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.

Acknowledgments.—This investigation was carried out under the sponsorship of the Naval Research Laboratory. We are deeply indebted to members of the staff of the Chemical Division for valuable suggestions and encouragement during its progress.

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.

CLEVELAND, OHIO RECEIVED[20] AUGUST 17, 1946

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[20] Original manuscript received July 18, 1945.

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

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*-$C_3H_7SiF_3$, 75-70% (2) *i*-$C_3H_7SiF_2Cl$, 8-10%
(3) *i*-$C_3H_7SiFCl_2$, 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).

TABLE I

SUMMARY OF PHYSICAL PROPERTIES

No.			1	2	3	4
Formula			$i\text{-}C_3H_7SiCl_3$	$i\text{-}C_3H_7SiCl_2F$	$i\text{-}C_3H_7SiClF_2$	$i\text{-}C_3H_7SiF_3$
Composition, %	Cl	Calcd.	59.92	44.03	24.53	.....
		Found	59.8 59.7	44.1 44.0	24.6 24.5	...
	F	Calcd.	.....	11.80	26.28	44.48
		Found	.....	11.9 11.8	25.8	44.2 44.6
Mol. wts.	Calcd.		177.52	161.06	144.60	128.15
	Found		.....	163.7 ± 1.0	149.9 ± 1.0	130.7 ± 1.0
Freezing pt., °C.			−87.7 ± 0.2	Glass	Glass	−127.6 ± 0.2
Boiling pt., °C.			119.4 ± 0.1	84.0 ± 0.1	48.8 ± 0.1	15.7 ± 0.1
Heat of vapn., cal.			8270	7570	6890	6400
Trouton const., cal./deg.			21.1	21.2	21.4	22.2
Vap. press., log p mm. =	(for 1)		$-1836/T + 7.5593$			
	(for 2)		$-2588.1/T + 6.2103 \log T + 25.9813$			
	(for 3)		$-1525/T + 7.6180$			
	(for 4)		$-2337.2/T - 7.974 \log T + 30.5926$			
Av. random deviation, mm.			±1.0	±0.6	±1.9	±1.1
Maximum deviation, mm.			+3.3	+1.4	+2.8	−2.9

a partial condensation type of gas column.[10] The cooling agent used in the column head was acetone cooled by a Dry Ice–acetone bath. The *i*-propyl trichlorosilane was distilled at pressures ranging from 500 to 700 mm.; the *i*-propyl chlorodifluorosilane at pressures from 180 to 240 mm.; the *i*-propyl dichlorofluorosilane at pressures lower than 70 mm.

Analyses.—The method of taking samples and preparing them for analysis was carried out as described by Booth and Suttle.[6] Chlorine was determined by the Volhard method and fluorine by the lead chlorofluoride method,[11] and the results are shown in Table I. The presence of carbon and silicon was established qualitatively.

Determination of Physical Constants.—Freezing points were determined as described by Booth and Martin.[12] *i*-Propyl trichlorosilane and *i*-propyl trifluorosilane gave easily reproducible freezing points. The latter compounded tended to supercool as much as 12° at times. While no satisfactory freezing points could be obtained for *i*-propyl monofluorodichlorosilane, and for *i*-propyl difluoromonochlorosilane, on account of glass formation, the latter did occasionally crystallize at approximately −141°.

Vapor pressures were determined as described by Booth and W. F. Martin,[5] and are given in Table I in the form of equations and in Fig. 1 as a graph of the original data.[13]

Physical and Chemical Properties.—None of these compounds hydrolyzes rapidly on exposure. Consequently they have their own characteristic odor as well as that of the hydrogen halides. They are all readily hydrolyzed and dissolved by strong alkaline hydroxides. The trifluoride has no action on mercury at room temperature but mercury is smutted slightly in time by the *i*-propyl halogeno silanes containing chlorine.

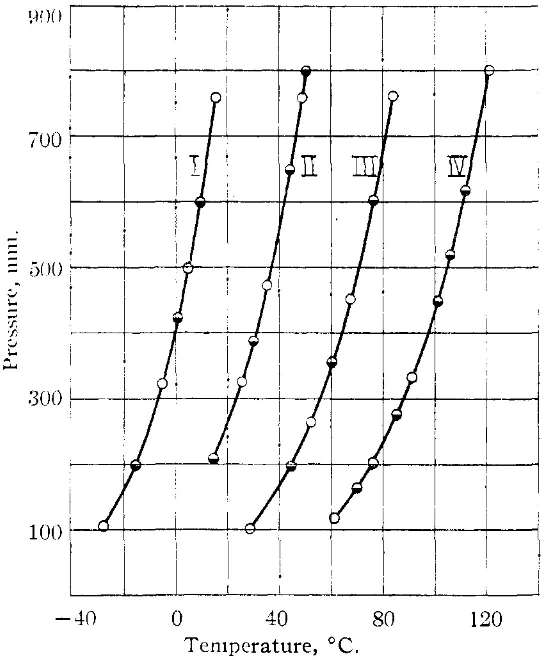

Fig. 1.—Vapor pressure of: I, $i\text{-}C_3H_7SiF_3$; II, $i\text{-}C_3H_7SiClF_2$; III, $i\text{-}C_3H_7SiCl_2F$; IV, $i\text{-}C_3H_7SiCl_3$: sample A, ○; sample B, ●.

Swarts[14] observed that the replacement of chlorine in a polychlorinated organic compound by fluorine, gave a regular almost constant lowering of the boiling point. Table II shows that the Swarts rule, which is so useful in the prediction of

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

[11] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. 11, 8th ed., Wiley and Sons, New York, 1935, p. 418.

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

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

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

boiling points is applicable to the ethyl and *i*-propyl trihalogenosilanes.

TABLE II

BOILING POINT DIFFERENCES OF ETHYL AND *i*-PROPYL TRIHALOGENO SILANES

Compound	B. p., ° C.	Diff.	Av.
$C_2H_5SiCl_3$	97.9	35.7	34.1
$C_2H_5SiCl_2F$	62.2	35.0	
$C_2H_5SiClF_2$	27.2	31.0	
$C_2H_5SiF_3$	−4.2		
i-$C_3H_7SiCl_3$	119.4	35.4	34.5
i-$C_3H_7SiCl_2F$	84.0	35.2	
i-$C_3H_7SiClF_2$	48.8	33.1	
i-$C_3H_7SiF_3$	15.7		

Acknowledgments.—This investigation was carried out under the sponsorship of the Naval Research Laboratory. We are deeply indebted to members of the staff of the Chemical Division for valuable suggestions and encouragement during its progress.

Summary

Methods are described for the preparation and purification of *i*-propyl trichloro-, dichlorofluoro-, chlorodifluoro- and trifluorosilane. All of these compounds are new substances not previously mentioned in the literature. Certain of their physical constants and chemical properties are described.

CLEVELAND, OHIO RECEIVED[15] AUGUST 17, 1946

(15) Original manuscript received July 18, 1945.

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

VI. Preparation and Fluorination of *n*-Butyl Trichlorosilane[1]

BY HAROLD SIMMONS BOOTH AND ALBERT A. SCHWARTZ

The use of the alkyl chlorosilanes in the preparation of silicones by hydrolysis and condensation has necessitated more adequate information on their properties. Little has been known about the alkyl halogeno silanes containing fluorine. This article presents the results of continued systematic study[2,3,4,5,6] of these compounds and their fluorination products.

In this investigation *n*-butyl trichlorosilane (*n*-$C_4H_9SiCl_3$) was prepared, and fluorinated by the Swarts reaction.[7,8] The fluorination yielded *n*-butyl dichlorofluorosilane (*n*-$C_4H_9SiCl_2F$), *n*-butyl chlorodifluorosilane (*n*-$C_4H_9SiClF_2$), and *n*-butyl trifluorosilane (*n*-$C_4H_9SiF_3$).

Experimental

Preparation and Purification of *n*-Butyl Trichlorosilane.—The *n*-butyl trichlorosilane used in these studies was prepared by the Grignard synthesis as described by Bygden[9] save that excess silicon tetrachloride (2 moles for each mole of butylmagnesium bromide) and rapid stirring were necessary in order to reduce to a minimum the yields of the di-, tri- and tetra-*n*-butylsilane derivatives, which tended to form in considerable amounts, particularly if the ratio of silicon tetrachloride to butylmagnesium bromide was not kept well above about 1.5:1.

The final purification of the *n*-butyl trichlorosilane for the purposes of analysis and determination of physical constants was achieved in an electrically heated, liquid distillation column with an inside diameter of 10 mm. packed for a length of 50 cm. with single turn glass helices and equipped with a Whitmore–Lux[10] total condensation, variable take-off type head[11] containing a thermocouple well. The middle fraction was redistilled and used for study.

Fluorination of *n*-Butyl Trichlorosilane.—The apparatus and experimental technique and procedures used in the fluorination were the same as that described by Booth and Spessard.[6] In every experiment the quantity of antimony fluoride used was in excess of the amount needed to fluorinate completely all the *n*-butyl trichlorosilane present.

The fluorination of *n*-butyl trichlorosilane proceeds sluggishly below about 70°. At any given temperature there appeared to be a minimum pressure at which fluorination proceeded smoothly. This minimum pressure increased with increasing temperature.

A study of the log of various preparations (Table I) indicates that perhaps the most significant factor in increasing the yields of the intermediate chlorofluorides is the use of the catalyst. When the catalyst was omitted, only traces of these materials were obtained; when it was used, the yields were appreciably better.

The formation of *n*-butyl dichlorofluorosilane appears to be favored by relatively low temperatures and pressures. For any given pressure, increasing the temperature reduced the yield of this substance. At any given temperature an increase in pressure had the same effect.

Apparently the formation of *n*-butyl chlorofluorosilane is favored by somewhat higher temperatures and pressures than is the formation of the *n*-butyl dichlorofluorosilane. These results are contrary to what we might expect, but they may be due to the effect of two factors which do not show up in the table, namely, rate of mixing of the reaction mixture and rate of addition of the antimony fluoride. In the last four experiments the stirring was much more rapid than in the first three. Furthermore, in the first three runs the antimony fluoride was fed into the

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(1) From a thesis submitted by Albert A. Schwartz to the Graduate School of Western Reserve University, June, 1945, in partial fulfilment of the requirements of 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) (I) H. S. Booth and Paul Carnell, THIS JOURNAL, **68**, 2650 (1946).

(3) (II) H. S. Booth and H. S. Halbedel, *ibid.*, **68**, 2652 (1946).

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

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

(6) (V) H. S. Booth and Dwight R. Spessard, *ibid.*, **68**, 2660 (1946).

(7) F. Swarts, *Bull. Acad. Roy. Belg.*, **24**, 309, 474 (1892).

(8) H. S. Booth and C. F. Swinehart, THIS JOURNAL, **54**, 4751 (1932); **57**, 1333 (1935).

(9) A. Bygden, *Ber.*, **44**, 2646 (1911).

(10) F. C. Whitmore and A. R. Lux, THIS JOURNAL, **54**, 3448 (1932).

(11) A. A. Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Co., New York, N. Y., 1938, pp. 83–85.