Anal. Calcd. for $C_{50}H_{41}NO_2SSi_2$: Si, 7.21. Found: Si, 6.09, 6.14. An attempt to prepare this material by the reaction of triphenylchlorosilane with 3,7-dilithio-10-ethylphenothiazine-5,5-dioxide gave essentially the same results.

Reaction of triphenylsilyllithium with 3,7-dichloro 10-ethylphenothiazine-5,5-dioxide in ether gave a 44.2% yield of hexaphenyldisilane and 17.5% yield of coupled product, slightly impure, m.p. 270–275°.

4-Triphenylsilyl-10-ethylphenothiazine. Triphenylsilyllithium (0.0135 mole) was added cautiously to 5 g. (0.0135 mole) of 4-iodo-10-ethylphenothiazine[30] in 50 ml. of ether over a period of 1 hr. Color Test I was strongly positive after the addition was completed. After stirring for 24 hr., Color Test I was negative. Subsequent to hydrolysis, 1.8 g. (46.3%) of hexaphenyldisilane, m.p. 358–360°, was separated by filtration.

The yellow organic layer was separated, dried, and the solvents were removed to leave a viscous light yellow oil. Chromatographing on alumina of the yellow oil obtained subsequent to evaporation of the organic layer gave 2.3 g. (46%) of recovered starting material, identified by the method of mixture melting points; and 0.5 g. (14.8%) of 4-triphenylsilyl-10-ethylphenothiazine, m.p. 164–166°. Recrystallization from ethanol raised the melting point to 166.5–168°. The infrared spectrum showed the presence of the silicon-phenyl absorption band and 1,2,3-trisubstitution.

Anal. Calcd. for $C_{32}H_{27}NSSi$: Si, 5.78. Found: Si, 5.88, 5.98.

Acknowledgment. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa State University, and special acknowledgment is made to Dr. V. A. Fassel and Mr. R. Kniseley for the spectra.

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Fluoroalkyl- and 3-(Fluoroalkoxy)propylpolysiloxanes

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The synthesis of seven fluoroalkyl- and 3-(fluoroalkoxy)propylpolysiloxanes is reported. The intermediates obtained were also characterized. An attempt to synthesize β-cyanoethylpolysiloxane was not successful.

This paper describes a convenient laboratory method for the preparation of fluoroalkyl- and 3-(fluoroalkoxy)propylpolysiloxanes.

Fluoroalkylpolysiloxanes have been prepared previously by alternate routes. Holbrook[1] obtained small yields of 1H,1H,2H,2H-perfluoroalkyldichlorosilanes by heating 1H,1H,2H-perfluoro-1-alkenes with dichlorosilane in an autoclave at 250°. Extensive disproportionation of the dichlorosilane was observed. Hydrolysis of the fluoroalkyldichlorosilanes gave the corresponding fluoroalkylpolysiloxanes. Geyer *et al.*[2] reported the addition of 3,3,3-trifluoropropene to dichlorosilane using ultraviolet light to yield 3,3,3-trifluoropropyldichlorosilane which would give 3,3,3-trifluoropropylpolysiloxane on hydrolysis. The above addition was slow and gave only a moderate yield. Dichlorosilane is difficult to obtain and hard to handle in large quantities.

RESULTS AND DISCUSSION

The general synthetic method is given below:

$$\begin{matrix} R_fCH{=}CH_2 \\ \text{or} \\ R_fOCH_2CH{=}CH_2 \end{matrix} + HSiCl_3 \xrightarrow{H_2PtCl_6}$$

$$—CH_2CH_2SiCl_3 \xrightarrow[\text{ether or THF}]{LiAlH_4} —CH_2CH_2SiH_3 \xrightarrow[2\ C_2H_5OH]{H_2PtCl_6}$$

$$—CH_2CH_2Si(H)(OC_2H_5)_2 \xrightarrow{0.01N\ HCl}$$

$$[—CH_2CH_2Si(H)O]_n \quad R_f = \text{fluoroalkyl}$$

The allyl αH,αH,ωH-perfluoroalkyl ethers and the allyl αH,αH-perfluoroalkyl ethers have not been previously reported. They were synthesized by three variations of the Williamson ether synthesis: (1) addition of the allyl halogenide to the sodium fluoroalkoxide in dimethyl carbitol followed by distillation of the allyl fluoroalkyl ether directly from the reaction mixture; (2) addition of the allyl halogenide to the sodium fluoroalkoxide in ether followed by hydrolysis; (3) refluxing a mixture of allyl bromide, the fluoro alcohol and anhydrous potassium carbonate in a ketone solvent followed by hydrolysis.

In general, the yields of the allyl fluoroalkyl ethers (21–67%) were lower than would be expected for two reasons. The boiling points of the starting alcohols and the ethers are very close, particularly in the first member of each series (allyl 2,2,2-trifluoroethyl ether and allyl 2,2,3,3-tetrafluoropropyl ether). To prepare these two ethers in a pure state, it was necessary to use Method 1 in which the unchanged alcohol remains in the flask as the sodium salt. With the long chain fluoro alcohols, preparation of the sodium salt was difficult and heating caused decomposition.[3,4]

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(1) G. W. Holbrook, private communication.

(2) A. M. Geyer, R. N. Haszeldine, K. Leedham, and R. J. Marklow, *J. Chem. Soc.*, 4472 (1957).

(3) E. J. P. Fear, J. Thrower, and J. Veitch, *J. Chem. Soc.*, 1322 (1958).

(4) E. T. McBee, C. R. Roberts, and G. W. Wilson, Jr., *J. Am. Chem. Soc.*, **80**, 1721 (1958).

In these cases Method 3 was generally superior.

Anhydrous potassium carbonate has been widely used as the condensing agent in the Williamson ether synthesis to prepare alkyl aryl ethers where phenols are used. It was found that potassium carbonate is an effective condensing agent in preparing allyl fluoroalkyl ethers with the more acidic fluoro alcohols.

Trichlorosilane was added to 3,3,3-trifluoropropene according to the method of Pierce[5] to produce both 3,3,3-trifluoropropyltrichlorosilane and 2-(trifluoromethyl) - 5,5,5 - trifluoropentyltrichlorosilane.

Trichlorosilane and methyldichlorosilane readily added to the allyl fluoroalkyl ethers in the presence of chloroplatinic acid at 80–100° (Table II). Addition of the silyl group was terminal as shown by the NMR spectra of two of the ethers. The H^1 spectra of 3-(2,2,2-trifluoroethoxy)propylmethyldichlorosilane and 3-(1H,1H-heptafluorobutoxy)propylmethyldichlorosilane showed a triplet for the $—OCH_2^*—CH_2—$ group. If addition was not terminal, a doublet would be expected from the $—OCH_2^*—CH(CH_3)—$ group. The remaining H^1 peaks and the F^{19} spectra were consistent with the structural assignments. A. D. Petrov *et al.*[6] reported terminal addition of various silanes to allyl 1,1,2,2-tetrafluoroethyl ether and gave a proof of structure.

The 3-(fluoroalkoxy)propyltrichlorosilanes and fluoroalkyltrichlorosilanes were reduced with lithium aluminum hydride in ether to the corresponding silanes. With 3,3,3-trifluoropropyltrichlorosilane it was necessary to use a different solvent, tetrahydrofuran, since the boiling points of 3,3,3-trifluoropropylsilane (32°) is very close to the boiling point of ether.

β-Trichlorosilylpropionitrile[7] was also included in this study. This material was reduced using a reversed lithium aluminum hydride reduction after the method of Steward.[8] A reversed addition with an equivalent amount of lithium aluminum hydride was necessary since the cyano group can also be reduced. A 39% yield of β-silylpropionitrile was obtained.

The 3-(fluoroalkoxy)propylsilanes, fluoroalkylsilanes and β-silylpropionitrile were converted to the corresponding diethoxysilanes using a variation of the reaction reported by Barnes and Schweitzer.[9] Addition of two equivalents of ethanol to the silanes dissolved in ether with a catalytic amount of chloroplatinic acid gave only the diethoxysilanes (64–84%) except with β-silylpropionitrile where two products were obtained—β-diethoxysilylpropionitrile (39%) and β-triethoxysilylpropionitrile (28%).

An attempt to prepare 3,3,3-trifluoropropyldiethoxysilane by addition of two equivalents of ethanol containing a catalytic amount of sodium ethoxide to 3,3,3-trifluoropropylsilane gave only 3,3,3-trifluoropropyltriethoxysilane and unchanged starting material.

Hydrolysis of the diethoxysilanes with 0.01*N* hydrochloric acid gave the corresponding polysiloxanes, $[RSi(H)O]_n$, with the exception of β-diethoxysilylpropionitrile. The 3-(fluoroalkoxy)-propylpolysiloxanes and fluoroalkylpolysiloxanes are colorless viscous fluids except 3-(1H,1H,11H-eicosylfluoroalkoxy)propylpolysiloxane which is a crystalline solid (m.p. 91–110°). The infrared spectrum of 3,3,3-trifluoropropylpolysiloxane shows a strong absorption band at 9.13 μ indicating a cyclic siloxane structure, a medium Si—H stretching band at 4.59 μ, and four C—F stretching bands, 7.61 μ (m), 7.91 μ (s), 8.25 μ (s), 8.79 μ (s). The C—F absorption band at 7.91 μ also includes the C—Si band. No Si—O—C or Si—OH structure was detected. No attempt was made to separate the various isomeric polysiloxanes.

Hydrolysis of β-diethoxysilylpropionitrile with 0.01*N* hydrochloric acid resulted in hydrogen evolution. The product isolated was β-cyanoethylsilsesquioxane with a few β-cyanoethylsiloxy units incorporated in the structure.

EXPERIMENTAL

Starting materials. The αH,αH,ωH-perfluoro alcohols [$H(CF_2CF_2)_nCH_2OH$; $n = 1, 2, 3$, and 5] were obtained from the E. I. du Pont de Nemours & Co. 2,2,2-Trifluoroethanol, 1H,1H-heptafluorobutan-1-ol and perfluorooctanoic acid were obtained from the Minnesota Mining and Manufacturing Co. 3,3,3-Trifluoropropyltrichlorosilane[10] and 2-(trifluoromethyl)-5,5,5-trifluoropentyltrichlorosilane were prepared by the method of Pierce.[5] β-Trichlorosilylpropionitrile[7] was available in research quantities in this laboratory.

1H,1H-Pentadecafluorooctan-1-ol. Ethyl perfluorooctanoate,[11] b.p. 62–63° (8 mm.), n_D^{25} 1.3093, d_4^{25} 1.623, was prepared in an 83% yield by esterification of perfluorooctanoic acid with ethanol using a sulfuric acid catalyst. Reduction with lithium aluminum hydride in ether gave 1H,1H-pentadecafluorooctan-1-ol,[12] b.p. 68.5° (8 mm.), an 89% yield.

Preparation of the allyl fluoroalkyl ethers. A detailed description of each general method used is described below using a typical example.

a. *Method 1.* Sodium (23 g., 1.0 g.-atom) was added in small pieces to 2,2,2-trifluoroethanol (100 g., 1.0 mole) dissolved in dimethyl carbitol (250 ml.). In order to obtain complete reaction, the mixture was heated until the sodium melted. After complete reaction, allyl chloride (115 g., 1.5 moles) was added dropwise, and the mixture was stirred for

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(5) O. R. Pierce, U. S. Patent 2,894,969 (1959).

(6) A. D. Petrov, V. A. Ponomarenko, G. V. Odabashyan, and S. I. Krokhmalev, *Doklady Akad. Nauk S.S.S.R.*, **124**, 838 (1959).

(7) J. C. Saam and J. L. Speier, *J. Org. Chem.*, **24**, 427 (1959).

(8) O. W. Steward, Ph.D. Thesis, The Pennsylvania State University, 1957, pp. 132–4; *Dissertation Abstr.*, **17**, 2827 (1957).

(9) G. H. Barnes, Jr. and G. W. Schweitzer, Fr. Patent **1,209,131** (1959).

(10) P. Tarrant, G. W. Dyckes, R. Dunmire, and G. B. Butler, *J. Am. Chem. Soc.*, **79**, 6536 (1957).

(11) E. Bergman, *J. Org. Chem.*, **23**, 476 (1958).

(12) R. Filler, J. V. Fenner, C. S. Stokes, J. F. O'Brien, and M. Hauptschein, *J. Am. Chem. Soc.*, **75**, 2693 (1953).

TABLE I

ALLYL FLUOROALKYL ETHERS

$ROCH_2CH{=}CH_2$		Yield,					Carbon, %		Fluorine, %		MR$_D$	
R	Method	%	B.P.	Mm.	n_D^{25}	d_4^{25}	Calcd.	Found	Calcd.	Found	Calcd.	Found
CF_3CH_2	1	66	75.5	746	1.3352	1.089	42.9	42.2	40.7	41.2	26.7	26.6
$CF_3(CF_2)_2CH_2$	2	67	105.5	747	1.3205	1.310	35.0	35.0	55.4	55.4	36.05	36.4
	3	52	106	741	1.3206							
$CF_3(CF_2)_6CH_2$	3	37	178	745	1.3202	1.561	30.0	30.2	64.7	63.9	54.8	56.0
$H(CF_2)_2CH_2$	1	43	110	740	1.3471	1.183	41.9	42.0	44.2	44.3	31.3	31.1
$H(CF_2)_4CH_2$	1	21	150–151	749	1.3392	1.392	35.3	35.7	55.9	55.9	40.7	40.9
$H(CF_2)_6CH_2$	2	24	90.6	25	1.3341	1.515	32.3	32.3	61.3	61.4	50.1	50.7
$H(CF_2)_{10}CH_2$	3	25	105[b]	4.5	1.3306	1.659	29.4	29.4	66.4	66.9	68.85	70.5
	3[a]	35	104[c]	4	1.3306							

[a] Methyl isobutyl ketone was used as the solvent. [b] White needles, m.p. 23.5–24.5°. [c] White needles, m.p. 23.0–24.5°.

TABLE II

3-(FLUOROALKOXY)PROPYLCHLOROSILANES

$RO(CH_2)_3Si(X)Cl_2$		Yield,					Chlorine, %		Silicon, %		MR$_D$	
R	X	%	B.P.	Mm.	n_D^{25}	d_4^{26}	Calcd.	Found	Calcd.	Found	Calcd.	Found
CF_3CH_2	CH_3	69	92	23	1.4010	1.231	11.0	11.3	27.8	27.5	49.9	50.3
$CF_3(CF_2)_2CH_2$	CH_3	67	96	14	1.3766	1.358	20.0	20.6	7.9	8.0	59.3	60.0
$CF_3(CF_2)_2CH_2$	Cl	72	112	32	1.3790	1.459	28.3	28.5	7.5	7.6	58.9	59.5
$CF_3(CF_2)_6CH_2$	Cl	66	125	7.5	1.3613	1.609	18.5	18.2	4.9	5.3	77.7	79.2
$H(CF_2)_{10}CH_2$	Cl	54	143–145	2[a]			15.0	14.8				

[a] M.p. 29–30° in a sealed tube.

20 hr. at approximately 80°. The reaction mixture was filtered and the filtrate was placed in a distillation flask. The material boiling below dimethyl carbitol (160°) was removed by distillation under reduced pressure. Fractional distillation of the distillate gave allyl 2,2,2-trifluoroethyl ether (92.2 g., 0.66 mole), in a 66% yield.

b. *Method 2.* Sodium (92 g., 4.0 g.-atoms) was added in small pieces to 1H,1H-heptafluorobutan-1-ol (800 g., 4.0 moles) dissolved in anhydrous ether (1 l.). The mixture was refluxed until all of the sodium reacted. Allyl bromide (455 g., 4.5 moles) was added dropwise, and the mixture was refluxed for 16 hr. The reaction mixture was hydrolyzed by pouring onto cracked ice, and the ether layer was dried over anhydrous calcium sulfate. The mixture was filtered, and the filtrate was placed in a distillation flask. The ethyl ether was removed through a Vigreux column. Fractional distillation of the remaining material gave a mixture of 1H, 1H-heptafluorobutan-1-ol and allyl 1H,1H-heptafluorobutyl ether (132 g.), b.p. 95–105° (745 mm.), and the desired product allyl 1H,1H-heptafluorobutyl ether (648 g., 2.7 moles), in a 67% yield.

c. *Method 3.* A mixture of 1H,1H-heptafluorobutan-1-ol (200 g., 1.0 mole), acetone (200 ml.), anhydrous potassium carbonate (152 g., 1.1 moles), and allyl bromide (121 g., 1.2 moles) was refluxed for 3 days. The mixture was filtered to remove the salts, and the acetone was removed through a Vigreux column. The residue was washed with water, and benzene (50 ml.) was added. Any remaining water was removed via the benzene-water azeotrope. Fractional distillation of the remaining material gave allyl 1H,1H-heptafluorobutyl ether (125 g., 0.52 mole) in a 52% yield.

Addition of trichlorosilane and methyldichlorosilane to the allyl fluoroalkyl ethers. The procedure given below is typical of the method used. Allyl 1H,1H-heptafluorobutyl ether (110 g., 0.46 mole) and chloroplatinic acid dissolved in dimethyl carbitol, 0.00122 g. of platinum/ml. (0.3 ml.), were heated to 90°, and trichlorosilane (81.2 g., 0.60 mole) was slowly added as the reaction proceeded. After all of the trichlorosilane was added the mixture was refluxed for 8 hr. The excess trichlorosilane was removed through a Vigreux column. Fractional distillation of the higher-boiling material gave 3-(1H,1H-heptafluorobutoxy)propyltrichlorosilane (125 g., 0.30 mole) in a 72% yield.

Reduction of the organotrichlorosilanes. The procedure used is the same as reported by West[13] except the excess lithium aluminum hydride was decomposed using trimethylchlorosilane. In the following cases a different procedure was necessary because of the properties of the compounds.

a. *3,3,3-Trifluoropropylsilane.* A 1-l. three-necked flask was equipped with a stirrer, dropping funnel with a side arm, and distillation head. The dropping funnel was connected to a nitrogen cylinder *via* a sulfuric acid trap. The distillation head was connected to a Dry Ice trap exited through a drying tube. Tetrahydrofuran (250 ml.), distilled from calcium hydride, was placed in the flask, and the system was purged with nitrogen. Lithium aluminum hydride (8.0 g., 0.21 mole) was dissolved in the tetrahydrofuran. 3,3,3-Trifluoropropyltrichlorosilane (57.9 g., 0.25 mole) dissolved in 50 ml. of tetrahydrofuran was slowly added over a period of 4 hr. with a positive nitrogen pressure throughout the system. The head temperature stayed between 40° and 50° throughout the addition. The stopcock of the distillation head was kept open so that the material which condensed was collected in the Dry Ice trap along with any material swept over by the nitrogen. After all of the 3,3,3-trifluoropropyltrichlorosilane was added, the reaction mixture was heated until the head temperature reached 60°. Fractional distillation of the material collected in the trap under a nitrogen atmosphere using ice water for cooling the head gave 3,3,3-trifluoropropylsilane (13.9 g., 0.11 mole).

b. *β-Silylpropionitrile.* The procedure used is described by Steward.[8] Under a nitrogen atmosphere, lithium aluminum hydride (42.4 g., 1.12 moles) dissolved in ether (900 ml.) was added dropwise to β-trichlorosilylpropionitrile (281 g. 1.49 moles) dissolved in ether (500 ml.). The addition was carried out over a period of 6 hr. with the flask cooled in an ice bath. The mixture was allowed to stir for 16 hr. The reaction mixture was poured onto cracked ice, and the ether layer was dried over anhydrous calcium sulfate. After re-

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(13) R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954).

TABLE III

ORGANOSILICON HYDRIDES

Formula	Yield, %	B.P.	Mm.	n_D^{25}	d_4^{25}	Silane Hydrogen, % Calcd.	Silane Hydrogen, % Found	Silicon, % Calcd.	Silicon, % Found	Carbon, % Calcd.	Carbon, % Found	MR_D Calcd.	MR_D Found
$CF_3CH_2CH_2SiH_3$	44	31	742	1.3211	0.974			21.9	21.9			26.5	26.2
$CF_3CH_2CH_2Si(H)(OC_2H_5)_2$	79	63	38	1.3578	1.031	0.47	0.46	13.0	12.9	38.9	39.0	46.0	46.1
$[CF_3CH_2CH_2Si(H)O]_n$	91			1.3689	1.348	0.71	0.65	19.7	20.2	25.3	25.4		
$CF_3CH_2CH_2CH(CF_3)CH_2SiH_3$	70	110–111	749	1.3458	1.186	1.35	1.26	12.5	12.5			40.5	40.8
$CF_3CH_2CH_2CH(CF_3)CH_2Si(H)(OC_2H_5)_2$	84	68	8	1.3597	1.152	0.32	0.30	9.0	9.5			60.0	59.8
$[CF_3CH_2CH_2CH(CF_3)CH_2Si(H)O]_n$	86			1.3731	1.437	0.43	0.41	11.8	11.8				
$CF_3(CF_2)_2CH_2O(CH_2)_3SiH_3$	70	59.5	43	1.3433	1.217	1.11	1.11			30.9	31.0	46.9	47.3
$CF_3(CF_2)_2CH_2O(CH_2)_3Si(H)(OC_2H_5)_2$	77	97	11	1.3613	1.191	0.28	0.28	7.8	8.2	36.7	37.1	66.45	67.0
$[CF_3(CF_2)_2CH_2O(CH_2)_3Si(H)O]_n$	91			1.3648	1.432	0.35	0.36	9.8	10.1	29.4	29.6		
$CF_3(CF_2)_6CH_2O(CH_2)_3SiH_3$	78	83	9	1.3350	1.458	0.64	0.63			28.0	28.4	65.7	67.0
$CF_3(CF_2)_6CH_2O(CH_2)_3Si(H)(OC_2H_5)_2$	74	115–116	4	1.3493	1.388	0.18	0.18			32.2	32.4	85.2	86.7
$[CF_3(CF_2)_6CH_2O(CH_2)_3Si(H)O]_n$	90			1.3507	1.631	0.21	0.19			27.2	27.6		
$H(CF_2)_{10}CH_2O(CH_2)_3SiH_3$[a]	84	96–97	1			0.50	0.515			27.8	28.0		
$[H(CF_2)_{10}CH_2O(CH_2)_3Si(H)O]_n$[b]	93					0.163	0.165			27.2	27.4		
$H(CF_2)_{10}CH_2O(CH_2)_3Si(H)(OC_2H_5)_2$	61	133	0.9	1.3522	1.478	0.15	0.14			31.2	31.3	99.3	101.4
$N{\equiv}CCH_2CH_2SiH_3$	39	39	16	1.4255	0.836	3.55	3.55	32.9	33.0			26.3	26.1
$N{\equiv}CCH_2CH_2Si(H)(OC_2H_5)_2$	39	97	12	1.4132	0.945	0.58	0.52			16.2	16.1	45.8	46.0

[a] White needles, m.p. 25.3–26.1°. [b] M.p. 91–110°.

moval of the ether, fractional distillation gave β-silylpropionitrile (49.6 g., 0.58 mole).

Preparation of the organodiethoxysilanes. The procedure is similar to that reported by Barnes and Schweitzer.[9] A typical example of the procedure is given below. Absolute ethanol (28.6 g., 0.62 mole), distilled from calcium hydride, was added to a mixture of 2-(trifluoromethyl)-5,5,5-trifluoropentylsilane (69.0 g., 0.31 mole), anhydrous ether (100 ml.), and chloroplatinic acid dissolved in dimethyl carbitol, 0.00122 g. of platinum/ml. (0.3 ml.), over a period of 1.5 hr. As the alcohol was added, hydrogen was evolved. The reaction mixture was allowed to stir for 16 hr. Fractional distillation gave 2-(trifluoromethyl)-5,5,5-trifluoropentyldiethoxysilane (80.9 g., 0.26 mole).

Using the above procedure β-silylpropionitrile gave two products: β-diethoxysilylpropionitrile, a 39% yield, and β-triethoxysilylpropionitrile,[7] b.p. 114 (12 mm.), n_D^{25} 1.4108, d_4^{25} 0.974, a 28% yield (a 43% yield based on the ethanol).

Reaction of 3,3,3-trifluoropropylsilane with sodium ethoxide. Sodium (0.23 g.) was dissolved in absolute ethanol (25.0 g., 0.54 mole). This solution was added dropwise over a period of 1 hr. to 3,3,3-trifluoropropylsilane (34.6 g., 0.27 mole) dissolved in tetrahydrofuran (98 g.). Throughout the addition, the flask was kept in an ice bath. The reaction mixture was allowed to stir for 16 hr. The volatile material was distilled under reduced pressure to separate the product from sodium ethoxide. Fractional distillation of the distillate gave unchanged 3,3,3-trifluoropropylsilane (7.1 g., 0.055 mole), b.p. 31° (760 mm.), n_D^{25} 1.3231, a 20% recovery, and 3,3,3-trifluoropropyltriethoxysilane (32.3 g., 0.12 mole), b.p. 81° (27 mm.), n_D^{25} 1.3648, a 69% yield based on the ethanol.

Anal. Calcd. for $C_9H_{19}F_3O_3Si$: C, 41.5; F, 21.9. Found: C, 41.7; F, 21.7.

Hydrolysis of the organodiethoxysilanes. The procedure given below is typical of the method used. 3,3,3-Trifluoropropyldiethoxysilane (36.9 g., 0.17 mole) was added rapidly to 0.01 *N* hydrochloric acid (200 ml.). The mixture was allowed to stir for 30 min. Benzene (100 ml.) was added, and the layers were separated. The benzene layer was washed with water and was placed in a distillation flask connected to a Dean-Stark distilling trap. Any remaining water was removed *via* the benzene-water azeotrope. The remaining benzene was removed under reduced pressure. The fluid remaining in the flask (22.0 g.) was filtered and analyzed. The analysis showed the material to be 3,3,3-trifluoropropylpolysiloxane.

The 3-(fluoroalkoxy)propylpolysiloxanes containing long fluoroalkoxy groups were not soluble in benzene; therefore, methyl isobutyl ketone was substituted.

Hydrolysis of β-diethoxysilylpropionitrile under the above conditions gave anomalous results. Hydrogen was rapidly evolved, and a white solid precipitated. The precipitate was washed with water and dried at a pressure of <1 mm. The solid was a white granular material which did not melt below 300°.

Anal. Found: $H_{(SiH)}$, 0.029; Si, 25.7; C, 34.6; H, 4.4.

The above anaylyses are much closer to the values calculated for β-cyanoethylsilsesquioxane than β-cyanoethylpolysiloxane.

Calcd. for $C_3H_4NO_{3/2}Si$: $H_{(SiH)}$, 0.0; Si, 26.4; C, 34.0; H, 3.8.

Calcd. for C_3H_5NOSi: $H_{(SiH)}$, 1.02; Si, 28.3; C, 36.3; H, 5.1.

An infrared spectrum of the solid (potassium bromide plate) shows a C≡N absorption band at 4.41 μ and a broad absorption band throughout the siloxane region. From the above data it would appear that the material is mainly β-cyanoethylsilsesquioxane incorporating a small number of β-cyanoethylsiloxy units.

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Organoboron Compounds. I. The Preparation of 2-Chlorovinyl- and 2-Chlorovinylethylboranes by Vinylation, Disproportionation and Exchange Reactions[1]

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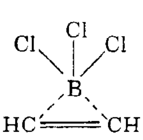
2-Chlorovinyl- and 2-chlorovinylethylboranes have been prepared by synthetic routes which do not require the use of metals, metal alkyls or Grignard reagents. These routes comprise vinylation, disproportionation, and exchange reactions. The methods of preparation and mechanisms are discussed.

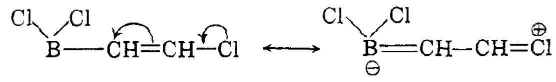
The alkylhaloboranes are versatile intermediates which can be utilized for the preparation of many organoboron compounds containing one, two, or three boron-carbon bonds. The halides are very reactive and readily undergo reactions in which the halogen is replaced without affecting the boron-carbon bonds. In general, synthetic routes to alkylhaloboranes require the use of metals, metal alkyls, or Grignard reagents.[2] It was the purpose of this investigation to prepare alkylhaloboranes from boron halides without metallic compounds.

The present investigation has developed a synthesis of 2-chlorovinyl- and 2-chlorovinylethylboranes by vinylation (reaction with acetylene), disproportionation, and exchange reactions. The vapor-phase reaction of boron trichloride with acetylene in the presence of typical vinylation catalysts has been found to give (2-chlorovinyl)-dichloroborane (I) primarily and very small quantities of bis(2-chlorovinyl)chloroborane (II) and tris(2-chlorovinyl)borane (III).[3] Further investigation of this reaction to obtain better yields of $ClCH{:}CHBCl_2$ (I), $(ClCH{:}CH)_2BCl$ (II), $(ClCH{:}CH)_3B$ (III), bis(2-chlorovinyl)chloroborane, and tris(2-chlorovinyl)borane indicated that acetylene could not be added easily to compounds containing the chlorovinyl group.

Presumably this reaction proceeds through an intermediate complex.



While the electrophilic character of the boron atom in boron trichloride is high, the electrophilicity of the boron atom attached to the chlorovinyl group is decreased by the following resonance form:



Thus a second chlorovinyl group was added to (2-chlorovinyl)dichloroborane with difficulty in poor yields (6%) while no addition occurred with either (2-chlorovinyl)ethylchloroborane[4] or bis(2-chlorovinyl)chloroborane. It is interesting to note that acetylene adds readily to ethyldichloroborane and not to diethylchloroborane.[4] The formation of the π-complex with acetylene is apparently prevented by the inductive effect of the ethyl groups and by steric hinderance.

In an attempt to find other methods for preparing bis- and tris(2-chlorovinyl)boranes, the disproportionation of (2-chlorovinyl)dichloroborane was investigated. Hennion *et al.*[5] found that alkyldichloroboranes disproportionate into dialkylchloroboranes in the presence of trialkylboranes as catalyst. They also found that dialkylchloroboranes could be disporportionated into trialkylboranes and alkyldichloroboranes by slow fractional distillation at atmospheric pressure at temperatures above 100°. We found that when (2-chlorovinyl)dichloroborane was refluxed without catalyst no disproportionation occurred. Upon addition of activated carbon, disproportionation occurred between 100–125° to give equimolar quantities of bis(2-chlorovinyl)chloroborane and boron trichloride.[6] Activated carbon inhibited the disproportionation of bis(2-chlorovinyl)chloroborane into tris(2-chloro-

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[2] For a review of this subject see M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956).

[3] H. R. Arnold, U. S. Patent **2,402,589** (1946); *Chem. Abstr.*, **40**, 5769 (1946).

[4] E. Gipstein, P. R. Kippur, M. A. Higgins, and B. F. Clark, *J. Org. Chem.*, **26**, 943 (1961).

[5] G. F. Hennion, P. A. McCusker, and E. C. Ashby, *J. Am. Chem. Soc.*, **79**, 5192–5194 (1957).

[6] B. F. Clark, E. Gipstein, M. A. Higgins, and P. R. Kippur, U. S. Patent **2,919,291**, Dec. 29, 1959; *Chem. Abstr.*, **54**, 7506 (1960).