[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

IV. The Preparation and Fluorination of Dimethyl and Trimethyl Chlorosilanes[1]

BY HAROLD SIMMONS BOOTH AND JOHN FRANCIS SUTTLE[2]

The recent development of silicones derived chiefly from the dimethylchlorosilanes prompted us to study the dimethyl and trimethyl chlorosilanes and their fluorination products. The information on these chlorosilanes was, at the time this investigation was carried out, incomplete and in some cases incorrect. Previous investigations in this Laboratory have shown that alkyl chlorosilanes may be fluorinated by antimony trifluoride to yield chlorofluorides and fluorides.[3,4,5]

Methyl trichlorosilane and dimethyl dichlorosilane were not[6] reported until 1941 by Gilliam, Liebhafsky, and Winslow.[7] Hyde and DeLong[8] also prepared dimethyldichlorosilane by means of a Grignard reaction. The preparation and purification of trimethyl chlorosilane had not been described in the literature until after this investigation was completed. Taylor and Walden[9] have recently made it by chlorination of trimethylsilane.

Experimental

Preparation and Purification of Dimethyl Dichlorosilane.—The procedure first used in preparing dimethyl dichlorosilane was similar to that used by Gilliam and coworkers.[7] Since the boiling points of methyl trichlorosilane and dimethyl dichlorosilane are only four degrees apart, a mixture of these two compounds proved to be very difficult to separate. This difficulty was surmounted in this investigation, by using a ratio of three moles of methylmagnesium bromide (based on the amount of magnesium used) in 1500 ml. ethyl ether to one mole of silicon tetrachloride in 1000 ml. ether. Any methyl trichlorosilane formed was thus converted either to dimethyl dichlorosilane or to trimethyl chlorosilane. These two latter compounds are easily separated from each other, by fractional distillation in a Dufton type gas column[10] at 100 mm. pressure with the head temperature at 17°. Each of the two main fractions, consisting of crude dimethyl dichloro silane and crude trimethyl monochlorosilane, were then fractionally distilled twice before their use for determination of properties and analysis.

Fluorination of Dimethyl Dichlorosilane and of Trimethylmonochlorosilane.—The apparatus and procedures used in fluorination studies in this laboratory have been adequately described.[10,11] Three fluorinations of dimethyl dichlorosilane under different conditions were tried with the object of getting as much dimethyl chlorofluorosilane as possible, since the yield of the intermediate chlorofluorides of a series is generally smaller than the yield of the fully fluorinated compound.[11] In the third fluorination, no pressure control was used. The antimony trifluoride was fed into the generator rapidly, and the products were condensed in ampules as fast as possible, regardless of the pressure; however, it never was above 300 mm. All fluorinations were carried out at room temperature. Results are shown in Table I.

TABLE I

LOG OF RUNS USING DIFFERENT CONDITIONS FOR FLUORINATION OF $(CH_3)_2SiCl_2$

$(CH_3)_2SiCl_2$, g.	SbF_3, g.	$SbCl_5$, ml.	Press. control, mm.	$(CH_3)_2SiClF$, ml.	$(CH_3)_2SiF_2$, ml.
146.5	140	None	180	10	34
133	120	10	180	22	22
179	170	10	None	35	35

These results indicate that use of the catalyst, antimony pentachloride, is advisable in this reaction in order to increase the yield of the chlorofluoride. This has been found true previously in this Laboratory: the antimony pentachloride lowers the threshold temperature necessary for fluorination.[10]

In the preparation of trimethyl monofluorosilane, since the purified trimethyl chlorosilane was needed elsewhere, the crude 62–66° fraction was added dropwise to the antimony trifluoride at one atmosphere pressure, where it reacted immediately, no heating of the reaction vessel being necessary.

Purification of Fluorination Products.—The fluorination products were readily purified by fractional distillation in the low temperature column previously mentioned.

Analysis.—The dimethyl and trimethyl halogenosilanes were analyzed quantitatively by decomposition in sodium hydroxide solution and titration by the Volhard method for chlorine and by the lead chlorofluoride method[12] for fluorine. Silicon and carbon were determined qualitatively.

Determination of Physical Constants.—Molecular weights in this investigation were determined by the Regnault method similar to the manner suggested by Germann.[13] The freezing points of all compounds were obtained without difficulty by the procedure standard for this Laboratory.[14] Vapor pressures below room temperature were measured directly while those above room temperature were measured by the isoteniscope method[15] as modified by Booth and Halbedel.[4] For the temperature control and measurement of the vapor pressure bath a five junction copper–constantan thermocouple, calibrated against a platinum resistance thermometer using a Mueller bridge[16] for resistance measurement, actuated a Leeds and Northrup Speedomax electronic Recorder Controller. Curves graphed from the vapor pressure data[17] are given in

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[1] From a thesis presented by John Francis Suttle to the Graduate School of Western Reserve University, February, 1944, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, and based upon work done in connection with a research project sponsored by the Naval Research Laboratory, Office of Research and Inventions, U. S. Navy Department. Publication delayed for security reasons.

[2] Present address: University of Portland, Portland, Oregon.

[3] I, H. S. Booth and Paul Carnell, THIS JOURNAL, **68**, 2650 (1946).

[4] II, H. S. Booth and H. Halbedel, *ibid.*, **68**, 2652 (1946).

[5] III, H. S. Booth and W. F. Martin, *ibid.*, **68**, 2655 (1946).

[6] G. Martin, *Ber.*, **46**, 2442 (1913).

[7] W. F. Gilliam, H. A. Liebhafsky and A. F. Winslow, THIS JOURNAL, **63**, 801 (1941).

[8] J. F. Hyde and R. C. DeLong, *ibid.*, **63**, 1194 (1941).

[9] A. C. Taylor and B. V. Walden, *ibid.*, **66**, 842 (1944).

[10] H. S. Booth and A. R. Bozarth, *ibid.*, **61**, 2927 (1939); *Ind. Eng. Chem.*, **29**, 470 (1937).

[11] H. S. Booth and W. C. Morris, THIS JOURNAL, **58**, 90 (1936).

[12] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," 8th ed., John Wiley and Sons, New York, 1935, p. 418.

[13] A. F. O. Germann, *J. Phys. Chem.*, **19**, 437 (1915).

[14] H. S. Booth and D. R. Martin, THIS JOURNAL, **64**, 2198 (1942).

[15] H. S. Booth, H. M. Elsey and P. E. Burchfield, *ibid.*, **57**, 2064 (1935).

[16] The purchase of this equipment was made possible by assistance from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

[17] For the data for these vapor pressure curves consult the original thesis at Western Reserve University Library.

TABLE II

METHYL HALOGENOSILANES

Formula			$(CH_3)_2SiCl_2$[a]	$(CH_3)_2SiClF$	$(CH_3)_2SiF_2$	$(CH_3)_3SiCl$[b]	$(CH_3)_2SiF$
Composition, %	Chlorine	Calcd.	54.95	31.49	.....	32.64	.....
		Found	54.94 54.92	31.43 31.52	.....	32.75 32.73	.....
	Fluorine	Calcd.	.....	16.87	39.52	.....	20.61
		Found	.....	16.44 17.15	39.36 39.31	.....	20.51 20.72
Molecular weight	Calcd.		129.06	112.6	96.14	108.64	92.18
	Found		130.4	113.4	96.2	110.7	92.9
Freezing pt., °C., ±0.2			−76.1	−85.1	−87.5	−57.7	−74.3
Boiling pt., °C., ±0.1			70.0	36.4	2.7	57.3	16.4
Heat of vapn., cal.			7530	6790	6160	7220	6430
Trouton const., cal./deg.			21.9	21.9	22.3	21.8	22.2
Vapor pressure equation constants[c]	A		−1645	−2269.4	−1809.76	−1578	−1405
	B		0	−6.0833	−3.9471	0	0
	C		+7.6738	+25.3626	+19.0738	+7.6559	+7.7326
Av. random devn., mm.			3.8	1.4	1.6	2.1	1.8
Maximum deviation, mm.			−7.3	+5.7	−4.9	−5.4	+3.6

[a] Gilliam, Liebhafsky and Winslow[7] reported a boiling point of 69.0–70.2° (745 mm.) and a freezing point of −86°. [b] Taylor and Walden[9] reported a boiling point of +59° and a freezing point of approximately −40° on $(CH_3)_3SiCl$ (made by chlorination of trimethylsilane) using a pentane thermometer. [c] Constants for the equation, $\log p_{(mm)} = A/T + B \log T + C$.

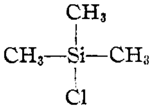
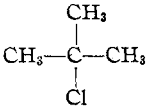
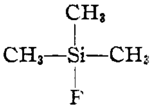
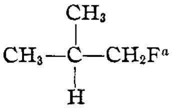
Figure 1. Physical constants and the constant for the vapor pressure equations are given in Table II.

Discussion

The preparation and purification of dimethyldichlorosilane offered no serious difficulties as long as the amount of methylmagnesium bromide was sufficient to prevent the formation of methyl trichlorosilane. Dimethyldichlorosilane and trimethylchlorosilane are both colorless liquids that fume slightly in air, the trimethylchlorosilane having this tendency to a lesser degree. Both dimethyldichlorosilane and trimethylchlorosilane have a camphor-like odor that becomes sickening on prolonged exposure.

The fluorination of dimethyldichlorosilane, using antimony pentachloride as catalyst, resulted in equal amounts of dimethyl chlorofluorosilane and dimethyldifluorosilane; however, when no catalyst was used, the amount of dimethyldifluorosilane was much greater than the amount of dimethylchlorofluorosilane formed.[18]

TABLE III

Formula	B. p., ° C.	Formula	B. p., ° C.
$CH_3SiCl_2CH_3$	70.0	$CH_3CCl_2CH_3$	69.7
$CH_3SiClFCH_3$	36.4	$CH_3CClFCH_3$	35.0
$CH_3SiF_2CH_3$	2.7	$CH_3CF_2CH_3$	−0.6 to −0.2°
 $CH_3-\underset{Cl}{\overset{CH_3}{Si}}-CH_3$	57.3	 $CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_3$	51–52
 $CH_3-\underset{F}{\overset{CH_3}{Si}}-CH_3$	16.4	 $CH_3-\underset{H}{\overset{CH_3}{C}}-CH_2F$[a]	16.0

[a] Corresponding carbon analog could not be found. This compound is nearly analogous.

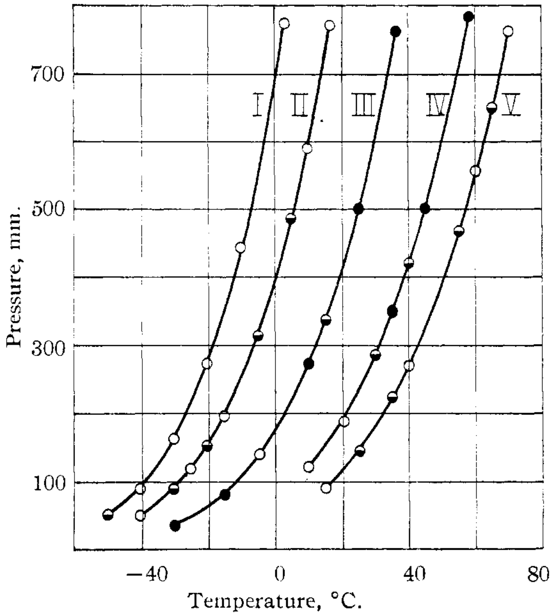


Fig. 1.—Vapor pressure: I, $(CH_3)_2SiF_2$; II, $(CH_3)_3SiF$; III, $(CH_3)_2SiClF$; IV, $(CH_3)_3SiCl$; V, $(CH_3)_2SiCl_2$· sample A, ○; sample B, ; sample C, ●.

Swarts[19] found that with a given polyhalide, the lowering of the boiling point for each fluorine substituted was a constant. This rule with a few exceptions has been found to hold true. Dimethyldichlorosilane has a boiling point of 70.0°, dimethyldifluorosilane has a boiling point of 2.7°, the two fluoride atoms have lowered the boiling point 67.3°: therefore, according to the Swarts rule, dimethylchlorofluorosilane should have a boiling point of 36.4°; actually the boiling point was found to be 36.4°.

Silicon compounds are often compared to car-

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[18] H. S. Booth and C. F. Swinehart, THIS JOURNAL, **57**, 1333 (1935).

[19] F. Swarts, *Bull. soc. chim.*, **35**, 1557 (1924).

bon compounds because of the periodic table relationship. If in the five compounds just studied, each silicon atom is replaced by a carbon atom, a surprising equality in boiling points exists.

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Summary

Dimethyldichlorosilane and trimethylchlorosilane were prepared, purified, their physical properties studied, and fluorinated. By using a higher ratio of Grignard reagent to silicon chloride than hitherto used, it was found that formation of methyltrichlorosilane was avoided, with consequent ease of purification of the dimethyl and trimethyl chlorosilanes. Three fluorination products were obtained and identified as dimethyl difluorosilane, dimethyl chlorofluorosilane, and trimethyl fluorosilane. The boiling points, freezing points, vapor pressures and molecular weights were determined and recorded for these five compounds. Dimethyl chlorofluorosilane, dimethyl difluorosilane, and trimethyl fluorosilane have not previously been reported.

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V. *i*-Propyl Trichlorosilane and its Fluorination Products[1]

BY HAROLD SIMMONS BOOTH AND DWIGHT R. SPESSARD

The stepwise fluorination of silicon tetrachloride[2] led to the application of this method to the stepwise fluorination of several alkyl chlorosilanes[3,4,5,6] in this Laboratory. So far as known, no mention of *i*-propyl trichlorosilane is made in the literature, nor of its fluorination products.

Experimental

Preparation and Purification of *i*-Propyl Trichlorosilane.—In the preparation of *i*-propyl trichlorosilane by the Grignard synthesis two moles of the Grignard mixture containing 1 liter of dry ethyl ether, was added dropwise with vigorous stirring to four moles of silicon tetrachloride in 100 ml. ether. To minimize side reactions, *i*-propyl chloride rather than bromide was used to prepare the Grignard reagent. Over-all yields of *i*-propyl trichlorosilane ranged from 35 to 50%.

Purification.—The reaction mixture was first stripped of its ether and most of the silicon tetrachloride and the resulting residual mixture in the stillpot, which was principally isopropyl trichlorosilane, was then distilled in a liquid fractionating column having a total condensation head, and take-off of the design of those used by Whitmore and Lux.[7]

Fluorination of *i*-Propyl Trichlorosilane.—The fluorination of *i*-propyl trichlorosilane was carried out by means of the Swarts reaction, using antimony trifluoride[7a] as the fluorination agent with antimony pentachloride as a catalyst. The reaction flask was identical with that described by Booth and Morris.[8] As a departure from the technique formerly used in this laboratory by Booth and Bozarth[9] and others,[3,4] the reaction was forced in order to favor the preparation of partially fluorinated products. That is, in place of a reflux condenser surmounting the flask together with an automatic take-off to bleed off higher boiling products as they were formed, a 10-mm. tube led directly from the generator to a trap and through a large bore stopcock to ampules and to the vacuum line so that everything that could be withdrawn from the flask was taken off as rapidly as possible, the vapors being condensed by means of liquid nitrogen into the ampules. At the same time, sublimed antimony trifluoride[7a] was added continuously to the mixture in the generating flask. The large bore stopcock was opened sufficiently to keep the pressure as constant and as low as possible. The initial pressure was 130 mm. and was kept under 300 mm. for most of the reaction. Although considerable amounts of the unfluorinated material, *i*-propyl trichlorosilane, distilled over into the trap, sufficient quantities of the *i*-propyl dichlorofluorosilane and *i*-propyl chlorodifluorosilane were obtained to justify this method. The unfluorinated *i*-propyl trichlorosilane was later recovered and refluorinated.

The average yields of several different fluorinations have been estimated to be as follows

(1) $i\text{-}C_3H_7SiF_3$, 75–70% (2) $i\text{-}C_3H_7SiF_2Cl$, 8–10%
(3) $i\text{-}C_3H_7SiFCl_2$, 17–20%

It is possible that by further varying the conditions, the yields of the partially fluorinated products can be increased.

Even at higher temperatures the fluorination of isopropyl trichlorosilane proceeds smoothly. The threshold fluorination temperature is below 20°.

Purification of the Products of Fluorination.—The products of fluorination, *i*-propyl trifluorosilane, *i*-propyl chlorodifluorosilane, and *i*-propyl dichlorofluorosilane, were fractionally distilled in

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[1] From a thesis presented by Dwight R. Spessard to the Graduate School of Western Reserve University, February, 1944, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, and based upon work done in connection with a research project sponsored by the Naval Research Laboratory, Office of Research and Inventions, U. S. Navy Dept. Publications delayed for security reasons.

(2) H. S. Booth and C. F. Swinehart, *ibid.*, **57**, 1333 (1935).

(3) (I) H. S. Booth and P. H. Carnell, *ibid.*, **68**, 2650 (1946).

(4) (II) H. S. Booth and H. S. Halbedell, *ibid.*, **68**, 2652 (1946).

(5) (III) H. S. Booth and W. F. Martin, *ibid.*, 2655 (1946).

(6) (IV) H. S. Booth, and J. F. Suttle, *ibid.*, **68**, 2658 (1946).

(7) A. A. Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Co., New York, N. Y., 1938, p. 83.

(7a) Supplied by courtesy of the Harshaw Chemical Co.

(8) H. S. Booth and W. Morris, THIS JOURNAL, **58**, 90 (1936).

(9) H. S. Booth and A. R. Bozarth, *ibid.*, **61**, 2927 (1939).