ride and 4-chloro-*m*-xylene hexafluoride have been measured at temperatures ranging from 2–80°.

The data have been fitted to a suitable equation.

Heats of vaporization have been calculated at 25°.

DURHAM, NORTH CAROLINA RECEIVED AUGUST 10, 1946

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

I. Ethyl Trichlorosilane and its Fluorination Products[1]

BY HAROLD SIMMONS BOOTH AND PAUL HERBERT CARNELL[2]

Fifty years ago Swarts[3] discovered that the stepwise replacement of halogens by fluorine in organic aliphatic halides could be accomplished by the use of antimony trifluoride with antimony pentachloride, or chlorine, as a catalyst. More recently this method has been applied in this Laboratory to inorganic non-polar halides. Booth and Swinehart[4] applied the method to silicon tetrachloride and obtained a series of mixed chlorofluorides of silicon.

The present investigation was carried out to determine whether or not the Swarts reaction could be applied successfully to alkyl chlorosilanes, specifically ethyl trichlorosilane. Upon application of the Swarts reaction this substance may be expected to yield three products: ethyl dichloromonofluorosilane ($C_2H_5SiCl_2F$), ethyl monochlorodifluorosilane ($C_2H_5SiClF_2$) and ethyl trifluorosilane ($C_2H_5SiF_3$).

Experimental

The Preparation of Ethyl Trichlorosilane.—The method of Kipping[5] was followed, but to avoid the formation of diethyl- and triethyl-chlorosilanes the Grignard reagent from 1 mole of ethyl bromide was added to 5 moles of silicon tetrachloride rather than in the ratio of 5:1 used by Kipping. When the reaction was complete all of the liquid in the generator was distilled from the solid residue and this product was then redistilled in a column packed with nichrome wire. For further purification 200-g. lots were redistilled at atmospheric pressure through a column wound with a heating unit and protected from access of moisture; the middle fraction was then re-distilled several times and the final, constant boiling middle third used for the physical measurements. The yields averaged 59% based on 80% yield of the Grignard reagent.

Fluorination of Ethyl Trichlorosilane.—The method and apparatus used for stepwise fluorination have been sufficiently described elsewhere[6] except that here no catalyst was employed. The product obtained was roughly separated into fractions in the same column that was used in the final purification of the ethyl trichlorosilane, the column head in this case being cooled with Dry Ice and acetone.

A log of three fluorination runs is as follows:

TABLE I

$C_2H_5SiCl_3$, g.	Generator temp., °C.	Generator press., mm.	Cooling agent	Liquid vol. of fractions Visual, cc. F_3	F_2	F
215	35–40	225 ± 25	None	70	8	15
200	80–90	525 ± 25	H_2O (cold)	60	5	15
150	25	85 ± 15	H_2O (25°)	40	2	2

These products were then combined and distilled either at atmospheric or at reduced pressure in a low temperature still, the distillation curves being automatically graphed by a Leeds and Northrup Micromax recording potentiometer. Each fraction was then carefully redistilled at various pressures. No unusual difficulty was encountered in the purification of these products. It was necessary to re-grease the stopcocks before each distillation as these substances, particularly the higher boiling material, appeared to dissolve the grease.

Analysis.—The samples weighed in 1-cc. sealed glass ampules[7] were hydrolyzed with 15 g. of sodium hydroxide per 1 g. of sample. Since reaction was slow, heat was applied to hasten the hydrolysis. When this was complete the chlorine was determined by the Volhard method and fluorine by precipitation as lead chlorofluoride.[8] The presence of carbon and silicon was established qualitatively.

Determination of Physical Constants.—The molecular weights were all determined by the standard Regnault method[9]; that of the trifluoride was also determined with a gas density balance.[10]

The freezing points were determined in the usual type of glass tubular cell used in this Laboratory.[11] Only ethyl trifluorosilane gave a definite, reproducible freezing point. Ethyl dichloromonofluorosilane and ethyl monochlorodifluorosilane, upon cooling, became more and more viscous and solidified to glassy, transparent solids. Attempts were made to obtain melting points by slow warming of the solid glasses. However, no break was obtained in the heating curve, apparently because of the gradual change from the glass to the liquid state with no sharp boundary between the two states. Ethyl trichlorosilane would form crystals only if the following technique was followed carefully:

The sample was considerably supercooled in liquid air. Upon removal of the liquid air, the sample was warmed rapidly by touching the outside of the cold cell with a cloth soaked in acetone. Usually, but not always, this would start the formation of a few crystals. The sample was then carefully warmed, keeping the seed crystals present, until the stirrer was in operation. A D'Arsonval tube was then placed around the cell and a Dewar flask containing a small amount of liquid air was placed around

---

[1] From a thesis submitted by Paul Herbert Carnell to the Graduate School of Western Reserve University, May, 1943, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Publication delayed for security reasons.

[2] Present address: Phillips Petroleum Company, Bartlesville, Oklahoma.

[3] F. Swarts, *Acad. Roy. Belg.*, **24**, 309, 474 (1892).

[4] H. S. Booth and C. F. Swinehart, THIS JOURNAL, **54**, 4751 (1932).

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

[6] H. S. Booth and A. R. Bozarth, THIS JOURNAL, **61**, 2927 (1939).

[7] H. S. Booth and W. D. Stillwell, *ibid.*, **56**, 1531 (1934).

[8] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," John Wiley and Sons, New York, N. Y., 1935, 8th ed., pp. 418–420.

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

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

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

TABLE II

Formula			$C_2H_5SiCl_3$	$C_2H_5SiCl_2F$	$C_2H_5SiClF_2$	$C_2H_5SiF_3$[a]
Composition, %	Chlorine	Calcd.	65.05	48.23	27.16	.....
		Found	64.95 64.83	47.88 47.97	26.80 27.30	.....
	Fluorine	Calcd.	.....	12.92	29.10	49.95
		Found	.....	12.75 13.09	29.21 29.03	49.68 50.05
Boiling pt., °C.			97.9	62.2	27.2	−4.2
Freezing pt., °C.			−105.6 ± 0.1	.....	.....	−113.3 ± 0.5
Molecular weight	Calcd.		163.5	147.0	130.6	114.1
	Found		163.4	148.6	132.6	115.6
Heat of vapn., cal.			7700	7360	6730	6120
Trouton const., cal./deg.			20.8	22.0	22.4	22.8
Vapor pressure eq. constants	*A*		−1684.3	−1609.5	−1470.7	−1338
	B		7.420	7.681	7.778	7.855
Random deviations	Av.		±2.2	±1.1	±2.9	±1.5
	Max.		+4.5	−3.6	+6.0	−4.4

[a] Since this investigation was completed, Emeléus and Wilkins, *J. Chem. Soc.*, 454 (1944), have reported the synthesis of ethyl trifluorosilane by the reaction of zinc fluoride on ethyl trichlorosilane. They report its boiling point to be −4.4° and its freezing point −105° (pentane thermometer).

the tube. This operation had to be done at precisely the right moment or the seed crystals would melt and, on cooling, a glassy solid would result. Using this technique definite breaks were obtained in the cooling curves but reproducible results were difficult to obtain. The best checks observed are reported. It was observed that when either of these compounds was transferred from one ampule to another some crystal formation was evident. However, when these crystals were melted and solidified again, glassy solids resulted. It would appear that either a metastable crystalline state exists or polymerization takes place to yield a glassy solid. If the clear, glassy solids were considerably supercooled with liquid air and then allowed to warm rapidly, they became shot through with irregular cracks accompanied by a considerable cracking noise. The material then took on the appearance of fractured glass with no evidence of crystal formation. On one occasion this sudden change of form shattered the glass freezing point tube.

The vapor pressures were determined by the static method of Booth, Elsey and Burchfield.[12] The vapor pressure of ethyl trifluorosilane, a gas at room temperature, was measured directly.[6] The vapor pressure curve for a particular compound was determined with a sample which had been distilled at a given pressure. The points of this curve were then checked with a sample distilled at a different pressure. The data thus obtained are plotted in Fig. 1.[13] Expressions of the usual form $\log p$ (mm.) = $A/T + B$ were derived and found to fit the observed data, except for one observation, with an average random deviation of ±1.8 mm. and a maximum deviation of 6.8 mm.

Chemical Properties.—At ordinary temperatures none of the four ethyl halogenosilanes prepared and purified as above react with mercury or nichrome, and ethyl trichlorosilane does not react with iron. When this silane is added to absolute alcohol the only evidence of reaction is a warming of the solution. All of the ethyl halogenosilanes prepared in this investigation are hydrolyzed slowly by sodium hydroxide.

An attempt was made to discover whether or not ethyl trifluorosilane coördinates with sodium fluoride to form a compound of the type $Na_2(SiC_2H_5F_5)$. A sample of dry, C. P. sodium fluoride was placed in an ampule provided with a stopcock and a conical joint. The ampule was then attached to the manifold system and, after being evacuated and dried, was weighed against a counterpoise. The ampule was again connected to the manifold and a few ml. of ethyl trifluorosilane was condensed upon the sodium fluoride. The ampule was allowed to stand for several days at room temperature with occasional shaking. At the end of that time it was attached to the manifold system and excess ethyl trifluorosilane was distilled off. The ampule was again weighed against the counterpoise. The fact that no gain in weight was observed would seem to indicate that, under the conditions described, dry sodium fluoride does not coordinate with the ethyl trifluorosilane.

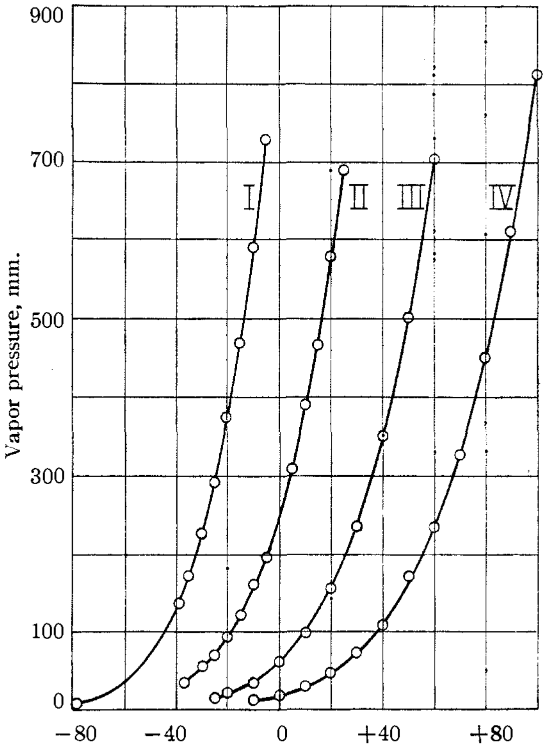

Fig. 1.—Vapor pressures of: I, $C_2H_5SiF_3$; II, $C_2H_5SiClF_2$; III, $C_2H_5SiCl_2F$; IV, $C_2H_5SiCl_3$.

Discussion

The small yields of intermediate ethyl chlorofluorosilane formed in the fluorinations described

---

[12] H. S. Booth, H. M. Elsey and P. E. Burchfield, This Journal, 58, 63 (1936).

[13] For data for these vapor pressure curves consult original thesis at Western Reserve University Library (see ref. 1).

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

---

[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

---

[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).