CH_2CH_2CFClCF_2Br}} \xrightarrow{H_2O} \underset{\text{XI}}{\left(CF_2BrCFClCH_2CH_2\overset{CH_3}{\underset{CH_3}{Si}}\right)_2O} \xrightarrow{Zn} \underset{\text{XII}}{\left(CF_2{=}CFCH_2CH_2\overset{CH_3}{\underset{CH_3}{Si}}\right)_2O} \quad (5)$$

This compound had been prepared previously,[6] but the yields by the method described here are much greater. An attempt to prepare $CF_2{=}CFCH_2CH_2Si(CH_3)_2Cl$ directly by the addition of dimethylchlorosilane to 1,1,2-trifluorobutadiene in a sealed tube at 70° was unsuccessful, as an explosion occurred. The chloroplatinic acid initiated addition of methyldichlorosilane to $CH_2{=}CHCFClCF_2Br$ was carried out successfully to give the adduct $CF_2BrCFClCH_2CH_2Si(CH_3)Cl_2$ (XIII) in 71% yield.

The last member of the trimethyltrifluorovinylalkylsilanes prepared was $CF_2{=}CFCH_2CH_2CH_2Si(CH_3)_3$ (XV). It was made by the sequence shown in eq 6. Thus, dimethylchlorosilane shows the same preference for reaction with a hydrocarbon vinyl group rather than a trifluorovinyl group that is displayed by CCl_3Br which gives $CCl_3(CH_2)_3CF{=}CF_2$ as reported by Muramatsu and Tarrant.[7]

The chlorosilane XIV so formed was hydrolyzed to the corresponding disiloxane XVI.

Seyferth[8] has studied the reaction of nucleophilic



$$\overset{CH_3}{\underset{CH_3}{HSiCl}} + CH_2{=}CHCH_2CF{=}CF_2 \longrightarrow \overset{CH_3}{\underset{CH_3}{ClSi}}{-}CH_2CH_2CH_2CF{=}CF_2 \xrightarrow{CH_3MgBr} \underset{\text{XV}}{(CH_3)_3Si(CH_2)_3CF{=}CF_2} \quad (6)$$

reagents with trifluorovinyltriethylsilane, and found in general that the normal reactions of fluoro olefins containing the $CF_2{=}$ group occurred. An exception was the reaction with sodium ethoxide in ethanol, which led to the cleavage of the carbon–silicon bond predominantly.

Trifluorovinyltrimethylsilane was found to react in a similar manner with nucleophilic reagents. Several organolithium compounds were allowed to react with trifluorovinyltrimethylsilane, and the products obtained were further treated with base to produce 1,2-difluoro olefins. These results will be published in a subsequent paper.

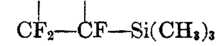
Surprisingly, $CF_2CFCH_2CH_2Si(CH_3)_3$ (XV) was found to be resistant to attack by certain nucleophilic reagents. No reaction occurred on refluxing with a mixture of sodium ethoxide in ethanol over a period of 20 hr or when the mixture was heated to 150° in a sealed tube for 12 hr. However, phenyllithium reacted with the olefin to give the substituted compound in good yield eq 7. The product was identified by elemental analysis and infrared spectroscopy.

$$C_6H_5Li + CF_2{=}CFCH_2CH_2Si(CH_3)_3 \longrightarrow \underset{\text{XVII}}{C_6H_5CF{=}CFCH_2CH_2Si(CH_3)_3} \quad (7)$$

It should be noted that other compounds containing the $CF_2{=}CFCH_2CH_2{-}$ group have been found to be resistant to attack by reagents which attack simpler fluoro olefins containing the $CF_2{=}$ group. For example, allylmagnesium bromide has been found to react with $CF_2{=}CF_2$, $CF_2{=}CFBr$, $CF_2{=}CFCl$, etc., but no reaction occurred with $CF_2{=}CFCH_2CH_2Br$.[9] These results suggest that 1,1,2-trifluoro olefins containing an electron-releasing group such as the alkyl group are not as susceptible to attack by nucleophiles as are such olefins containing electronegative groups.

Fluoroethylenes containing the $CF_2{=}$ group upon heating dimerize to cyclobutane derivatives. A study was made of this reaction with a number of the vinylsilanes prepared.

Trifluorovinyltrimethylsilane was heated for 2 days at 200° in a sealed tube to give a small amount of a product tentatively identified as the dimer by elemental analysis and infrared data. An attempt was made to obtain either a Diels–Alder adduct or a cyclobutane derivative with butadiene, but polymeric products were obtained.



XVIII

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[6] C. Tomasino, Ph.D. Dissertation, University of Florida, 1959.

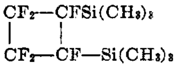
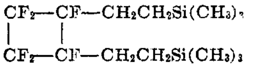
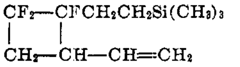
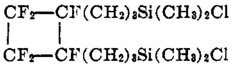
[7] H. Muramatsu and P. Tarrant, *J. Org. Chem.*, **29**, 1796 (1964).

[8] D. Seyferth and T. Wada, *Inorg. Chem.*, **1**, 78 (1962).

[9] P. Tarrant and J. Heyes, *J. Org. Chem.*, **30**, 1485 (1965).

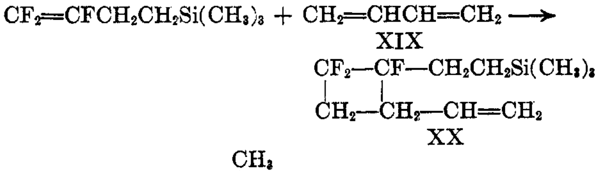
Table I

Physical Properties and Analyses of Compounds Prepared

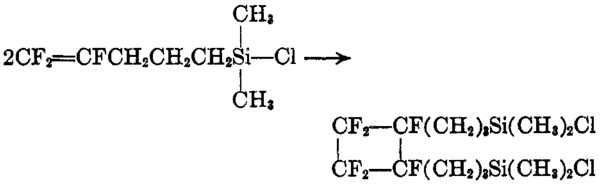
Compd	Structure	Yield, %	Bp, °C (mm)	n^{20}_D	d^{20}_{20}	Calcd % C	Calcd % H	Calcd % F	Calcd MR_D[a]	Found % C	Found % H	Found % F	Found MR_D
I	$CF_2{=}CFSi(CH_3)_3$	65	67[b]	1.3580	0.983								
II	$(CF_2{=}CF)_2Si(CH_3)_2$	56	98	1.3633	1.272	32.73	2.74	51.77	38.3	32.43	2.97	51.48	38.5
III	$CF_2{=}CFSi(CH_3)_2(OC_2H_5)$	50	104	1.3642	1.028	39.12	6.02	30.94	39.9	38.90	6.26	31.05	40.3
IV	$CF_2{=}CFSi(CH_3)_2Cl$	55	87	1.3764	1.154	27.51	3.46	32.64	34.2	27.74	3.68	32.81	34.7
V	$[CF_2{=}CFSi(CH_3)_2]_2O$	50	54 (20)	1.3691	1.136	32.60	4.11	38.72	57.4	32.54	4.23	38.46	58.3
VI	$CF_2{=}CFSi(CH_3)_2H$	25	50	1.3513	0.976	34.26	5.03	40.65	30.2	34.55	5.28	40.29	30.9
VII	$CF_2{=}CFSi(CH_3)_2C_6F_5$	57	89 (20)	1.4214	0.976	38.22	1.97	49.64	...	38.45	2.18	49.40	...
VIII	$CF_2{=}CFCH_2Si(CH_3)_3$	42	89	1.3745	0.949	42.84	6.59	33.89	39.2	43.16	6.61	33.49	40.4
IX	$CF_2{=}CFCH_2CH_2Si(CH_3)_3$	75	112–114[c]	1.3808	0.962								
X	$CF_2BrCFClCH_2Si(CH_3)_2$	44	205	1.4400	1.513	22.65	3.16	17.91	56.4	22.69	3.57	18.97	56.0
XI	$[CF_2BrCFClCH_2CH_2Si(CH_3)_2]_2O$	82	125 (1)	1.4345	1.4712	24.78	3.47	19.62	101.9	24.93	3.52	19.74	102.7
XII	$[CF_2{=}CFCH_2CH_2Si(CH_3)_2]_2O$	42	95 (6)[d]	1.3932	1.085								
XIII	$CF_2BrCFClCH_2CH_2Si(CH_3)Cl_2$	71	220	1.4451	1.6076	17.74	2.08	16.84	56.1	17.92	2.23	17.07	56.0
XIV	$CF_2{=}CFCH_2CH_2CH_2Si(CH_3)_2Cl$	85	163	1.4046	1.116	38.79	5.58	26.30	48.0	38.85	5.55	26.16	47.6
XV	$CF_2{=}CFCH_2CH_2CH_2Si(CH_3)_3$	85	136	1.3885	0.959	48.94	7.73	29.04	48.4	48.71	17.52	28.77	48.3
XVI	$[CF_2{=}CFCH_2CH_2CH_2Si(CH_3)_2]_2O$	88	117 (10)	1.4016	1.078	44.42	6.40	30.12	85.2	44.60	6.43	30.31	85.6
XVII	$C_6H_5CF{=}CFCH_2CH_2Si(CH_3)_3$	69	90 (2)	1.4990	1.007	64.93	7.56	15.82		65.01	7.67	15.82	
XVIII		4	96 (24)			38.94	4.88	36.96		39.19	6.07	37.22	
XIX		33	70 (0.8)	1.4059	1.069	46.12	7.19	31.26	84.3	46.31	7.19	31.52	83.9
XX						55.85	8.11			56.87	8.11		
XXI		42	145 (5) Mp 53–56			38.79	5.58	26.30		39.65	5.58	27.07	
XXII	$CF_2ClCFNO(CH_2)_2Si(CH_3)$					33.89	5.29			33.76	5.43		

[a] Bond refractions according to E. L. Warrick, *J. Am. Chem. Soc.*, **68,** 2455 (1946). [b] Lit.[3] bp 65°, n^{25}_D 1.3569, λ 5.83 μ. [c] Lit.[6] bp 114°, n^{23}_D 1.3790. [d] Lit.[6] 95° (6 mm), n^{20}_D 1.3975.

Heating $CF_2{=}CFCH_2CH_2Si(CH_3)_3$ for 2 days at 200° gave a 33% yield of the cyclic dimer XIX which was identified by elemental analysis and infrared and nmr spectra. Furthermore, the unsaturated silane reacted with butadiene to give a vinylcyclobutane derivative (eq 8). The thermal dimerization of a pentenyl derivative occurred in 42% yield (eq 9).



(8)



(9)

XXI

It was also found that nitrosyl chloride reacted with $CF_2{=}CFCH_2CH_2Si(CH_3)_3$ to give a nitroso compound with a characteristic deep blue color. It was separated by passage of a pentane solution through an alumina column, and the material from the passage of the narrow blue band through the column was collected after evaporation of the pentane. The product

$$CF_2{=}CFCH_2CH_2Si(CH_3)_3 + NOCl \longrightarrow \underset{\text{XXII}}{CF_2ClCF(NO)CH_2CH_2Si(CH_3)_3}$$

was tentatively identified by elemental analysis and nmr data. Nitrosyl chloride is known to add chlorine preferentially to the CF_2 end of a double bond with the NO going to the other carbon atom.

The infrared spectra of compounds containing the trifluorovinyl group attached directly to silicon show an absorption peak associated with the double bond at 5.83 μ. The same group attached to carbon, hydrogen, bromine, or chlorine absorbs between 5.5 and 5.6 μ. Triphenyltrifluorovinyltin, prepared in this laboratory, absorbs at 5.88 μ, while tris(trifluorovinyl)boron absorbs at 5.95 μ. All of the metal compounds mentioned have empty p or d orbitals which are perhaps responsible for the large shift from the usual absorption frequency. Stone, *et al.*,[10] use this shift as evidence of carbon–boron π bonding.

The infrared absorption for the double bond in $CF_2{=}CFCH_2Si(CH_3)_3$ was also found to be 5.57 μ, which would again indicate that the d orbitals on the silicon do not significantly affect the trifluorovinyl group in this case. The double bond absorption for $CF_2{=}CFCH_2CH_2Si(CH_3)_2Cl$ occurred at 5.52 μ, indicating a normal trifluorovinyl group.

Experimental Section[11]

Trifluorovinyllithium.—Methyllithium was prepared by the reaction of methyl bromide with freshly cut lithium chips in enough ethyl ether to make an approximately 1 *M* solution. The solution was then cooled to −78° in a Dry Ice–acetone bath and a slight excess of bromotrifluoroethylene (previously condensed in a cold trap) was bubbled into the solution. The solution turned dark blue after about 30 min. Stirring was continued for about 2 hr to allow completion of the exchange reaction before the chlorosilane was added.

Trifluorovinyltrimethylsilane (I).—Trimethylchlorosilane (28 g, 0.26 mole) was added dropwise to a stirred solution of the trifluorovinyllithium (0.26 mole) in ethyl ether at −78°. The reaction mixture was allowed to come to room temperature slowly. The mixture was then hydrolyzed with water, and the ethereal solution was separated and dried over calcium chloride. Distillation gave I (26 g, 65%), the properties and analysis of which are given in Table I.

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(10) T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.*, 3103 (1961).

(11) Analyses were by Galbraith Laboratories, Knoxville, Tenn.

Bis(trifluorovinyl)dimethylsilane (II).—Trifluorovinyllithium (1.0 mole) in ether at −78° was added to dichlorodimethylsilane (65 g, 0.5 mole) at −78°. The mixture was allowed to come to room temperature. The lithium chloride was filtered and the filtrate was distilled. The only product, in addition to recovered dichlorodimethylsilane, was II (30.5 g, 56%).

Trifluorovinyldimethylethoxysilane (III).—Dimethylchloroethoxysilane was prepared by adding dropwise 1 mole of absolute ethanol to 1 mole of dimethyldichlorosilane in triamylamine with stirring. Fractional distillation gave a yield of *ca.* 50% of the desired product with small amounts of the dichloro and diethoxy compounds as impurities.

Dimethylchloroethoxysilane (30 g, 0.22 mole) was slowly added to a stirred solution of trifluorovinyllithium (0.22 mole) at −78°. The mixture was allowed to come to room temperature slowly. The lithium chloride was filtered, and the remaining solution was distilled to give III (20 g, 50%).

Trifluorovinyldimethylchlorosilane (IV).—Trifluorovinyldimethylethoxysilane (III) (15 g, 0.085 mole) was slowly added to PCl_3 (6.1 g, 0.045 mole) at 0° with stirring. Stirring was continued for 5 hr and the solution was distilled, yielding IV (8.1 g, 55%).

***sym*-Tetramethylbis(trifluorovinyl)disiloxane** (V).—*sym*-Tetramethyldichlorodisiloxane was prepared by adding water in dioxane slowly to a solution of dichlorodimethylsilane in ether in the manner described by Patnode and Wilcox.[12] The product (11.5 g, 0.056 mole) was then added to a stirred solution of trifluorovinyllithium (0.12 mole) at −78°. The mixture was allowed to come to room temperature, water was added, and the organic layer was separated and dried. Distillation yielded V (8.3 g, 50%).

Trifluorovinyldimethylsilane (VI).—Bromotrifluoroethylene was bubbled into tetrahydrofuran (THF) (120 ml) and magnesium (5 g, 0.2 g-atom). When the reaction had started, the mixture was cooled in an ice–water bath, and dimethylchlorosilane (17 g, 0.2 mole) was added. Bromotrifluoroethylene was added slowly until most of the magnesium had disappeared. A fraction with a boiling range of 40–63° was distilled from the mixture. This fraction was washed twice with cold water and dried over calcium chloride. Distillation yielded VI (7.0 g, 25%).

Pentafluorophenyltrifluorovinyldimethylsilane (VII).—Pentafluorophenylmagnesium bromide was prepared in ether from bromopentafluorobenzene (10 g, 0.04 mole). The mixture was filtered and the solution was added dropwise to trifluorovinyldimethylchlorosilane IV (7.1 g, 0.04 mole) in ether. The mixture was refluxed 4 hr, then hydrolyzed. The ether layer was dried and distillation yielded VII (7.2 g, 57%).

2,3,3-Trifluoroallyltrimethylsilane (VIII).—Bromomethyltrimethylsilane (8.4 g, 0.05 mole) was allowed to react with an excess of dispersed lithium in ether (50 ml). Excess lithium was filtered off. The filtrate and tetrafluoroethylene (6 g, 0.06 mole) were kept in a 100-ml evacuated thick-walled glass tube at 0° for 16 hr and at room temperature for 12 hr. The volatile products were condensed out under reduced pressure and distilled to give VIII (3.6 g, 42%).

(3,4,4-Trifluoro-3-butenyl)trimethylsilane (IX).—A stirred mixture of isopropyl alcohol (200 ml) and zinc dust (130 g, 2 g-atoms) was heated to reflux. (1,4-Dibromo-3-chloro-3,4,4-trifluorobutyl)trimethylsilane (188 g, 0.50 mole) was added at a rate to maintain reflux without further heating. The mixture was refluxed for an additional 1 hr, and on cooling hydrochloric acid (100 ml, 38%) was added slowly. Upon completion of the reaction, the mixture was filtered to remove the zinc. Water and ether were added to the two-phase system. The ethereal solution was washed twice more with water and dried over $CaCl_2$. Distillation yielded IX (68.5 g, 75%): lit.[6] bp 114°, n^{23}_{D} 1.3790.

(3,4,4-Trifluoro-3-chloro-4-bromobutyl)dimethylchlorosilane (X).—A solution of dimethylchlorosilane (25 g, 0.37 mole), 3,4,4-trifluoro-3-chloro-4-bromo-1-butene (57 g, 0.26 mole), and a 1 *M* solution of H_2PtCl_6 in isopropyl alcohol (0.5 ml) was refluxed for 24 hr. Distillation of the two products gave dimethyldichlorosilane (11 g) and X (35.8 g, 44%).

1,3-Bis(3,4,4-trifluoro-3-chloro-4-bromobutyl)-1,1,3,3-tetramethyldisiloxane (XI).—(3,3,4-Trifluoro-3-chloro-4-bromobutyl)-dimethylchlorosilane (36 g, 0.11 mole) and water (25 ml) were heated with stirring for 16 hr. The organic layer was separated and dried over $CaCl_2$. Distillation yielded XI (23 g, 82%).

1,3-Bis(3,4,4-trifluoro-3-butenyl)-1,1,3,3-tetramethyldisiloxane (XII).—XI (22 g, 0.045 mole) was slowly added to a refluxing mixture of zinc (10 g) in isopropyl alcohol. Water was added and the product was extracted with ether. The ethereal solution was washed twice and dried over $CaCl_2$. Distillation yielded XII (6.8 g, 42%).

(3,4,4-Trifluoro-3-chloro-4-bromobutyl)methyldichlorosilane (XIII).—A solution of methyldichlorosilane (23 g, 0.020 mole), 3,4,4-trifluoro-3-chloro-4-bromo-1-butene (40 g, 0.18 mole), and 1 *M* H_2PtCl_6 solution in isopropyl alcohol (0.5 ml) was refluxed for 24 hr. Distillation gave XIII (45 g, 71%).

(4,5,5-Trifluoro-4-pentenyl)dimethylchlorosilane (XIV).—1,1,2-Trifluoro-1,4-pentadiene (50 g, 0.41 mole), prepared by the method of Tarrant and Gilman,[13] was sealed in a thick-walled glass tube with dimethylchlorosilane (40 g, 0.42 mole) and 1 *M* H_2PtCl_6 solution in isopropyl alcohol (0.5 ml). The tube was heated at 75° for 16 hr. Distillation of products yielded XIV (75 g, 85%).

(4,5,5-Trifluoro-4-pentenyl)trimethylsilane (XV).—XIV (34.5 g, 0.16 mole) was added slowly to CH_3MgBr (*ca.* 0.2 mole) in ether (150 ml) with cooling. The resulting mixture was hydrolyzed with water, and the ethereal solution was separated and dried over calcium chloride. Distillation yielded XV (26 g, 85%).

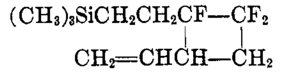
1,3-Bis(4,5,5-trifluoro-4-pentenyl)-1,1,3,3-tetramethyldisiloxane (XVI).—XIV (16 g, 0.074 mole) was heated overnight with stirring in 20 ml of water. The organic layer was extracted with ether and dried over calcium chloride. Distillation yielded XVI (12 g, 88%).

(4-Phenyl-3,4-difluoro-3-butenyl)trimethylsilane (XVII).—IX (9.1 g, 0.05 mole) was slowly added to a solution containing phenyllithium (0.05 mole) in ether. The mixture was stirred for 2 hr and hydrolyzed, and the organic layer was dried. Distillation gave XVII (8.3 g, 69%).

Dimerization of I.—I (7.0 g, 0.045 moles) was sealed in a glass tube and heated to 200° for 2 days. Considerable decomposition was evident but distillation gave XVIII (0.25 g, 3.8%).

Thermal Dimerization of IX.—IX (25 g, 0.14 mole) and hydroquinone (*ca.* 0.2 g) were heated at 210° for 47 hr. Distillation of the reaction mixture yielded the dimer XIX (8 g, 33%).

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



XX

Infrared analysis showed a vinyl group to be present. Butadiene is known to react with $CF_2{=}CFX$ compounds to give products with the CH_2 group adjacent to the CF_2 group.

Thermal Dimerization of (4,5,5-Trifluoro-4-pentenyl)dimethylchlorosilane (XXI).—XIV (25 g, 0.12 mole) was heated in a sealed tube at 200° for 48 hr. Distillation yielded XXI (10 g, 42%).

Reaction of IX with NOCl (XXII).—Nitroyl chloride was bubbled into a mixture of dimethylformamide (DMF) (160 ml), $AlCl_3$ (11 g, 0.082 mole), and IX (11 g, 0.06 mole) until no further reaction was obvious. (The reaction was exothermic.) The solution was extracted with *n*-pentane, and the pentane layer, containing the blue product, was passed through an alumina (acid) column. The blue material was collected and the pentane was evaporated under vacuum. A deep blue product, tentatively identified as $(CH_3)_3SiCH_2CH_2C(NO)FCF_2Cl$ (XXII), was obtained.

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