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A Study of the Chlorination of Methylchlorosilanes

BY JOHN L. SPEIER

The relative rates of chlorination of trimethylchlorosilane, *t*-butyl chloride and trimethylchlorosilane and dimethyldichlorosilanes were determined and the anomalous tendency for the exhaustive chlorination of one methyl group in the methylchlorosilanes was investigated and discussed. The following new compounds were isolated: tris-(chloromethyl)-methylsilane, dichloromethylchloromethyldimethylsilane, trichloromethyltrimethylsilane and trichloromethyldimethylchlorosilane.

Several investigators have studied the chlorination of alkylsilanes since Friedel and Crafts[1] in 1865 discovered that tetraalkylsilanes could be successfully chlorinated without breaking the silicon-carbon linkages. The photo chlorination of the methylchlorosilanes was first reported by Krieble and Elliott[2] who noted that a chloromethyl group was chlorinated in preference to an unsubstituted methyl group. The peroxide catalyzed chlorination of trimethylchlorosilane and *t*-butyl chloride was later studied by McBride and Beachell.[3]

The observations of Krieble and Elliott have been confirmed in this Laboratory during several years and further data concerning the anomalies found during the chlorination of methylsilicon compounds were obtained. Very interesting results have been found which shed new light on the role of silicon in organosilicon compounds during chlorination. Several new chlorinated methylchlorosilanes were isolated.

Experimental

Method.—All chlorinations were carried out in the presence of light from a 60-watt incandescent lamp, unless otherwise stated, at 55–60° in a round-bottom flask equipped with a chlorine inlet tube, a thermometer well and a knockdown condenser cooled to about −70°. The gases that escaped the condenser were passed through a cold-trap and then through an aqueous alkali scrubber. No detectable amount of organic material ever reached the scrubber and usually only a few grams was found in the cold-trap. The extent of chlorination was checked by measuring the amount of alkali neutralized and then by weighing the chlorinated mixture to determine the gain in weight. The two values agreed reasonably well with one another, with the alkali consumed generally being slightly more than the gain in weight would allow.

Chlorination of Me_3SiCl and Me_3CCl.—Trimethylchlorosilane (434 g., 4 moles) was chlorinated with about 3.2 moles of chlorine, and *t*-butyl chloride (185 g., 2 moles) was chlorinated with about 1.6 moles of chlorine. The products were distilled in a simple column 4 feet long, of 8 mm. diameter containing a single nichrome spiral for a packing. This column has been found capable of separating components boiling 20° apart with only about 1 g. between plateaus. Components boiling 10° apart are separated only poorly. Table I lists the products obtained.

TABLE I

PRODUCTS FROM THE CHLORINATION OF Me_3XCl

(X = Si OR C)

Formula	X = Si B.p., °C. at 734 mm.	Mole %	X = C B.p., °C. at 747 mm.	Mole %
Me_3XCl	56.5	41.5	51.5	36.2–36.7
Me_2XClCH_2Cl	113–115[a]	39.0	105	51
$Me_2XClCHCl_2$	148[a]	11.7	145	
$Me_2XClCCl_3$[b]	161 at 739 mm. m.p. 95–96°	1.2	No trace on distillation curve	
$MeXCl(CH_2Cl)_2$	168–173[a]	2.4	140–160[c]	8.8
Residue taken as $C_3H_5Cl_4X$	>173[d]	2.6	>160	2.0
Total		98.4		98–98.5
Lost over-all		1.6		2–1.5

[a] Reference 2 reports for compounds 2, 3 and 5 b.p.'s of 115, 149, 172°. Reference 3 reports for compound 2, a b.p. of 115.2–116° at 762 mm. [b] Compounds 4 and 5 were not separated. The distillation curve showed a slight inflection at 160–162° and a better plateau at 168–172°. The fraction at 148–162° had 18.7% hydrolyzable chlorine. The fraction at 168–173° had 18.5% hydrolyzable chlorine corresponding to $SiC_3H_6Cl_4$ and $SiC_3H_7Cl_3$ in the amounts shown. The 148–173° material was refractionated through a column of about 50 plates and a small amount, about 8 g., of sludgy crystals were obtained, b.p. 161°. The identity of the components was assumed on the basis of their known boiling points (see next part). [c] This fraction was mixed isomers of $C_4H_7Cl_3$. No effort was made to separate these. [d] A small amount of material (6 g.) was found boiling at 193°. This was not investigated and is included in the residue, but was probably $MeSiCl(CHCl_2)(CH_2Cl)$.

Chlorination of Dichloromethyldimethylchlorosilane.—It seemed likely from the boiling point that the substance described in the footnotes of Table I as boiling in the range of 148–173° was trichloromethyldimethylchlorosilane, a compound not previously known. In order to prepare a sample of this compound so that its boiling point could be determined, dichloromethyldimethylchlorosilane (b.p. 148° at 734 mm., $n^{25}D$ 1.4588, 177.5 g., 1 mole) was chlorinated until it gained 12 g. in weight.

The product was distilled and after the unreacted starting material was recovered 32 g. of a crystalline fraction was obtained which proved to be slightly impure trichloromethyldimethylchlorosilane, b.p. 161° at 739 mm., f.p. from a time-temperature plot, about 95–96°.

Anal. Hydrolyzable chlorine calculated for Cl_3CMe_2SiCl, 16.7; found, 17.1.

The identity of the compound was established by hydrolysis in ammonia water which is known to cleave Cl_3C groups from silicon[2] and distillation of the hydrolyzate. Chloroform, b.p. 60.5°, $n^{25}D$ 1.4428, $d^{25}{}_4$ 1.48, sp. ref. 0.179 (calculated[4] 0.179), was obtained, leaving a residue of dimethylpolysiloxane polymer, $n^{25}D$ 1.3930, $d^{25}{}_4$ 0.95; sp. ref. 0.251, calculated 0.252.

Anal. Calcd. for $(Me_2SiO)_x$: Si, 37.9. Found: Si, 38.1.

It appears reasonably certain, therefore, that the identity of the impurity found boiling in the 148–173° range was actually trichloromethyldimethylchlorosilane.

Discussion

The chlorination of trimethylchlorosilane may be considered as a series of consecutive reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C, \text{ etc.}$$

where A is trimethylchlorosilane, B is chloromethyldimethylchlorosilane and C is any more highly chlorinated product. The process may then be treated as outlined by Glasstone[5]

$$C_a = ae^{-k_1t} \qquad (1)$$

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(1) A. Friedel and J. Crafts, *Compt. rend.*, **61**, 792 (1865).

(2) R. H. Krieble and J. R. Elliott, THIS JOURNAL, **67**, 1810 (1945).

(3) J. J. McBride and H. C. Beachell, *ibid.*, **70**, 2532 (1948).

(4) E. L. Warrick, *ibid.*, **68**, 2455 (1946).

(5) S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 1055.

$$C_b = a\frac{k_1}{k_2 - k_1}(e^{-k_1t} - e^{-k_2t}) \qquad (2)$$

where C_a and C_b are the concentrations of A and B at any time; k_1 and k_2 are the respective rates of chlorination, and a is the original concentration of A, *i.e.*, unity.

If t is taken as unity, these equations are soluble for k_1 and k_2; though they will be of unknown units they should be comparable.

Solving equation 1 with the data of Table I in mole fractions, we find for trimethylchlorosilane $0.415 = 1e^{-k_1}$; $k_1 = 0.88$. From equation 2 and this value for k_1, the expression

$$C_b = 1\frac{0.88}{k_2 - 0.88}(0.415 - e^{-k_2})$$

is obtained. Graphical solution of this equation, plotting C_b *vs.* k_2, shows k_2 is about 0.75 at the experimental value of 0.39 for C_b. The ratio $k_1/k_2 = 1.2$. Thus the rates of chlorination are nearly the same for trimethylchlorosilane and for chloromethyldimethylchlorosilane.

The same treatment shows that $k_1 = 1.01$; $k_2 = 0.39$ and $k_1/k_2 = 2.6$ for the chlorination of *t*-butyl chloride.

From these ratios it is evident that the presence of the second chlorine in the butane structure results in a considerable deactivation of the entire molecule toward further chlorination, but that such deactivation is present to an almost negligible amount in the exactly analogous silicon-containing structure.

The distribution of the di- and trichlorinated products of Me_3SiCl as listed in Table I are found to be most unusual when compared with the analogous products from the chlorination of *t*-butyl chloride. Rogers and Nelson[6] chlorinated *t*-butyl chloride under nearly the same conditions used here. Their data, although not comparable in detail since the extent of chlorination, the amounts of recovered *t*-butyl chloride and residue are not known, indicate pronounced differences in the distribution of products. Table II summarizes their data and compares them with the data concerning the silicon compounds.

TABLE II

CHLORINATION PRODUCTS OF Me_3XCl

Formula	B.p., °C. at 760 mm. X = C[6]	B.p., °C. at 760 mm. X = Si	Mole % yield from chlorination X = C[6]	Mole % yield from chlorination X = Si
Me_2XClCH_3	51.5[a]	57	No data	41.5
Me_2XClCH_2Cl	107	115	8.4	39.0
$Me_2XClCHCl_2$	144.5–145.4	149	15.5	11.7
$Me_2XClCCl_3$	M.p. 178.6–179.6	M.p. 95–96	Trace	1.2
$MeXCl(CH_2Cl)_2$	162.0–163.1	172	22.9	2.4
$XCl(CH_2Cl)_3$	206–210	...	3.1	
$MeXCl(CH_2Cl)$-$(CHCl_2)$	190.6–191.3	...	10.9	Trace (?)

[a] Huntress, E. H., "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 955.

That exhaustive chlorination of one methyl group is much more the tendency in trimethylchlorosilane than in *t*-butyl chloride is shown plainly by comparing the ratios

$$\frac{Me_2CClCHCl_2}{MeCCl(CH_2Cl)_2} = 0.67; \text{ and } \frac{Me_2SiClCHCl_2}{MeSiCl(CH_2Cl)_2} = 4.9$$

Experimental: Competitive Chlorination of Me_3SiCl and Me_2SiCl_2.—To determine the relative ease of chlorination of trimethylchlorosilane and dimethyldichlorosilane, a mixture of these compounds was prepared from one mole of trimethylchlorosilane (3 equivalents of methyl groups) and 1.5 moles of dimethylchlorosilane (3 equivalents of methyl groups). This mixture was chlorinated until it gained 32 g. in weight. The mixture was then distilled using a Stedman column of about 50 theoretical plates. The distillation curve showed the amounts of products listed in Table III.

TABLE III

CHLORINATION OF $Me_3SiCl + 1.5\ Me_2SiCl_2$

Formula	B.p., °C. at 737 mm.	Grams	Mole % of charged compounds
Me_3SiCl	57	39	36
Me_2SiCl_2	70	172	89
$Me_2SiClCH_2Cl$[a]	114	70.5	49
$MeSiCl_2CHCl_2$[a]	122	15	6.3
$Me_2SiClCHCl_2$[a]	147	18.2	*ca.* 10
Residue		17	
Lost over-all		2	

[a] Reference 2 reports for compounds 3 through 5 the following b.p.'s: 115, 122 and 149°.

Discussion.—Table III indicates that 64% of the Me_3SiCl and only 11% of the Me_2SiCl_2 was chlorinated. If the rate of chlorination of the first methyl group in each compound is expressed as

$$-dMe/dt = k_1(Me)(Cl_2)_2$$

and

$$-dMe'/dt = k_2(Me')(Cl_2)$$

where k_1 and Me refer to methyl groups on Me_3SiCl and k_2 and Me′ refer to methyl groups in Me_2SiCl_2, one finds from these data that $k_1/k_2 = 9$. It appears that the rate of disappearance of Me_3SiCl is about 9 times that of Me_2SiCl_2. The presence of the additional chloride substituent on silicon thus clearly resulted in a strong deactivation of the neighboring methyl groups toward chlorination, as might be expected.

Experimental.—Competitive Chlorination of Me_3SiCl and Me_3CCl.—A mixture of one mole of trimethylchlorosilane and one mole of *t*-butyl chloride was chlorinated until it gained 22.4 g. The mixture was then fractionated into two fractions and a residue by means of the small still. Fraction 1, b.p. 51–57°, and fraction 2, b.p. 107–119°, were poured upon ice to hydrolyze the chlorosilanes, dried immediately and redistilled to separate the butyl chlorides from the disiloxanes. The hydrolyzed mixtures were easily separable as *t*-butyl chloride, b.p. 51°, and hexamethyldisiloxane, b.p. 100°, from fraction 1, and 1,2-dichloro, 2-methylpropane, b.p. 107°, and *sym*-bis-chloromethyltetramethyldisiloxane, b.p. 205°, from fraction 2. The residue boiling above 119° was not investigated. By this means the chlorination mixture was analyzed and found to have contained the products listed in Table IV.

TABLE IV

PRODUCTS FROM THE CHLORINATION OF 1/1 Me_3SiCl AND Me_3CCl

Formula	Grams	Mole % charge
Me_3CCl	65.4	71
Me_3SiCl	75.6	70
Me_2CH_2ClCCl	34.0	27
$Me_2CH_2ClSiCl$	34.3	24
Polychlorides, b.p. 119°	12.0	..
Total	221.3	
Lost over-all	2.5	

Discussion.—Despite the different orientation effects of silicon and carbon during chlorination,

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(6) A. O. Rogers and R. E. Nelson, THIS JOURNAL, **58**, 1027 (1936).

TABLE V

PRODUCTS FROM THE CHLORINATION OF Me_3SiCH_2Cl

Formula	B.p., °C. at 749 mm.	$n^{25}D$	d^{25}_4	Mole %	Sp. ref. Calculated	Sp. ref. Found
Me_3SiCH_2Cl[a]	97.2	1.4148	0.8765	35.5	0.2865	0.2856
$Me_3SiCHCl_2$[b]	133–134	1.4430	1.04	20.0	0.2544	0.254
Me_3SiCCl_3[c]	146–156	M. p. 60–66°		1.3	%Cl, 55.54	55.4
$Me_2Si(CH_2Cl)_2$[b]	160–161	1.4573	1.08	30.5	0.2544	0.253
$Me_2SiCH_2ClCHCl_2$[c]	183–184	1.4753	1.209	8.5	0.2338	0.2330
					%Cl, 55.54	55.45
$MeSi(CH_2Cl)_3$[c]	205	1.4857	1.24	2.1	0.2338	0.231
					%Cl, 55.54	55.53
Residue as $SiC_4H_8Cl_4$		1.490		1.1		
Total				99.0		

[a] F. C. Whitmore and L. H. Sommer, THIS JOURNAL, **68**, 481 (1946), report: b.p. 97.1° at 734 mm., $n^{20}D$ 1.4180, d^{25}_4 0.8791. [b] J. L. Speier and B. F. Daubert, *ibid.*, **70**, 1400 (1948), report for $Me_3SiCHCl_2$, b.p. 133° at 730 mm., d^{25}_4 1.0395, $n^{25}D$ 1.4430; for $Me_2Si(CH_2Cl)_2$, b.p. 160° at 724 mm., d^{25}_4 1.075, $n^{25}D$ 1.4579. [c] These were previously unreported compounds. Their configurations were assigned on the basis of their boiling points.

the rates of chlorination for the substitution of the first chlorine were nearly identical for the analogous structures Me_3CCl and Me_3SiCl, but the presence of less $Me_2ClSiCH_2Cl$ than Me_2ClCCH_2Cl showed again that the former was chlorinated more rapidly than the latter.

Experimental. Chlorination of Me_3SiCH_2Cl.—Two moles of chloromethyltrimethylsilane (b.p. 97.2° at 740 mm., $n^{25}D$ 1.4148, 245 g.) was chlorinated until it weighed 300 g. Approximately 1.6 moles of chlorine were used. The products were then distilled carefully and the products listed in Table V were found.

Discussion.—The chlorination of chloromethyltrimethylsilane revealed that in this compound no unusual orientation effects of silicon were apparent. The most symmetrical products were the chief ones formed as is typical of hydrocarbon chlorinations. The chlorination of *t*-butyl chloride gave a ratio of $Me_2CClCHCl_2/MeCCl(CH_2Cl)_2 = 0.67$. The ratio of $Me_3SiCHCl_2/Me_2Si(CH_2Cl)_2 = 0.66$. The symmetrical trichloride was obtained, and this is the first example of such a structure ever reported. No trace of the corresponding structure from trichlorosilane has ever been found.

The typical hydrocarbon character toward chlorination of the chloromethyltrimethylsilane shows that silicon alone is not responsible for the anomalous distribution of products obtained from methylchlorosilanes. The halogen is essential on silicon if the effect is to be noted. Probably other negative substituents on silicon give rise to the same phenomenon, and we have qualitatively observed this same distribution in chlorinated methylsiloxanes.

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[CONTRIBUTION FROM THE MELLON INSTITUTE]

Bromination of Methylchlorosilanes

BY JOHN L. SPEIER

A solution of bromine in compounds difficult to brominate reacted smoothly in the presence of chlorine and light to yield brominated derivatives. The process was equally applicable for brominating hydrocarbons such as benzene, toluene and cyclohexane as for methylchlorosilanes. New compounds described were: bromomethyltrimethylsilane; bromomethyldimethylchlorosilane; bromomethylmethyldichlorosilane; dibromomethylmethyldichlorosilane; *sym*-bis-(bromomethyl)-tetramethyldisiloxane; bromomethylpentamethyldisiloxane; bromophenyltrichlorosilane.

Except for one instance, a thorough search of the literature revealed no reference concerning the direct bromination of organosilicon compounds. E. Larsson and L. O. Knopp[1] have brominated tetraethylsilane at reflux temperature with bromine. A similar procedure using trimethylchlorosilane, dimethyldichlorosilane or hexamethyldisiloxane produced no reaction in this Laboratory.

The addition of chlorine to a solution of bromine in any of these or related compounds caused immediate reaction to occur with the formation of only brominated organosilicon compounds and hydrogen chloride. No carrier or catalyst of any kind was found necessary.

Remick[2] states that bromine chloride is a powerful brominating agent. This is true, but a reasonably thorough literature search brought to light no examples of bromine chloride as a brominating agent until McBee, Sanford and Graham[3] used it with a carrier to brominate trifluoromethylbenzenes.

The reagent is excellent for the bromination of methylsilicon compounds as well as for many organic compounds. The bromine in some cases is nearly quantitatively converted to bromides.

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(1) E. Larsson and L. O. Knopp, *Acta Chem. Scand.*, **1**, 268 (1947).

(2) A. E. Remick, "Electronic Interpretation of Organic Chemistry," J. Wiley and Sons, Inc., New York, N. Y., 1943, p. 129.

(3) E. T. McBee, R. A. Sanford and P. J. Graham, THIS JOURNAL, **72**, 1651 (1950).