THE CHLORINATION OF (3,3,3-TRIFLUOROPROPYL)TRICHLOROSILANE

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INTRODUCTION

The reactivities of C–H bonds in aliphatic compounds toward attack by a chlorine free radical vary quite markedly with structure**. The chlorine radical preferentially attacks at the carbon atom bearing the highest electron density which is controlled by the inductive and resonance effects of the substituent groups[1–6].

In this paper, we report a study of the chlorination of (3,3,3-trifluoropropyl)-trichlorosilane to determine the effect of the trifluoromethyl and trichlorosilyl groups on the distribution of the chlorinated products. Particular emphasis is placed on the isolation, determination of structure and yield of each chlorinated (3,3,3-trifluoropropyl)trichlorosilane present in the reaction mixture.

RESULTS

The chlorination of (3,3,3-trifluoropropyl)trichlorosilane was accomplished in the liquid phase (25–100°) using chlorine gas and ultraviolet light. Two separate experiments were carried out to simplify the isolation of the chlorinated products, partial and exhaustive chlorination.

In the partial chlorination experiment, the ratio of moles of chlorine added to moles of silane was 1.5. The composition of the reaction mixture was determined by vapor phase chromatography and fractional distillation (Table 1).

In the exhaustive chlorination experiment, chlorine gas was added until no further reaction occurred. The chlorination was exothermic until approximately two moles of chlorine gas per mole of silane were added. Beyond this point, the chlorination was carried out with an external source of heat (90–100°). The composition of the reaction mixture is given in Table 1.

The structures of the compounds isolated were determined from the analytical data and the NMR spectra, Tables 2 and 3. The number of chlorine atoms substituted for hydrogen atoms was assigned from the analytical data; the positions of the chlorine atoms, α or β to silicon, were assigned from the ^{19}F NMR spectra. The ^{19}F absorption signal for the trifluoromethyl group consisted of 1, 2 or 3 peaks depending on the number of adjacent hydrogens.

Fractional distillation and vapor phase chromatographic data indicated that only

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** For a recent review, see ref. 1.

TABLE 1

MOLE PER CENT OF THE COMPOUNDS PRESENT AFTER CHLORINATION OF (3,3,3-TRIFLUOROPROPYL)-TRICHLOROSILANE

Formula	*Partial chlorination*		*Exhaustive chlorination*	
	Vapor phase chromatography	*Fractional distillation**	*Vapor phase chromatography*	*Fractional distillation**
$CF_3CH_2CH_2SiCl_3$	36	34	—	—
$CF_3CH_2CHClSiCl_3$** $CF_3CHClCH_2SiCl_3$	44	46	2	—
$CF_3CH_2CCl_2SiCl_3$	19	20	58	67
$CF_3CHClCCl_2SiCl_3$	—	—	21	17
$CF_3CCl_2CCl_2SiCl_3$	—	—	19	15

* Calculated from the yields of the isolated compounds. ** Isomers not separated by above methods, see EXPERIMENTAL section.

TABLE 2

PHYSICAL PROPERTIES AND ANALYSES OF THE CHLOROFLUOROALKYLSILANES

Formula[a,b]	*B.p.*		n_D^{25}	d_4^{25}	*Carbon, %*		*Fluorine, %*		*Silicon, %*	
	°C	*mm*			*Calcd.*	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*
$RSiCl_3$	59–60	36	1.4112	1.530	13.5	14.0	21.4	21.6	10.6	10.8
$CF_3CH_2CCl_2SiCl_3$	77	36	1.4341	1.625	11.9	12.6	18.1	19.0	9.4	9.6
$CF_3CHClCCl_2SiCl_3$	71.5	10	1.4570	1.725	10.8	10.8	17.8	17.8	8.4	8.7
$CF_3CCl_2CCl_2SiCl_3$[c]	89.5	10	1.4759[d]	1.810[d]	9.8	10.1	15.4	15.3	7.6	7.7
$RSi(CH_3)_3$	138–139	739	1.3911	1.095	35.2	35.3	27.8	28.0	13.7	14.1
$RSi(CH_3)_2(OC_2H_5)$[e]	69–72	28	1.3878	1.121	35.8	36.0	24.3	24.6		
$RSi(CH_3)(OC_2H_5)_2$[f]	87–91	28	1.3864	1.133	36.3	36.2	21.5	21.4		
$RSi(OC_2H_5)_3$[g]	102–103	28	1.3834	1.136	36.7	37.0	19.3	19.3		
$[RSi(CH_3)O]_n$	104–160	0.2	1.4076	1.418	25.2	25.5	29.9	29.6	14.7	14.4

[a] R = CF_3CH_2CHCl– and $CF_3CHClCH_2$–, see Table 4. [b] % $Cl_{hydr.}$ gives high results for all compounds with more than one chlorine on the α-carbon. [c] Melting point 27.5–29.0° in a sealed tube. [d] Supercooled liquid. [e] Molecular weight (cryoscopically in benzene) 224. [f] Molecular weight (cryoscopically in benzene) 258. [g] Molecular weight (cryoscopically in benzene) 296.

TABLE 3

^{19}F CHEMICAL SHIFTS AND COUPLING CONSTANTS OF THE CHLOROFLUOROALKYLSILANES

Formula	*Vol. % in* CCl_3F	*Group*	Φ^* *(ppm)**	J_{F-H} *(cps)*	*Relative intensity*
$CF_3CH_2CHClSiCl_3$ (80%)** and	70.0	$CF^*_3CH_2$–	65.113 ± 0.003	9.31 ± 0.03	1:2:1
$CF_3CHClCH_2SiCl_3$ (20%)**		CF^*_3CHCl–	77.344 ± 0.005	6.10 ± 0.01	1:1
$CF_3CH_2CCl_2SiCl_3$	50.0	$CF^*_3CH_2$–	59.419 ± 0.002	8.82 ± 0.03	1:2:1
$CF_2CHClCCl_2SiCl_3$	54.3	CF^*_3CHCl–	65.830 ± 0.002	5.41 ± 0.03	1:1
$CF_3CCl_2CCl_2SiCl_3$	60.0	$CF^*_3CCl_2$–	69.381 ± 0.001		singlet
$CF_3CH_2CHClSi(CH_3)_3$ (98%)**	52.9	$CF^*_3CH_2$–	65.499 ± 0.002	9.68 ± 0.05	1:2:1
$CF_3CHClCH_2Si(CH_3)_3$ (2%)**		CF^*_3CHCl–	77.611 ± 0.002	6.35 ± 0.04	1:1

* Ref. 10. ** Estimated from the relative peak heights, precision ± 1%, accuracy not known.

TABLE 4

ISOMERIC COMPOSITION OF THE (CHLORO-3,3,3-TRIFLUOROPROPYL)SILICON COMPOUNDS*

Compound	*R*	
	CF_3CH_2CHCl– (%)	*$CF_3CHClCH_2$–* (%)
$RSiCl_3$	80	20
$RSi(CH_3)_3$	98	2
$RSi(CH_3)_2OC_2H_5$	88	12
$RSi(CH_3)(OC_2H_5)_2$	82	18
$RSi(OC_2H_5)_3$	91	9
$[RSi(CH_3)O]_n$	87	13

[*] Estimated by NMR from the relative peak heights of the ^{19}F spectra, precision ± 1%, accuracy not known.

one species was present in the monochlorinated product. However, the ^{19}F NMR spectrum showed that there were actually two isomers present, (1-chloro-3,3,3-trifluoropropyl)trichlorosilane (80 %) and (2-chloro-3,3,3-trifluoropropyl)trichlorosilane (20 %). The amount of each isomer was estimated from the relative peak heights of the ^{19}F spectrum. Attempts to separate the two isomers by vapor phase chromatography using a variety of conditions were not successful.

The following reactions were carried out with the monochlorinated mixture, (1- and 2-chloro-3,3,3-trifluoropropyl)trichlorosilane:

$$RSiCl_3 \xrightarrow[\text{ether}]{CH_3MgBr} RSi(CH_3)_3 \qquad (1)$$

$$RSiCl_3 \xrightarrow{\text{ethanol}} \xrightarrow[\text{ether}]{CH_3MgBr} RSi(OC_2H_5)_n(CH_3)_{3-n} \qquad n = 1\text{–}3 \qquad (2)$$

In the second reaction, conditions were controlled in order to obtain the maximum yield of the diethoxysilane. The diethoxysilane was hydrolyzed to the polysiloxane.

$$RSi(CH_3)(OC_2H_5)_2 \xrightarrow[\text{water/toluene}]{1\ N\ HCl} [RSi(CH_3)O]_n \qquad (3)$$

In the above equations, R = CF_3CH_2CHCl– and $CF_3CHClCH_2$–. The isomeric composition of the products as estimated from the ^{19}F NMR spectra are given in Table 4.

DISCUSSION

The chlorination of compounds containing trifluoromethyl and trichlorosilyl groups has been reported. The C–H bonds in the 2-position of 1,1,1-trifluoropropane show a remarkable resistance toward attack by a chlorine radical. Henne and Whaley[7] obtained only one monochlorinated isomer, 3-chloro-1,1,1-trifluoropropane, using the following conditions: chlorine gas, light, vapor phase, and room temperature.

$$\underset{1.0}{C}—\underset{0.0}{C}—CF_3^{*}$$

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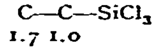
[*] The numbers below the carbon atoms refer to the relative reactivities of the C–H bonds in these positions[1].

Sommer and Whitmore[8] obtained both (1- and 2-chloroethyl)trichlorosilane from the sulfuryl chloride chlorination (room temperature) of ethyltrichlorosilane. The C–H bonds in the β-position are more susceptible to the substitution reaction.

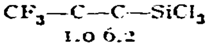


$\underset{1.7}{C}—\underset{1.0}{C}—SiCl_3$

In the above examples, the decrease in reactivity of the C–H bonds α to the substituent trifluoromethyl and trichlorosilyl groups is undoubtedly due mainly to the electron-withdrawing power (—*I*) of these groups, the trifluoromethyl group having the largest —*I* effect.

In (3,3,3-trifluoropropyl)trichlorosilane, the inductive effects of the two groups are acting in opposition, and one would expect both the α- and β-C–H bonds, relative to the silicon atom, to be deactivated toward attack by chlorine. The relative magnitude of the directive effects of these two groups can be determined from the partial chlorination experiment.

In the partial chlorination experiment, the product distribution was determined. In addition to the monochlorinated products, only one dichlorinated product was detected, (1,1-dichloro-3,3,3-trifluoropropyl)trichlorosilane, which must arise from (1-chloro-3,3,3-trifluoropropyl)trichlorosilane since both chlorine atoms are on the same carbon. The relative reactivities toward chlorination in the two positions are given below:



$CF_3—\underset{1.0}{C}—\underset{6.2}{C}—SiCl_3$

These values represent only the relative magnitude of the directive effects, since the accuracy of the measurements is not known.

When polychlorination occurs, other factors in addition to the inductive effect must be considered. The importance of resonance effects on the position of attack by a chlorine atom on 1- and 2-chloroalkanes has been demonstrated by the work of Fredricks and Tedder[5,6]. However, the powerful inductive effect (—*I*) of the trifluoromethyl group remains the prime factor in controlling the product distribution. Only the products with the smallest number of chlorine atoms in the β-position to silicon were isolated, (1,1-dichloro-, 1,1,2-trichloro- and 1,1,2,2-tetrachloro-3,3,3-trifluoropropyl)trichlorosilane. The 1,2-dichloro, 2,2-dichloro and 1,2,2-trichloro compounds were not detected by vapor phase chromatography or NMR.

EXPERIMENTAL

(1) *Chlorination of (3,3,3-trifluoropropyl)trichlorosilane*

(*a*) *Partial chlorination.* (3,3,3-Trifluoropropyl)trichlorosilane[9] (463 g, 2.0 moles) was placed in a one-liter, three-necked flask equipped with a thermometer, a dry-ice-cooled condenser, an ultraviolet lamp in a quartz well and a gas dispersion tube. Chlorine gas, dried by passing through a sulfuric acid trap, was slowly added via the gas dispersion tube below the surface of the liquid. The chlorination was stopped when the chlorine to silicon ratio reached 1.5. During the chlorination, the reaction temperature varied from 25° to 100°. Fractional distillation gave: (3,3,3-trifluoropropyl)trichlorosilane (135 g, 0.58 mole), a 29% recovery; a mixture of (1- and 2-chloro-3,3,3-trifluoropropyl)trichlorosilane (212 g, 0.80 mole), a 40% yield; (1,1-dichloro-3,3,3-trifluoropropyl)trichlorosilane (104 g, 0.35 mole), a 17% yield. Vapor phase chromatographic analysis indicated the products isolated were > 99% one component; however, NMR measurements indicated a mixture of two isomers in the monochlorinated product (Tables 3 and 4). The structures of the compounds were assigned on the basis of the NMR spectra (Table 3) and analyses (Table 2). The physical properties are given in Table 2.

(*b*) *Exhaustive chlorination.* Using the apparatus and procedure described above, (3,3,3-trifluoropropyl)trichlorosilane (231 g, 1.0 mole) was chlorinated. During the first part of the chlorination, the reaction temperature rose rapidly from 25° to 100° and remained between 90–100°. When approximately two moles of chlorine had been added, the reaction temperature started to drop, and the reaction mixture became yellow. The chlorination was continued with heating (90–100°) until no further reaction appeared to occur (22 h). During the chlorination, the weight of the material in the flask increased 96 g, corresponding to the introduction of three chlorine atoms per molecule. Fractional distillation gave: (1,1-dichloro-3,3,3-trifluoropropyl)trichlorosilane (175 g, 0.58 mole), a 58% yield; (1,1,2-trichloro-3,3,3-trifluoropropyl)trichlorosilane (50 g, 0.15 mole), a 15% yield; (1,1,2,2-tetrachloro-3,3,3-trifluoropropyl)trichlorosilane (50 g, 0.13 mole), a 13% yield. Vapor phase chromatographic analysis indicated the products isolated were > 99% one component. The structure of the compounds were assigned on the basis of the NMR spectra and analyses (Tables 2 and 3). The physical properties are listed in Table 2.

(2) Reaction of (chloro-3,3,3-trifluoropropyl)trichlorosilane with methyl Grignard

(Chloro-3,3,3-trifluoropropyl)trichlorosilane (194 g, 0.73 mole), dissolved in ether (600 ml), was added over a period of one hour to methylmagnesium bromide (2.5 moles) dissolved in ether (1.2 liters). The reaction flask was cooled in an ice bath throughout the addition. The reaction mixture was stirred for 12 hours and hydrolyzed by pouring onto cracked ice. Fractional distillation of the dried ether layer gave (chloro-3,3,3-trifluoropropyl)trimethylsilane (85.6 g, 0.42 mole), a 57% yield. The isomeric composition of the product, analysis and physical properties are given in Tables 2, 3 and 4.

(3) Preparation of (chloro-3,3,3-trifluoropropyl)methyldiethoxysilane

(Chloro-3,3,3-trifluoropropyl)trichlorosilane (320 g, 1.2 moles) was placed in a three-liter, three-necked flask equipped with a stirrer, thermometer, condenser and dropping funnel. The system was vented to the atmosphere via a dry-ice-cooled trap. Absolute ethanol (110 g, 2.4 moles) was added over a period of 1.5 hours, and the reaction mixture was heated to 60° for one hour. After cooling to room temperature, the reaction mixtures was stirred, and the system was swept with dry nitrogen for 16 hours to remove any remaining hydrogen chloride. After addition of anhydrous ether (400 ml), methylmagnesium bromide (1.3 moles), dissolved in ether (600 ml), was added over a period of one hour. The flask was cooled in an ice bath throughout the addition. The resulting mixture was stirred for 20 hours. After pouring the reaction mixture onto a slurry of cracked ice, water and sodium bicarbonate (218 g, 2.6 moles), the ether layer was dried over anhydrous calcium sulfate. Fractional distillation gave: (chloro-3,3,3-trifluoropropyl)dimethylethoxysilane (28.3 g, 0.13 mole), an 11 % yield; (chloro-3,3,3-trifluoropropyl)methyldiethoxysilane (192 g, 0.72 mole), a 60 % yield; (chloro-3,3,3-trifluoropropyl)triethoxysilane (23.1 g, 0.078 mole), a 9.5 % yield. Vapor phase chromatographic analysis indicated each fraction was > 99 % one component. For the analyses, physical properties and isomeric compositions, see Tables 2 and 4.

(4) *Hydrolysis of (chloro-3,3,3-trifluoropropyl)methyldiethoxysilane*

(Chloro-3,3,3-trifluoropropyl)methyldiethoxysilane (165 g, 0.61 mole) was added rapidly to 1 *N* hydrochloric acid (500 ml). The mixture was stirred for two hours, toluene (500 ml) was added, and stirring was continued for 16 hours. The toluene layer was placed in a distillation flask, and any remaining water was removed via the toluene/water azeotrope. The toluene was removed by distillation, and the remaining material was distilled through a Vigreux column. (Chloro-3,3,3-trifluoropropyl)-methylpolysiloxane was obtained in a 77 % yield. The infrared spectrum indicated a mixture of linear and cyclic polysiloxanes with a small amount of silanol present; no ethoxy groups were detected. The analysis, physical properties and isomeric composition are given in Tables 2 and 4.

(5) *Vapor phase chromatography*

The vapor phase chromatographic analyses were carried out using a ten-foot column with a silicone, DC F60, (20 %) on Celite-545 packing. Helium was used as the carrier gas with a flow rate of approximately 60 cc/min. The area under the peaks were assumed to be proportional to the mole per cent of the components presence*. The chromatographic peaks from mixtures were identified by comparison with the retention times of the isolated compounds.

The above column did not separate the two monochloro isomers, (1- and 2-chloro-3,3,3-trifluoropropyl)trichlorosilane. Attempts to separate these isomers using the following conditions were not successful: (*a*) A ten-foot column with a silicone, DC F4050, (20 %) on Chromasorb P packing (helium carrier gas); (*b*) a ten-foot column with Ucon LB550X (20 %) on Celite-545 packing (hydrogen carrier gas).

(6) *Nuclear magnetic resonance*

The spectra were obtained using a Varian 4300B High Resolution NMR Spectrometer operating at 40 Mc/sec. The usual sample spinning and sideband modulation techniques were employed. Fluorotrichloromethane was used as the solvent, and the chemical shifts were measured relative to the ^{19}F resonance peak of the solvent.

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* If the components are not very different in type and helium or hydrogen is used as the carrier gas, the areas under the peaks of a gas chromatogram are a good estimate of the concentrations[11].

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SUMMARY

The chlorination of (3,3,3-trifluoropropyl)trichlorosilane is reported. The chlorinated products were isolated, when possible, and their structures were determined. The C–H bonds in the α-position to silicon were found to be about 6.2 times more susceptible to attack by a chlorine radical than the C–H bonds in the β-position. Some reactions of the monochlorinated products are reported.

REFERENCES

1 C. Walling, *Free Radicals in Solution*, Wiley, New York, 1957, pp. 352–369.
2 H. C. Brown and A. B. Ash, *J. Am. Chem. Soc.*, 77 (1955) 4019.
3 P. C. Anson, P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, (1959) 918.
4 P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, (1960) 144.
5 P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, (1961) 3520.
6 P. S. Fredricks and J. M. Tedder, *Chem. Ind. (London)*, (1959) 490.
7 A. L. Henne and A. M. Whaley, *J. Am. Chem. Soc.*, 64 (1942) 1157.
8 L. H. Sommer and F. C. Whitmore, *J. Am. Chem. Soc.*, 68 (1946) 485.
9 P. Tarrant, G. W. Dyckes, R. Dunmire and G. B. Butler, *J. Am. Chem. Soc.*, 79 (1957) 6536.
10 G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, 63 (1959) 761.
11 A. I. M. Keulemans, *Gas Chromatography*, Reinhold, New York, 2nd ed., 1959, pp. 32–33.