

with sodium bicarbonate solution. The hydrogen evolved during neutralization amounted to 0.5 mole. Distillation of the product *in vacuo* yielded 1.0 g. (1.9%) of benzyl alcohol (b. p. 91–93° (10 mm.)) and 45.6 g. (86.5%) of benzyl benzoate (b. p. 172–173° (10 mm.)). The ester was identified by hydrolysis to benzoic acid (m. p. 121°; m. p. of amide 128–129°) and benzyl alcohol (b. p. 91–93° (10 mm.); m. p. of 3,5-dinitrobenzoate 111.5°).

The reaction was also carried out using only 1.2 g. (0.05 mole) of sodium hydride to 106 g. (1.0 mole) of benzaldehyde. The yield of benzyl benzoate (b. p. 172–173° (10 mm.)) was 97.6 g. (92%).

Action on Methyl Benzoate.—A mixture of 12.0 g. (0.5 mole) of sodium hydride, 34.0 g. (0.25 mole) of methyl benzoate, and 75 ml. of xylene was stirred at 140° for three hours and then worked up as described for benzophenone. The evolved hydrogen on neutralization amounted to 0.49 mole and 29.4 g. (87%) of essentially pure methyl benzoate was recovered. No other product was found.

Summary

1. Certain carbonyl compounds having α -hydrogen are converted by sodium hydride to their anions, which may enter into Claisen condensations, whereas certain of those having no α -hydrogen are reduced.

2. Ethylisovalerate has been self-condensed and cyclohexanone has been benzoylated with methyl benzoate. Di-*i*-propyl and di-*i*-butyl ketones have been converted to their anions and recovered.

3. Benzophenone has been reduced to benzhydrol and benzaldehyde to benzyl benzoate. The mechanism for the latter reaction and the failure of methyl benzoate to reduce is discussed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Vapor Pressures of Some Organic Fluorides^{1,2}

BY FRANK H. FIELD AND JOHN H. SAYLOR

The measurements reported in this paper were made in connection with a general program of research in this Laboratory concerning the physical properties of fluorine compounds.

Experimental

The method used was a modification of that devised by Ramsay and Young³ and has been previously described.⁴

Two different manometers were used as before; a mercury U-gage⁵ for pressures above 15 mm. of mercury and an oil manometer⁶ for all pressures below 15 mm. of mercury.

All of the compounds used except the benzotrifluoride were prepared by workers in this Laboratory under the direction of Dr. C. K. Bradsher. The benzotrifluoride was procured from the Hooker Electrochemical Company. The materials were refluxed with sulfuric acid until the acid gave no test for chloride ion, were washed twice with sodium bicarbonate solution, three times with water and dried over Drierite. The dried material was distilled at a

high reflux ratio through a two-and-one-half foot glass column packed with glass helices using calibrated thermometers.

The extent of the purification was somewhat limited by the quantities of materials available. The 4-chloro-*m*-xylene hexafluoride boils within one degree of 2-chloro-*p*-xylene hexafluoride and was likely contaminated with a small amount of the latter compound. All boiling points were corrected to 760 mm. by means of Craft's rule.

Results

Approximately ten individual measurements were made on each compound at temperatures ranging from about 2 to 80°. The data were fitted by the method of least squares to the following equation.^{4,7}

$$\log p = -\frac{A}{T-C} + B$$

In the calculations, 0° = 273.16° K.

The mean deviation between the observed pressures and those calculated from the equation varied from 2 parts per 1000 for 5-chloro-*m*-xylene hexafluoride to 9 parts per 1000 for 4-chloro-*m*-xylene hexafluoride.

Heats of vaporization were calculated from the Clapeyron equation approximation obtained by differentiating the vapor pressure equation and multiplying the result by RT^2 . These values together with the constants for the vapor pressure equation are given in Table I.

Booth, Elsey and Burchfield⁸ have measured the vapor pressures of benzotrifluoride which are the only values reported for any of the four compounds measured here. The agreement with the present data is good.

Summary

The vapor pressures of benzotrifluoride, *m*-xylene hexafluoride, 5-chloro-*m*-xylene hexafluoride,

(7) Thomson, *Chem. Rev.*, **38**, 1 (1946).

(8) Booth, Elsey and Burchfield, *THIS JOURNAL*, **57**, 2066 (1935).

TABLE I

BOILING POINTS, CONSTANTS OF THE VAPOR PRESSURE EQUATION AND HEATS OF VAPORIZATION

Substance	B. p. range, °C.	Constants of the equation			ΔH at 25° kcal./mole
		$\log p = \frac{A}{T-C} + B$	A	B	
Benzotrifluoride	102.30 ± 0.05	1148.7	6.642	70.90	9.0
<i>m</i> -Xylene hexafluoride	116.0–116.1	1488.8	7.315	52.16	10.0
5-Chloro- <i>m</i> -xylene hexafluoride	138.20–138.25	1992.7	8.119	26.54	11.0
4-Chloro- <i>m</i> -xylene hexafluoride	149.1–149.2	1959.4	7.981	33.61	11.4

(1) This research program was sponsored by the Naval Research Laboratory.

(2) This paper was taken in part from the thesis submitted by Frank H. Field to the Graduate School of Duke University in partial fulfillment of the requirements for the degree of Master of Arts, June, 1944.

(3) Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).

(4) Stuckey and Saylor, *THIS JOURNAL*, **62**, 2922 (1940).

(5) Zimmerli, *Ind. Eng. Chem., Anal. Ed.*, **10**, 283 (1938).

(6) Hickman, *Rev. Sci. Instruments*, **5**, 161 (1934).

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°.

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

I. Ethyl Trichlorosilane and its Fluorination Products¹

BY HAROLD SIMMONS BOOTH AND PAUL HERBERT CARNELL²

Fifty years ago Swarts³ 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 Swinehart⁴ 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 (C₂H₅SiCl₂F), ethyl monochlorodifluorosilane (C₂H₅SiClF₂) and ethyl trifluorosilane (C₂H₅SiF₃).

Experimental

The Preparation of Ethyl Trichlorosilane.—The method of Kipping⁵ 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 elsewhere⁶ 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:

(1) From a thesis submitted by Paul Herbert Carnell to the Graduate School of Western Reserve University, May, 1943, in partial fulfillment 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).

C ₂ H ₅ SiCl ₃ , g.	Generator temp., °C.	Generator press., mm.	Cooling agent	Liquid vol. of fractions		
				Visual, cc.	F ₂	F
215	35–40	225 ± 25	None	70	8	15
200	80–90	525 ± 25	H ₂ O (cold)	60	5	15
150	25	85 ± 15	H ₂ O (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 ampules⁷ 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 method⁹; 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

(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).