above are understandable in the light of the earlier observations of Booth and Bozarth.[6] They found that there exists a definite threshold temperature at which fluorination of each chlorofluoride takes place. They also noted that the rate of fluorination increases as the fluorine content of the halide increases.

It has been pointed out by Turkevich[14] that the possible co-existence of two or more molecular shapes and irregularity of crystalline form favors vitrification. It is possible that these factors may serve to explain the formation of glasses on cooling as described above.

The boiling point of ethyl trichlorosilane calculated from the vapor pressure equation for this substance is 97.9 ± 0.1° at 760 mm. Ladenburg[15] prepared ethyl trichlorosilane by the reaction of ethyl silicon triethoxide with benzoyl chloride. He reported a boiling point of "about 100°" for the impure material. Kipping[16] did not purify the ethyl trichlorosilane he prepared. He stated that the fraction boiling from 97–103° was pure enough for the preparation of other derivatives. Bygden[17] reports a boiling point of 99.5–100.5° at 766 mm. He states, however, that the material studied was not pure. These high values reported for the boiling point of ethyl trichlorosilane could be accounted for by the presence of a small amount of the higher boiling diethyl dichlorosilane due to inadequate purification methods.

Swarts'[18] rule that the lowering of the boiling point per atom of fluorine substituted for chlorine in a given compound applied to the above four ethyl halogenosilanes would indicate a uniform lowering of 34° for each fluorine substituted in ethyl trichlorosilane, while the successive lowerings are 35.7, 35.0 and 31.4°.

Summary

The fluorination of ethyl trichlorosilane by the Swarts reaction (without a catalyst) yields three fluorination products, $C_2H_5SiF_3$, $C_2H_5SiF_2Cl$ and $C_2H_5SiFCl_2$. The boiling points, freezing points, vapor pressures, and molecular weights of these substances and of ethyl trichlorosilane have been determined. Some of their chemical properties have also been observed and recorded.

CLEVELAND, OHIO RECEIVED[19] AUGUST 9, 1946

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[14] A. Turkevich and C. P. Smyth, THIS JOURNAL, **64**, 737 (1942).

[15] A. Ladenburg, *Ann.*, **164**, 300 (1872).

[16] F. S. Kipping, *ibid.*, 5 (1872); *J. Chem. Soc.*, **91**, 209 (1907).

[17] A. Bygden. *Z. physik. Chem.*, **90**, 243 (1915).

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

[19] Original manuscript received, April 13, 1945.

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

II. The Fluorination of *n*-Propyl Trichlorosilane[1]

BY HAROLD SIMMONS BOOTH AND HAROLD SEIBERT HALBEDEL

The Swarts method of fluorination with antimony trifluoride in the presence of halogens or antimony pentachloride, recently used with success in this laboratory for the fluorination of ethyl trichlorosilane,[2] has now been applied to *n*-propyl dichlorosilane, and the properties of the resulting substances have been studied.

Experimental

***n*-Propyl Trichlorosilane.**—Best yields of *n*-propyl trichlorosilane were obtained by adding the Grignard reagent from one mole of *n*-propyl bromide dropwise to twice the theoretically needed amount of silicon tetrachloride in half its weight of dry ether cooled to the temperature of melting ice, while the mixture was being vigorously stirred. The product was refluxed for ten hours, separated from the ether, and then fractionally distilled several times, using only the middle third for determination of physical constants and for fluorination.

Fluorination.—The apparatus and procedure for the fluorination of the *n*-propyl trichlorosilane and for the purification of the products were those described by Booth and Bozarth.[3] In the most successful experiment using 145 g. of the *n*-propyl trichlorosilane, 10 g. of the catalyst ($SbCl_5$) and generating at a pressure of 460–480 mm. using water as the cooling agent in the reflux condenser, an approximately 80% yield of *n*-propyl trifluorosilane was obtained with none of the usual intermediate chlorofluorides. A lower distillation pressure (180–220 mm.) using air to cool the reflux gave a 70% yield with traces of the intermediate chlorofluorides. Omission of the catalyst at a distillation pressure of 100 mm. gave similar traces of the intermediates but only a 30% yield of the *n*-propyl trifluorosilane.

The best results for the separation and recovery of the reaction products were obtained by distillation at a pressure of 500 mm. when the trifluorosilane distilled off at 15–16°. Two other fractions were obtained boiling under atmospheric pressure at 55–57° and 88–90°, approximately the expected boiling point of the chlorodifluoro- and the dichlorofluoro-silanes, respectively.

It was found impossible to moderate the reaction sufficiently to obtain more than traces of the intermediates. The use of tetrachloroethylene as a diluent increased the yield of these substances slightly but the solvent could not be separated successfully from the *n*-propyl dichlorofluorosilane.

Analysis.—The products were analyzed for chlorine and fluorine as described by Booth and Carnell.[2] Chlorine was found to be absent from the *n*-propyltrifluorosilane by test. The fractions boiling at 55–57° (chlorodifluoro) were redistilled several times and finally yielded 0.5 g. boiling at 56°. The dichlorofluorosilane was similarly redistilled. The resulting analytical data are collected in Table I.

The analytical data indicate that the *n*-propyl trifluorosilane is quite pure and the propyl chlorodifluorosilane nearly pure, possibly containing some *n*-propyl trifluorosilane. The propyl dichlorofluorosilane, however, appears

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[1] From a thesis presented by Harold S. Halbedel, September 10, 1943, to the Graduate School of Western Reserve University, in partial fulfilment of the degree of Doctor of Philosophy in Chemistry. Publication delayed for security reasons.

[2] H. S. Booth and P. H. Carnell, THIS JOURNAL, **68**, 2650 (1946).

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

TABLE I

n-PROPYL TRIHALOGENOSILANES

Formula			n-$C_3H_7SiCl_3$	n-$C_3H_7SiCl_2F$	n-$C_3H_7SiClF_2$	n-$C_3H_7SiF_3$
Composition, %	Chlorine	Calcd.	59.92	44.03	24.52	.....
		Found	59.36 59.61	39.32 39.53	24.13 23.85	.....
	Fluorine	Calcd.	.....	11.80	26.28	44.48
		Found	.....	11.64 11.17	27.06	44.14 44.61
Boiling point, °C.			122.7 ± 1	88-89[a]	55-57[a]	24.9 ± 0.1
Molecular weight		Calcd.	177.5	161.5	144.6	128.2
		Found	.....	163.7	141.3	129.3
Heat of vapn., cal.			8700	.....	.....	6470
Trouton constant, cal./deg.			22.0	.....	.....	21.7
Vapor pressure equation constants		A	30.725	.....	.....	25.2715
		B	−3161.7	.....	.....	−2189.5
		C	−7.643	.....	.....	−6.0833
Random deviations		Av.	±1.7	.....	.....	±1.8
		Max.	+2.9	.....	.....	+5.8

[a] Barometer 745 mm.

to be quite impure. The material was again distilled and analyzed, but an almost identical value was obtained. A clue to the impurity present was furnished by the behavior on hydrolysis of 1 ml. of the material in 3 ml. of water. After hydrolysis was complete there remained a tiny globule of liquid insoluble in and heavier than water. This was probably some of the tetrachloroethylene which had been used as a diluent during the fluorination. The amount of material, however, was too small to permit us to identify it rigorously.

Physical Properties.—The molecular weights were determined by the method of Regnault substantially as developed by Germann.[4]

The freezing point of n-propyl trifluorosilane could not be obtained because on cooling the liquid became extremely viscous and finally a clear glass appeared. It then shattered with an audible report into a multitude of tiny particles that seemed to have no definite lines of fracture. No reproducible freezing curves could be obtained. The propyl chlorofluorosilanes and the trichlorosilane behaved similarly.

The vapor pressure of the n-propyl trifluorosilane was measured directly. The vapor pressures of the n-propyl trichlorosilane were measured by the static method as described previously[5] between 20 and 121°. However, the design shown in Fig. 1 was found to be much easier to construct and to use than types hitherto used in this Laboratory. The capacity of the reservoir C should be large enough to hold all the mercury in the isoteniscope, while the substance whose vapor pressure is to be measured is being introduced.

After the isoteniscope has been evacuated, flamed, and rinsed with dry air several times, sufficient mercury is introduced through stopcock B. It is attached to the gas apparatus by the flat joint A, evacuated, and warmed until air bubbles no longer appear between the mercury and the glass. It is detached from the apparatus and tilted until all the mercury is in the reservoir C. It is re-attached to the apparatus, and the sample for vapor pressure determination is condensed into the bulb E by immersion in liquid air until the bulb is filled. The bulb is warmed and part of the sample is boiled off to remove adsorbed air. The stopcock B is closed and the isoteniscope is removed from the apparatus. It is then tilted until all the mercury is in the manometer D. It is now ready for vapor pressure measurements

Duplicate determinations were made on samples taken from separate preparations The vapor pressure of the propyl trifluorosilane was measured directly, duplicate measurements being made on a second sample distilled at a different pressure.

The usual empirical equations were derived for the vapor pressures[5a] obtained of the form

$$\log p_{\text{mm.}} = A + \frac{B}{T} + C \log T$$

The values of the vapor pressure calculated from the formulas showed only random variations, the average deviation between the observed and calculated values being −1.6 mm. and a maximum deviation of 5.8 mm. No significant differences could be detected between the duplicate samples. The general course of the vapor pressure curves is shown in Fig. 2.

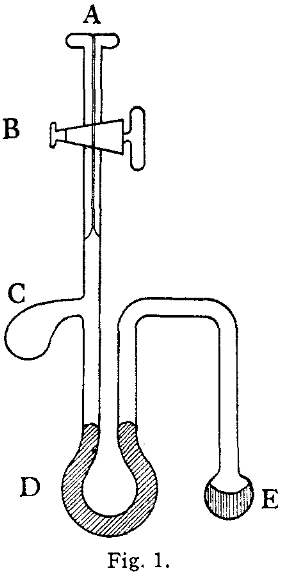

Fig. 1.

Chemical Properties.—n-Propyl trichlorosilane and its fluorination products are all water-white liquids with sharp, disagreeable, and irritating odors not at all like that of tetrachlorosilane. The trifluorosilane is somewhat lachrymatory.

These compounds do not fume in air. They are but slightly soluble in water and hydrolyze slowly in water to produce a gelatinous precipitate of the so-called propane siliconic acid. With excess of aqueous sodium or potassium hydroxides, the hydrolysis proceeds quite rapidly to form the corresponding salts of the acids, which are soluble in the solution.

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(4) A. F. O. Germann, *J. Phys. Chem.*, **19**, 437 (1915).

(5) H. S. Booth, H. M. Elsey and P. E. Burchfield, THIS JOURNAL, **57**, 2064 (1935).

(5a). For data for these vapor pressure curves consult original thesis at Western Reserve University Library.

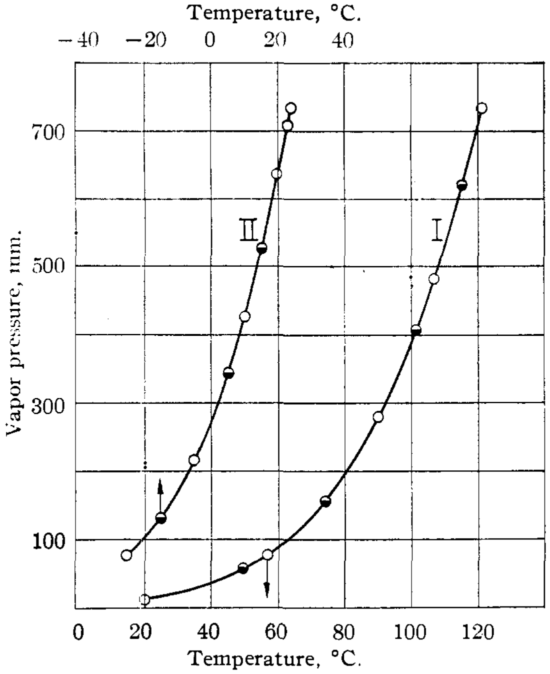

Fig. 2.—Vapor pressures of: I, n-$C_3H_7SiCl_3$; II, n-$C_3H_7SiF_3$: Sample A, ○; Sample B, ◒.

These silanes are soluble in ether and tetrachloroethylene and dissolve stopcock grease quite readily. They are unaffected by mercury or nichrome at their boiling points.

Glassware which has been wet by these silanes will resist wetting by water. Water in vessels treated in this manner presents a flat meniscus.

Discussion

The low yield of the n-propyl chlorodifluorosilane confirms our previous experience. Others[2,6,7] in this Laboratory have also found that in fluorination of silicon compounds containing chlorine, the chlorofluoride in which all but one of the chlorine atoms had been replaced was obtained in the smallest amount.

Booth and Bozarth[3] have shown that there is a definite threshold temperature for the fluorination of each covalent chlorofluoride or chloride, and with increased fluorine content the threshold temperature is lowered. Consequently, the rate of fluorination increases as the fluorine content of the halide is increased. If the threshold temperature for the fluorination of propyl chlorodifluorosilane were extremely low, then at the temperature needed to initiate the fluorination of trichlorosilane, the former reaction may be so extremely rapid as to prevent the removal from the reaction zone of any appreciable yield of this intermediate.

That these silanes exhibit such a strong tendency to vitrify is not surprising. Although symmetrical silicon dioxide and silicon tetrachloride crystallize readily, groups introduced into the molecule which destroy the symmetry thereof tend to cause the resulting substance to solidify as glasses: thus the alkali and alkaline earth silicates are glasses. Booth and Carnell[2] found that the ethyl chlorofluorosilanes were glasses, and they experienced difficulty in obtaining freezing points for the trifluoro and trichlorosilanes. These observations are in line with those presented by Turkevich and Smyth.[8]

Summary

n-Propyl trichlorosilane may be readily fluorinated by anhydrous antimony trifluoride with or without a catalyst to yield n-propyl trifluorosilane. Only traces of intermediate chlorofluorides are obtained normally but the yield of intermediate chlorofluorides may be increased to small amounts by dilution of the reactants with tetrachloroethylene. As usual the chlorodifluoride was obtained in smallest yield. Difficulty in separating the volatile diluent from the dichloromonofluoride interfered with its conclusive identification. None of these products have been previously reported.

CLEVELAND, OHIO RECEIVED[9] AUGUST 9, 1946

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(6) H. S. Booth and Wm. D. Stillwell, THIS JOURNAL, **56**, 1531 (1934).

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

(8) A. Turkevich and C. P. Smyth, THIS JOURNAL, **64**, 737 (1942).

(9) Original manuscript received April 21, 1945.