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	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 %Cl, 55.54	0.2330 55.45
$MeSi(CH_2Cl)_3{}^c$	205	1.4857	1.24	2.1	0.2338 %Cl, 55.54	0.231 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).

Very little, if any, hydrogen bromide is produced. The reaction is easily carried out on either aliphatic or aryl hydrocarbons as well as on silicon compounds.

Experimental

Bromination Using Bromine and Chlorine.—The following technique was employed in every case. As an example the bromination of trimethylchlorosilane will be described in detail.

Bromomethyldimethylchlorosilane.—Trimethylchlorosilane (119 g., 1.1 moles) was illuminated with a 60-w. incandescent lamp in a 500-ml. flask equipped with a reflux condenser topped by a Dry Ice cooled knock down condenser. From a separatory funnel a small amount of bromine was added. Chlorine was then passed through the mixture until the dark red color of bromine disappeared. More bromine was then added and the process was continued until 46.5 g., 0.64 equivalent, was added. The mixture then weighed 168 g. According to the equation $2RH + Cl_2 + Br_2 \rightarrow 2RBr + 2HCl$ the product should weigh 169 g.

The gases that escaped the condensers were trapped in aqueous alkali. Qualitative analysis showed no bromide in the trap at the end of the experiment. The product was distilled and yielded 61 g., 51% of recovered trimethylchlorosilane; no trace of trimethylbromosilane; a possible trace of chloromethyldimethylchlorosilane, and in addition to a residue of polybrominated products, 75 g. of bromomethyldimethylchlorosilane, b.p. 130° at 740 mm., $n^{25}\mathrm{D}$ 1.4630, d^{25}_{4} 1.375, sp. ref. 0.2002, calculated[4] sp. ref. 0.2005; yield 62% based on bromine. *Anal.* Calcd. for $C_3H_8BrClSi$: Cl, 18.91. Found: Cl, 18.83.

***sym*-Bis-bromomethyltetramethyldisiloxane.**—A sample of bromomethyldimethylchlorosilane so obtained was hydrolyzed by shaking it with water. The aqueous layer was tested qualitatively for bromide ion. None was found. Therefore, no readily hydrolyzable bromine was present and no isomer such as chloromethyldimethylbromosilane was present. The hydrolysate was washed with water, separated and dried over sodium sulfate. With no further purification *sym*-bis-(bromomethyl)-tetramethyldisiloxane was obtained with the following properties; b.p. 232–235° at 734 mm., $n^{25}\mathrm{D}$ 1.4719, d^{25}_{4} 1.3918, sp. ref. 0.2004, calculated[4] sp. ref. 0.2008. *Anal.* Calcd. for $C_6H_{16}OBr_2Si$: Si, 17.53. Found: Si, 17.5.

Bromomethyltrimethylsilane.—A sample of bromomethyldimethylchlorosilane was treated with 10% excess methylmagnesium bromide in ether. Worked up in the usual manner, a yield of 80% of theory of bromomethyltrimethylsilane was obtained, b.p. 115.5° at 742 mm., $n^{25}\mathrm{D}$ 1.4422–1.4424, d^{25}_{4} 1.170, sp. ref. 0.2254, calculated[4] sp. ref. 0.2272. *Anal.* Calcd. for $C_4H_{11}BrSi$: Br, 47.9. Found: Br, 47.7. A product of the same properties was prepared more easily by brominating tetramethylsilane.

Bromomethylmethyldichlorosilane and Dibromomethylmethyldichlorosilane.—Dimethyldichlorosilane (2 moles) with bromine (1 equiv.) by the same technique yielded bromomethylmethyldichlorosilane, b.p. 140–141° at 740 mm., $n^{25}\mathrm{D}$ 1.4750, d^{25}_{4} 1.57, sp. ref. 0.179; calculated sp. ref. 0.1789; yield 34%. *Anal.* Calcd. for $C_2H_5BrCl_2Si$: Cl, 34.10. Found: Cl, 34.5. Dibromomethylmethyldichlorosilane was also obtained, b.p. 86–91° at 25 mm., $n^{25}\mathrm{D}$ 1.5185; yield 24.8%, based on bromine used. Steam distillation of this compound from 5% aqueous sodium hydroxide yielded methylene bromide, b.p. 95° at 742 mm., d^{25}_{4} 2.4, $n^{25}\mathrm{D}$ 1.5290, sp. ref. 0.128, calculated, sp. ref. 0.127; yield 86%. The isolation of methylene bromide established the configuration of the brominated silicon compound. The higher boiling products were a crystalline mixture which was not separated.

Bromomethylpentamethyldisiloxane.—Hexamethyldisiloxane (286 g., 1.76 moles) similarly brominated with 1.54 equivalents of bromine yielded bromomethylpentamethyldisiloxane, b.p. 83° at 49 mm., $n^{25}\mathrm{D}$ 1.4279, d^{25}_{4} 1.097, sp. ref. 0.2345, calculated sp. ref. 0.2347; yield 25%. *Anal.* Calcd. for $C_6H_{17}OBrSi$: Si, 23.3; Br, 33.1. Found: Si, 23.1; Br, 34.5. Higher boiling isomeric dibromides were obtained (28 g.) b.p. 72–104° at 16 mm. which were extremely active lachrymators. This fraction turned dark and fumed soon after distillation. It obviously decomposed on storage before it was to be analyzed. Higher boiling fractions were also obtained, all of which appeared to be di- and tribromides. No pure compounds were isolated from this high boiling mixture. The lachrymatory properties of these fractions probably may be associated with two or more bromide substituents on the same carbon. Pure bisbromomethyltetramethyldisiloxane shows no such activity.

Other Brominations.—The procedure was used on hydrocarbons usually with the hydrocarbon:bromine ratio of 2:1. The following results were obtained with the yields based on bromine: toluene yielded 71% benzyl bromide; cyclohexane yielded 45% cyclohexyl bromide, and 38% cyclohexyl dibromides; benzene yielded 68% bromobenzene; phenyltrichlorosilane yielded 40% bromophenyltrichlorosilane, b.p. 126–128° at 23 mm.[5] *Anal.* Calcd. for $C_6H_4BrCl_3Si$: Cl, 36.6. Found: Cl, 36.6.

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

(5) G. Gruttner and E. Krause, *Ber.*, **50**, 1559 (1917), report a b.p. of 123° at 15 mm. for *p*-bromophenyltrichlorosilane.