$OCF_2CHFCl$ was obtained. However, the basic catalyst potassium hydroxide reacts with the ethylene chlorohydrin to form ethylene oxide so rapidly that the yield of adduct is necessarily low.

**Addition of Fluoroalcohols to Ethylene Oxide.**—A cooled solution of 5 g. of potassium hydroxide in 1.5 moles of the fluoroalcohol was placed in an autoclave having a capacity of 300 ml., which was cooled in a Dry Ice–acetone-bath; 44 g. (1.0 mole) of ethylene oxide was added to the contents of the autoclave, which was rocked at 70° for four hours. The reaction mixture was distilled through the 65-cm. fractionating column.

$CF_3CH_2OH$, available commercially, $C_2F_5CH_2OH$ and $C_3F_7CH_2OH$, prepared by reduction of the appropriate perfluoroacids with lithium aluminum hydride, and $CF_3C(CH_3)_2OH$, were added successfully to ethylene oxide by this procedure.

**Treatment of Hydroxyethyl Ethers with Phosphorus Pentachloride.**—Sixty grams (0.29 mole) of phosphorus pentachloride was added gradually to approximately 0.25 mole of the hydroxy-ether, in a 500-ml., three-necked flask, while the mixture was stirred vigorously. Immediate reaction occurred, as shown by the evolution of hydrogen chloride and heating of the mixture. After addition was complete, the reaction mixture was refluxed 20 minutes; it was then cooled, poured into ice-water, washed with sodium bicarbonate solution, dried over anhydrous sodium sulfate, and fractionated. Yields of 27% were consistently obtained by this procedure. When the reaction mixture was diluted with about 100 ml. of chloroform, yields of 45–67% were obtained.

Hydrolysis of two of the chloroethers was performed. $CH_2ClCH_2O\underset{\underset{O}{\|}}{C}CHFCl$ was obtained from $CH_2ClCH_2OCF_2CHFCl$ in 34% yield, b.p. 106° (47 mm.) 105° (45 mm.), $n^{23}$D 1.4369, $d^{25}_4$ 1.4256; *MR*D calcd. 32.06, *MR*D found 32.20.

*Anal.* Calcd. for $C_4H_5Cl_2FO_2$: Cl, 40.52. Found: Cl, 40.09.

$CH_2ClCH_2O\overset{\overset{O}{\|}}{C}CHCl_2$ was obtained from $CH_2ClCH_2OCF_2CHCl_2$ in 36% yield, b.p. 207–211° (atm. press.), $n^{25}$D 1.4719, $d^{25}_4$ 1.4544; *MR*D calcd. 36.93, *MR*D found 36.85.

*Anal.* Calcd. for $C_4H_5Cl_3O_2$: Cl, 55.56. Found: Cl, 54.85.

This compound is reported by Delacre[16] to have the constants b.p. 209–212° (767 mm.) and $d^{15}$ 1.200. However, this density value appears to be unreasonably low.

**Dehydrochlorination of the Chloroethyl Ethers.**—A solution of 18 g. (0.32 mole) of potassium hydroxide in 120 ml. of *n*-propyl alcohol was added dropwise to about 0.20 mole of the chloroethyl ether in a 500-ml. flask, with heating and vigorous stirring. Salt formation began immediately. A distillate consisting of a mixture of vinyl ether and alcohol was collected. It was poured into ice-water, and the organic layer was separated, washed, dried and distilled.

Only four of the seven desired vinyl ethers were isolated. Other dehydrochlorinating agents, including tri-*n*-butylamine, powdered sodium hydroxide and aqueous potassium hydroxide, were ineffective.

**Addition of Fluoroalcohols to Epichlorohydrin with Excess Sodium Hydroxide.**—The fluoroalcohol (0.50 mole) and epichlorohydrin (46 g., 0.50 mole) were added to a cooled solution of 25 g. (0.62 mole) of sodium hydroxide in 300 ml. of water. The reactants were mixed thoroughly, and the mixture was allowed to stand at room temperature overnight. The organic layer was then separated and treated in the usual manner.

**Addition of Trifluoroethyl Alcohol to Epichlorohydrin with a Catalytic Amount of Pyridine.**—One hundred grams (1.0 mole) of trifluoroethyl alcohol, 185 g. (2.0 moles) of epichlorohydrin and 2 ml. of pyridine were heated to 80–90° with stirring for 12 hr. The mixture was then fractionated.

**Infrared spectra** were determined with a Perkin–Elmer model 21 double-beam infrared recording spectrophotometer equipped with sodium chloride optics. Approximately 0.2 *M* solutions of the freshly distilled vinyl ethers in Eastman Spectro Grade carbon tetrachloride were prepared and placed in a cell of 0.1 mm. thickness, with compensating cell of about the same thickness containing carbon tetrachloride only. The higher boiling points of the glycidyl fluoroethers made it possible to obtain spectra of the liquids, using a demountable cell.

The study of the effect of temperature on the intensity of the carbon–carbon double-bond stretching bands was performed with a demountable cell which was heated by wrapping with heating tape. Freshly distilled vinyl 2-ethylhexyl ether, b.p. 177° (atm. press.), was used because of its relatively high boiling point. Low temperature spectra could not be obtained with the equipment available because of interfering absorption of water which immediately condensed on the cold cell upon exposure to air.

**Acknowledgments.**—We are indebted to the General Chemical Division, Allied Chemical and Dye Corporation, for financial assistance in the form of a grant-in-aid. We also appreciate the aid and advice freely given by Dr. G. B. Butler and Dr. A. H. Gropp in initiating the study and in interpreting the infrared spectra. Analyses of new compounds were performed by the Clark Microanalytical Laboratory, Urbana, Ill., with three exceptions: $CH_2OHCH_2OCF_2CHCl_2$, by the writer; and $CH_2OHCH_2OCF_2CHFCF_3$ and $\underset{\diagdown\!\diagup \atop O}{CH_2CH}CH_2OCH_2CF_3$, by the microanalytical laboratory of Dr. G. Weiler and Dr. F. B. Strauss, Oxford, England.

GAINESVILLE, FLA.

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[16] M. Delacre, *Bull. soc. chim.*, **48**, 708 (1887).

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[CONTRIBUTION FROM PENINSULAR CHEMRESEARCH, INC.]

# The Preparation of Some Fluoroalkylmethyldichlorosilanes and their Hydrolysis Products[1]

BY PAUL TARRANT, G. W. DYCKES, ROBERT DUNMIRE AND G. B. BUTLER

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Methyldichlorosilane has been added to various fluorine-containing olefins to give fluoroalkylmethyldichlorosilanes. Explosions occurred in attempts to treat silanes with chlorotrifluoroethene and perfluoropropene. Cyclic siloxanes obtained by hydrolysis of the dichlorosilanes were characterized.

Silicone elastomers are useful because of the wide temperature range over which they retain elasticity. These materials have some disadvantages, particularly in their lack of resistance to swelling by fuels and similar organic materials. Several years ago samples of bis-(heptafluoropentyl)-diethoxysilane and heptafluoropentylmethyldiethoxysilane

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[1] Presented at the Symposium on Fluorine-containing Polymers of the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 16, 1956. The research described was supported by funds from the Wright Air Development Center, Materials Laboratory; Lt. E. C. Stump served as project engineer.

prepared by the Grignard method[2] were treated with dimethyldichlorosilane to give copolymers which showed improved resistance to the swelling action of test fuels.[3] No homopolymers could be produced.

The present research was initiated to develop a method of preparation of fluoroalkylmethyldichlorosilanes, to hydrolyze such materials and to study their polymerization and copolymerization.

The most promising method of synthesis of the desired silanes seemed to be by the addition of trichloro- or methyldichlorosilane to a suitable olefin.[4-7]

Preliminary studies on the addition of trichlorosilane to 1-octene were made to correlate the effect of various initiators which have been used previously. It was found that benzoyl peroxide gave a 45% yield of octyltrichlorosilane and a 5% platinum-on-charcoal catalyst gave an 81% yield of adduct under the same conditions. No reaction occurred in the absence of either platinum or peroxide. Under comparable conditions in a stainless steel autoclave heated to 45°, a 61% yield of octyltrichlorosilane was obtained using the platinum catalyst. The experiments clearly demonstrate the effectiveness of platinum in aiding the addition of trichlorosilane; consequently, most of the reactions with silanes and fluoroölefins were carried out in the presence of this initiator.

It was found that trichlorosilanes added to 3,3,3-trifluoropropene to give excellent yields of (3,3,3-trifluoropropyl)-trichlorosilane, $CF_3CH{=}CH_2 + HSiCl_3 \rightarrow CF_3CH_2CH_2SiCl_3$. Attempts to react the product with methylmagnesium bromide to give the (trifluoropropyl)-methyldichlorosilane were unsuccessful because of the small difference in boiling points between the starting material and the desired product. However, it was found that methyldichlorosilane added readily to trifluoropropene at about 250° to give (3,3,3-trifluoropropyl)-methyldichlorosilane. The structure of the adduct was established as $CF_3CH_2CH_2Si(CH_3)Cl_2$ by its nuclear magnetic spectrum: the $F^{19}$ spectrum showed a triplet due to the adjacent $CH_2$ group.[8] The trifluoropropyltrichlorosilane was shown to be (3,3,3-trifluoropropyl)-trichlorosilane by its conversion to the known trimethoxy compound.[2] McBee and his associates[9] have reported similar results with methyldichlorosilane and trifluoropropene under somewhat different experimental conditions.

Both 3,3,4,4,4-pentafluorobutene and 3,3,4,4,-5,5,5-heptafluoropentene reacted with methyldichlorosilane to give good yields of adducts which were assigned the straight chain structure $R_fCH_2CH_2Si(CH_3)Cl_2$. (2-Trifluoromethyl)-propene gave (2-trifluoromethylpropyl)-methyldichlorosilane.

In general the reactions were carried out at 250° for 16 hours in a stainless steel reaction vessel, but good yields also were obtained in 4 hours. In one or two cases the platinum was omitted and the yields of adducts were still satisfactory. With the platinum catalyst the conversions averaged 60% and sometimes reached 75%.

Trichlorosilane also added to 2-fluoropropene to give (2-fluoropropyl)-trichlorosilane. The adduct shows the typical reaction of a β-halogen silane in losing the fluorine atom by hydrolysis in basic medium. Hydrolysis by distilled water removed only the chlorine bound to silicon. A very small amount (1.5%) of adduct[7] also was obtained from 1,1-difluoroethene.

Chlorotrifluoroethene was heated with trichlorosilane at 150° for 4 hours and a small amount of high boiling material was obtained. Reaction took place at 200° over a period of three hours to give a small amount of material differing considerably from the previous product. In an effort to determine the effect of higher reaction temperatures an experiment was carried out in the absence of platinum. At 250° an exothermic reaction began and the temperature of the reaction vessel suddenly increased to 300°, where an explosion occurred.

Methyldichlorosilane added to chlorotrifluoroethene in the presence of platinum catalyst at 200° to give a 25% yield of adduct which gave hydrolyzable chlorine values close to the theoretical value. Two other reactions were carried out without incident under similar conditions but a detonation occurred during a subsequent experiment. Because of the violence of the reaction of silanes with chlorotrifluoroethene, no further experiments were carried out with this olefin.

Perfluoropropene was heated with trichlorosilane in the absence of a catalyst for 18 hours at 180°, but only starting materials were obtained. An attempt was made to add methyldichlorosilane in the presence of platinum, but at 100° a violent explosion occurred. It is interesting that these explosions occurred in those cases where fluorine atoms were present on both unsaturated carbon atoms; no similar difficulties were observed during additions to compounds of the type $R_fCH{=}CH_2$ although these reactions were carried out a large number of times.

The physical properties of the various addition products are shown in Table I.

The hydrolysis of the (fluoroalkyl)-methyldichlorosilanes was carried out at 0° in a mixture of ether and water. The resulting oils were fractionated and the constant boiling materials separated. The fluorine-containing materials resemble their hydrocarbon analogs in giving cyclic siloxanes having 3 or 4 silicon atoms.

Hydrolysis of 3,3,3-trifluoropropylmethyldichlorosilane gave a 30% yield of the cyclic trimer and an 11% yield of the cyclic tetramer as well as higher-boiling oils. A number of molecular weights were determined by the freezing-point method using benzene, but no consistent results could be obtained with the samples used. The difficulty appears to

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[2] E. T. McBee, C. W. Roberts, G. F. Judd and T. S. Chao, THIS JOURNAL, **77**, 1292 (1955).

[3] Roy T. Clark, Jr., Technical Note WCRT 53-294, Addendum I, March, 1954.

[4] L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, THIS JOURNAL, **69**, 188 (1947).

[5] A. J. Barry, L. DePree, J. W. Gilkey and D. E. Hook, *ibid.*, **69**, 2916 (1947).

[6] C. A. Burkhard and R. H. Krieble, *ibid.*, **69**, 2687 (1947).

[7] G. H. Wagner, U. S. Patent 2,537,738, May, 1953.

[8] We are indebted to James N. Shoolery of Varian Associates for the determination and interpretation of the spectra.

[9] E. T. McBee, C. W. Roberts and G. W. R. Purckhauer, THIS JOURNAL, **79**, 2329 (1957).

TABLE I

ADDITION PRODUCTS FROM SILANES AND FLUOROÖLEFINS

| Adduct | Yield, % | B.p., °C. | $t$, °C. | $M^t_D$ | $d^t_4$ | Analyses[a] Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Fluorine, % Calcd. | Fluorine, % Found | Silicon, % Calcd. | Silicon, % Found | Chlorine, % Calcd. | Chlorine, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CF_3CH_2CH_2SiCl_3$ | 72 | 114 | 28 | 1.3845 | 1.3951 | | | | | | | | | 46.1 | 46.3[b] |
| $CF_3CH_2CH_2Si(CH_3)Cl_2$ | 60 | 122 | 20 | 1.3946 | 1.2611 | 22.83 | 22.87 | 3.34 | 3.37 | 27.01 | 27.28 | 13.27 | 13.02 | 33.61 | 33.59 |
| $C_2F_5CH_2CH_2Si(CH_3)Cl_2$ | 64 | 131 | 25 | 1.3691 | 1.3136$^{26}$ | 22.96 | 23.10 | 2.70 | 2.76 | 36.39 | 36.34 | 10.73 | 10.84 | 27.17 | 27.44 |
| $C_3F_7CH_2CH_2Si(CH_3)Cl_2$ | 60 | 147 | 23 | 1.3610 | 1.3996$^{30}$ | 23.16 | 23.28 | 2.27 | 2.37 | 42.77 | 42.98 | 9.00 | 9.22 | 22.78 | 22.88 |
| $CF_3CH(CH_3)CH_2Si(CH_3)Cl_2$ | 66 | 139 | 24 | 1.3936 | 1.2322$^{26}$ | 26.89 | 26.57 | 4.03 | 4.04 | 25.33 | 25.10 | 12.49 | 12.73 | 31.50 | 31.57 |
| $CH_3CHFCH_2SiCl_3$ | 7[c] | 123–124 | 21.5 | 1.4348 | 1.1924 | | | | | | | | | 54.5 | 54.0 |
| $C_2HClF_3Si(CH_3)Cl_2$ | 25[d] | 128.5–130 | 21.5 | 1.4036 | 1.4036$^{20}$ | | | | | | | | | 30.7 | 30.8[b] |

[a] Elemental analysis by Schwarzkopf Microanalytical Laboratory. [b] Hydrolyzable chlorine. [c] Platinum catalyst not used in this experiment. [d] Estimated from one run.

TABLE II

REACTION OF SILANES WITH FLUOROÖLEFINS[a]

| Olefin | Moles | Silane | Moles | Pt cat., g. | Temp., °C. | Time, hr. |
|---|---|---|---|---|---|---|
| 3,3,3-Trifluoropropene[b] | 1.0 | Trichloro- | 2.8 | .. | 250[c] | 16[c] |
| 3,3,3-Trifluoropropene[b] | 1.1 | Methyldichloro- | 3.0 | .5 | 250[d] | 16 |
| 3,3,4,4,4-Pentafluorobutene[e] | 1.4 | Methyldichloro- | 2.7 | .5 | 250 | 16 |
| 3,3,4,4,5,5,5-Heptafluoropentene | 1.1 | Methyldichloro- | 2.3 | .5 | 250 | 16 |
| 2-Trifluoromethylpropene[f] | 2.2 | Methyldichloro- | 4.4 | .5 | 250 | 16 |
| 2-Fluoropropene | 2.0 | Trichloro- | 4.1 | .. | 240 | 14 |

[a] The yield of product from a typical run is given in Table I. [b] P. Tarrant and A. M. Lovelace, THIS JOURNAL, **76**, 3466 (1954). [c] This treatment was followed by 4 hours heating at 275°. [d] A reaction time of 4 hr. gave a 49% yield of product. [e] E. T. McBee, O. R. Pierce and M. C. Chen, THIS JOURNAL, **75**, 2324 (1953). [f] A. L. Henne, J. W. Shepard and E. J. Young, *ibid.*, **72**, 3577 (1950).

TABLE III

PHYSICAL PROPERTIES OF CYCLIC SILOXANES

| Compound | Yield, % | B.p., °C. (3 mm.) | $n^t_D$ | $t$, °C. | $d^t_4$ | $t$, °C. | Analysis, %[a] Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Fluorine, % Calcd. | Fluorine, % Found | Silicon, % Calcd. | Silicon, % Found | Mol. wts. Calcd. | Mol. wts. Found | Infrared absorption, μ[d] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $[CF_3CH_2CH_2Si(CH_3)O]_3$ | 30 | 95 | 1.3696 | 20 | 1.241 | 26 | 30.76 | 31.45 | 4.52 | 3.70 | 36.50 | 38.23 | 17.97 | 17.30 | 469 | 462[b] | 9.8 |
| $[CF_3CH_2CH_2Si(CH_3)O]_4$ | 11 | 134 | 1.3724 | 19 | 1.255 | 26 | 30.76 | 31.58 | 4.52 | 3.90 | 36.50 | 36.78 | 17.97 | 17.41 | 625 | 615[c] | |
| $[CH_3CH(CF_3)CH_2Si(CH_3)O]_3$ | 15 | 117.5 | 1.3855 | 21 | 1.210 | 23 | 35.29 | 35.56 | 5.33 | 4.57 | 33.49 | 33.18 | 16.49 | 16.33 | 510 | 529[b] | 9.8 |
| $[CH_3CH(CF_2)CH_2Si(CH_3)O]_4$ | 8 | 152 | 1.3863 | 20 | 1.227 | 22 | 35.29 | 35.69 | 5.33 | 3.91 | 33.49 | 33.88 | 16.49 | 15.98 | 680 | 686[b] | 9.05–9.2 |
| $[CF_3CF_2CH_2CH_2Si(CH_3)O]_3$ | 15 | 107 | 1.3552 | 22 | 1.338 | 21 | 29.13 | 29.58 | 3.42 | 3.56 | 46.08 | 46.22 | 13.61 | 13.80 | 619 | 614[c] | 9.8 |
| $[CF_3CF_2CH_2CH_2Si(CH_3)O]_4$ | 11 | 147 | 1.3604 | 22 | 1.356 | 21 | 29.13 | 29.59 | 3.42 | 3.05 | 46.08 | 46.26 | 13.61 | 14.04 | 825 | 820[c] | |
| $[CF_3CF_2CF_2CH_2CH_2Si(CH_3)O]_3$ | 20 | 122 | 1.3470 | 24 | 1.425 | 23 | 28.13 | 28.35 | 2.75 | 2.86 | 51.92 | 51.98 | 10.93 | 10.96 | 769 | 765[c] | 9.8 |
| $[CF_3CF_2CF_2CH_2CH_2Si(CH_3)O]_4$ | 18 | 156 | 1.3496 | 22 | 1.438 | 23 | 28.13 | 28.29 | 2.75 | 2.65 | 51.92 | 51.98 | 10.93 | 10.71 | 1025 | 1066[c] | |

[a] Elemental analyses by Schwartzkopf Microanalytical Laboratory. [b] Freezing point depression in benzene. [c] Boiling point elevation in benzene. [d] The characteristic absorption maximum for cyclic trisiloxanes is 9.8 μ and for tetrasiloxanes is 9.15–9.25 μ.

be due to the limited solubility of the siloxanes in benzene. At lower temperatures other investigators[10] have encountered this difficulty in cryoscopic determinations and have corrected the molecular weights by using a different value of the constant for cyclohexane when used with polysiloxanes. However, infrared studies[11,12] made on cyclic disubstituted siloxanes show that the lower members have bands in their infrared spectra in the region between 9 and 10 μ which are characteristic of the number of atoms in the ring. This band is attributed to the stretch vibrations of the Si–O–Si bonds. Cyclic trimers from dimethyl-, diethyl-, diphenyl-, methylphenyl- and ethylphenyldichlorosilane have a maximum absorption at 9.8 to 9.9; tetramers from such materials have their characteristic absorption at 9.15 – 9.25. The cyclic materials from $CF_3CH_2CH_2Si(CH_3)Cl_2$ having a strong absorption at 9.8 is therefore the cyclic trimer. The higher boiling fraction is assigned the cyclic tetramer structure because of its absorption band at 9.2. The determination of molecular weights by the use of the boiling point elevation of benzene gave results consistent with infrared data.

## Experimental

**The Reaction of Trichlorosilane and Methyldichlorosilane with Fluoroölefins. General Method.**—A 1.4-liter stainless steel reaction vessel was cooled in Dry Ice and acetone and charged with trichloro- or methyldichlorosilane and olefin. The molar ratio of silane to olefin was about 3:1. The reaction vessel was heated to about 250° and rocked for several hours. The vessel was then cooled in ice and the contents removed. Fractionation was carried out in a 27″ column packed with glass helices. Yields were based on fractions having a two degree boiling range. Detailed conditions are given in Table II.

**Reaction of Trichlorosilane with 1-Octene.**—A 500-ml. round-bottom flask containing 56 g. (0.5 mole) of 1-octene was fitted with a stirrer, reflux condenser and addition funnel. The temperature was raised to 70° and 203 g. (1.5 moles) of trichlorosilane was added dropwise along with intermittent additions of benzoyl peroxide (10 g.) through the reflux condenser. The reaction mixture was refluxed 12 hours. Distillation of the reaction products through an 18″ fractionating column gave 53 g. (45%) of *n*-octyltrichlorosilane, b.p. 122–124° (28 mm.), $n^{24}D$ 1.4481; reported properties,[13] b.p. 231–232° (731 mm.), $n^{20}D$ 1.4480.

The experiment was repeated using 0.5 g. of 5% platinum-on-charcoal catalyst[14] instead of benzoyl peroxide. In this instance, the catalyst was placed in the 1-octene at the beginning of the reaction, then filtered off prior to distillation of the products. A 95.5 g. (81%) yield of *n*-octyltrichlorosilane, b.p. 124° (28 mm.), was obtained.

Under essentially the same conditions in the absence of any catalyst, only starting materials were obtained.

Carrying out the reaction in a 1.4-liter stainless steel reaction vessel for 12 hours at 45° with 0.5 g. of platinum-on-charcoal catalyst gave 76 g. (61%) of *n*-octyltrichlorosilane, b.p. 123–125° (28 mm.).

**Preparation of (3,3,3-Trifluoropropyl)-trimethoxysilane.**—Sodium methylate (81 g., 1.5 moles) was placed in a 1-liter flask and covered with 200 ml. of dry diethyl ether as rapidly as possible. 3,3,3-Trifluoropropyltrichlorosilane (115.8 g., 0.5 mole) was added dropwise with stirring, using an ice-bath to cool the reaction mixture. After standing overnight, the ether was recovered using a Claisen head and the remaining liquids were distilled rapidly from the salt under reduced pressure. Redistillation of these materials through an 18″ fractionating column gave 65 g. (60%) of (3,3,3-trifluoropropyl)-trimethoxysilane b.p. 80.5° (87 mm.), $n^{21}D$ 1.3547, $d^{26}_4$ 1.126; reported[15] properties, b.p. 79.8–80.5° (87 mm.), $n^{20}D$ 1.3547, $d^{20}_4$ 1.137.

*Anal.* Calcd. for $C_6H_{13}F_3O_3Si$: C, 33.02; H, 6.00; F, 26.12; Si, 12.83. Found: C, 33.54; H, 5.20; F, 26.56; Si, 12.87.[16]

**Preparation of 3,3,4,4,5,5,5-Heptafluoropentene.**—This compound was prepared in the same manner as 3,3,4,4,4-pentafluorobutene. Esterification of 2140.5 g. (10 moles of heptafluorobutyric acid using 921.4 g. (20 moles) of ethyl alcohol and 300 ml. of concd. sulfuric acid gave 2023 g. (82.5%) of ethyl heptafluorobutyrate, b.p. 95–98°. Grignard reduction of the ester (484 g., 2 moles) gave 1288 g. (75%) of 3,3,4,4,5,5,5-heptafluoropentanol-2, b.p. 102°, $n^{25}D$ 1.3109, $d^{29}_4$ 1.483. Dehydration of the secondary alcohol (616 g., 2.8 moles) with 468.6 g. (3.3 moles) of phosphorus pentoxide gave 303 g. (55%) of 3,3,4,4,5,5,5-heptafluoropentene, b.p. 32–37°.

**Preparation of 2-Fluoropropene.**—1,2,3-Trichloropropane (5 kg., 33.9 moles) was treated with 10% (by weight) sodium hydroxide solution to give 1693 g. of 2,3-dichloropropene-1, b.p. 92–95°. The 2,3-dichloropropene-1 (1.1 kg., 9.9 moles) and 210 g. (10.5 moles) of hydrofluoric acid were placed in a 1.4-liter stainless steel reaction vessel and mechanically rocked for 15 hours at room temperature. The organic layer was separated, neutralized with sodium carbonate and steam distilled. The products from two experiments were combined and treated with bromine until the color persisted. Distillation of the resulting mixture gave 950 g. (37%) of 1,2-dichloro-2-fluoropropane, b.p. 87–90°. Dechlorination of this compound (196 g., 1.5 moles) using 60 g. (2.5 moles) of magnesium turnings with 500 ml. of dry diethyl ether gave 64 g. (71%) of 2-fluoropropene, b.p. –20 to –24°.

**Reaction of Trichlorosilane with 1,1-Difluoroethene.**—Trichlorosilane (203 g., 1.5 moles) and 0.5 g. of platinum-on-charcoal catalyst were placed in a 1.4-liter stainless steel reaction vessel equipped with a pressure gage and valve assembly. 1,1-Difluoroethane was charged into the mixture to a pressure of 200 p.s.i. and the vessel was mechanically rocked for 4 hours at 150°. Distillation of the reaction mixture through a 12″ fractionating column gave only 3 g. of material (b.p. 104–106°) boiling within the expected range for the desired compound.

*Anal.* Calcd. for $C_2H_3Cl_3F_2Si$: Cl, 58.94. Found: Cl, 49.54.

**Reaction of Trichlorosilane with Chlorotrifluoroethene.**—A 1.4-liter stainless steel reaction vessel was cooled in a Dry Ice–acetone-bath and charged with 200 g. (2 moles) of trichlorosilane, 155 g. (1.3 moles) of chlorotrifluoroethene, 0.5 g. of platinum-on-charcoal catalyst and mechanically rocked for 4 hours at 150°. Distillation of the reaction mixture through a 27″ fractionating column gave only 5 g. of material (b.p. 95–125°) boiling within the expected range for the desired compound.

*Anal.* Calcd. for $C_2HCl_4F_3Si$: Cl, 56.38. Found: Cl, 60.36.

The experiment was repeated using reaction conditions of 3 hours at 200°. Distillation of the reaction mixture in this instance gave 10 g. of material, b.p. 123–131°.

*Anal.* Calcd. for $C_2HCl_4F_3Si$: hydrolyzable Cl, 42.23. Found: hydrolyzable Cl, 28.14.

Repetition of the experiment using a 250° reaction temperature resulted in a violent explosion causing considerable damage to the autoclave and the surrounding area.

**Reaction of Methyldichlorosilane with Chlorotrifluoroethene.**—A 1.4-liter stainless steel reaction vessel was cooled in a Dry Ice–acetone-bath and charged with 235 g. (2 moles) of methyldichlorosilane, 175 g. (1.5 moles) of chlorotrifluoroethene, 0.7 g. of platinum-on-charcoal catalyst and mechanically rocked for 3.75 hours at 200°. Distillation of the reaction mixture gave 28 g. of material, b.p. 128.6–129°. The experiment was repeated twice without incident. However, the fourth experiment resulted in a violent explosion. The material collected from the first three experiments,

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[10] M. J. Hunter, J. F. Hyde, E. L. Warrick and H. J. Fletcher, THIS JOURNAL, **68**, 670 (1946).

[11] N. Wright and M. J. Hunter, *ibid.*, **69**, 803 (1947).

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b.p. 110–145°, was redistilled through a micro-distilling apparatus giving 25 g. of material, b.p. 128.5–130°.

**Reaction of Trichlorosilane with Hexafluoropropene.**—A 1.4-liter stainless steel reaction vessel was cooled in a Dry Ice–acetone-bath and charged with 271 g. (2 moles) of trichlorosilane, 145 g. (1 mole) of hexafluoropropene,[17] and mechanically rocked 18 hours at 180°. Distillation of the reaction mixture through a 27″ fractionating column gave only starting materials.

**Reaction of Methyldichlorosilane with Hexafluoropropene.**—A 1.4-liter stainless steel reaction vessel was cooled in a Dry Ice–acetone-bath and charged with 300 g. (2.6 moles) of methyldichlorosilane, 240 g. (1.6 moles) of hexafluoropropene and 0.5 g. of platinum-on-charcoal catalyst. At 100° a violent explosion took place causing considerable damage to the autoclave.

**Hydrolysis of (3,3,3-Trifluoropropyl)-methyldichlorosilane.**—Hydrolysis of this compound was carried out using a procedure previously reported[18] for the hydrolysis of dimethyldichlorosilane except that the reaction temperature was held at approximately 2°. In this experiment 200 ml. of (3,3,3-trifluoropropyl)-methyldichlorosilane hydrolyzed in 400 ml. of water and 200 ml. of diethyl ether gave 58 g. (30%) of 2,4,6-trimethyl-2,4,6-tris-(3′,3′,3′-trifluoropropyl)-cyclotrisiloxane, b.p. 95° (3 mm.), and 16.7 g. (11%) of 2,4,6,8-tetramethyl-2,4,6,8-tetrakis-(3′,3′,3′-trifluoropropyl)-cyclotetrasiloxane, b.p. 134° (3 mm.).

**Hydrolysis of (2-Trifluoromethylpropyl)-methyldichlorosilane.**—Using the procedure described above, 200 ml. of this compound were hydrolyzed in 400 ml. of water and 200 ml. of diethyl ether. Fractionation of the hydrolysis products gave 30.2 g. (15%) of 2,4,6-trimethyl-2,4,6-tris-(2′-trifluoromethylpropyl)-cyclotrisiloxane, b.p. 117.5° (3 mm.), and 15.3 g. (8%) of 2,4,6,8-tetramethyl-2,4,6,8-tetrakis-(2′-trifluoromethylpropyl)-cyclotetrasiloxane, b.p. 152° (3 mm.).

**Hydrolysis of (3,3,4,4,4-Pentafluorobutyl)-methyldichlorosilane.**—Using the above procedure, 160 ml. of this compound was hydrolyzed in 320 ml. of water and 160 ml. of diethyl ether. Fractionation of the hydrolysis products gave 25.5 g. (15%) of 2,4,6-trimethyl-2,4,6-tris-(3′,3′,4′,4′-pentafluorobutyl)-cyclotrisiloxane, b.p. 107° (3 mm.), and 19 g. (11%) of 2,4,6,8-tetramethyl-2,4,6,8-tetrakis-(3′,3′,4′,4′-pentafluorobutyl)-cyclotetrasiloxane, b.p. 147° (3 mm.).

**Hydrolysis of (3,3,4,4,5,5,5-Heptafluoropentyl)-methyldichlorosilane.**—Using the above procedure, 200 ml. of this compound was hydrolyzed in 400 ml. of water and 200 ml. of diethyl ether. Fractionation of the hydrolysis products gave 45 g. (20%) of 2,4,6-trimethyl-2,4,6-tris-(3′,3′,4′,4′,-5′,5′,5′-heptafluoropentyl)-cyclotrisiloxane, b.p. 122° (3 mm.), and 41.5 g. (18%) of 2,4,6,8-tetramethyl-2,4,6,8-tetrakis-(3′,3′,4′,4′,5′,5′,5′-heptafluoropentyl)-cyclotetrasiloxane, b.p. 156° (3 mm.).

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[Contribution from the Department of Chemistry, University of North Dakota]

# Substituted Phenylsilanes. II. The Bromination of the Tolyltrimethylsilanes[1,2]

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The tolyltrimethylsilanes have been brominated with N-bromosuccinimide to give the trimethylsilylbenzyl bromides and the trimethylsilylbenzal bromides. The trimethylsilylbenzal bromides were hydrolyzed to the three isomeric trimethylsilylbenzaldehydes. *p*-Trimethylsilylbenzaldehyde also has been prepared from *p*-trimethylsilylbenzyl bromide by means of the Hass–Bender reaction. The trimethylsilylbenzyl bromides have been converted to the corresponding acetates and these acetates to the trimethylsilylbenzyl alcohols.

In a previous paper, the preparation of the trimethylsilylacetophenones by the autoxidation of the trimethylsilylethylbenzenes was described.[3] This work on substituted phenylsilanes has been extended and we are now reporting convenient syntheses for the trimethylsilylbenzaldehydes and some related compounds.

The easily accessible tolyltrimethylsilanes have been brominated, in good yield, with N-bromosuccinimide to form the trimethylsilylbenzyl bromides and the trimethylsilylbenzal bromides. These compounds serve as useful intermediates for the introduction of other functional groups into phenylsilanes. Thus, by refluxing the benzyl bromides with sodium acetate in glacial acetic acid, the trimethylsilylbenzyl acetates are formed easily. These acetates were saponified with methanolic sodium hydroxide to produce the trimethylsilylbenzyl alcohols.

The direct hydrolysis of the trimethylsilylbenzal bromides by refluxing with water in the presence of calcium carbonate under a nitrogen atmosphere gave the trimethylsilylbenzaldehydes. The pure aldehydes were obtained as colorless liquids in good yield from the reaction mixture by steam distillation followed by vacuum distillation. *p*-Trimethylsilylbenzaldehyde was also prepared in very good yield from *p*-trimethylsilylbenzyl bromide using the Hass–Bender[4] reaction. It is interesting to note that during the preparation of these compounds there has been no indication of cleavage of the phenyl–silicon bond.

*p*-Trimethylsilylbenzaldehyde was reported previously by Frisch and Shroff[5] to be a solid, m.p. 109–110°. We have not found this aldehyde to be a solid; however, on standing in air all three aldehydes are quite rapidly converted to solids melting in the vicinity of 100° which yield, on purification, pure samples of the corresponding benzoic acids. In order to get maximum yields of the aldehydes by our procedure, particularly with the *meta* and the *para* compounds, we found it necessary to carry out the reactions in an inert atmosphere; otherwise, considerable quantities of the acids were formed by the autoxidation of the aldehydes.

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(2) Presented in part in the Symposium on Carbon-Functional Silanes at the 125th Meeting of the American Chemical Society in Kansas City, Missouri, March, 1954.

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