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		
$C_2H_5SiCl_2F$	62.2	35.7	
$C_2H_5SiClF_2$	27.2	35.0	34.1
$C_2H_5SiF_3$	−4.2	31.0	
i-$C_3H_7SiCl_3$	119.4		
i-$C_3H_7SiCl_2F$	84.0	35.4	
i-$C_3H_7SiClF_2$	48.8	35.2	34.5
i-$C_3H_7SiF_3$	15.7	33.1	

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

---

[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.

TABLE I

LOG OF FLUORINATION OF n-BUTYL TRICHLOROSILANE UNDER DIFFERENT CONDITIONS

Expt.	Wt. of BuSiCl$_3$, g.	Wt. of SbF$_3$, g.	Catalyst (SbCl$_3$), ml.	Generator bath temp., ° C.	Generator pressure, mm. Hg	Diluent (c-C$_6$H$_4$Cl$_2$), ml.	Approx. % yield of products[a] BuSiCl$_2$F	BuSiClF$_2$	BuSiF$_3$
1	244	235	10	70–83	175–225		10	2	33
2	291	300	10	100–112	175–225		7	1	35
3	120	135	. .	118–125	175–225		Trace	Trace	33
4	138	153	10	113–117	300–350	125	8	4	35
5	192	196	20	108–112	375–425	165	6	3	35
6	172	187	20	112–117	300–350		6	3	40
7	169	174	15	108–110	375–425		5	2	40

[a] The material unaccounted for by these figures consisted very largely of n-butyl trichlorosilane which distilled out of the reaction flask before it could be fluorinated. Small amounts of hydrogen chloride, silicon tetrafluoride, and other decomposition products were also obtained. In each experiment there was a small loss of material which could not be accounted for. This was probably liquid which remained behind in the generator due to sorption by the antimony salts.

reaction mixture steadily and the fluorination was forced, whereas in the last four experiments the antimony fluoride was added very slowly and intermittently and no forcing of the reaction occurred.

Purification of Fluorination Products.—After preliminary separation in the liquid type column described, the tri- and di-fluorides were redistilled several times in a gas type column[12,13] and the middle fractions used for further study. The monofluoride was similarly purified in the liquid type column.

Analysis.—Chlorine was determined quantitatively, and the presence of carbon and silicon were verified qualitatively, as described by Booth and Suttle.[5] Fluorine was determined by the method devised by Siegel.[14]

Determination of Physical Constants.—Molecular weights were determined by the Regnault method in the manner described by Germann.[15] Freezing points were determined using the apparatus and techniques developed previously in this laboratory.[16,17]

n-Butyl trifluorosilane was the only one of the four compounds studied which gave a definite reproducible freezing point, and even in this case great care had to be exercised due to the tendency of liquid to supercool before freezing occurred. This supercooling was of the order of 15°.

The other compounds studied (n-butyl trichlorosilane, n-butyl dichlorofluorosilane and n-butyl chlorodifluorosilane) do not appear to possess definite freezing points. In each case as these substances were cooled, they became more and more viscous until finally a transparent glass was formed. If these glasses were cooled rapidly by liquid nitrogen and then kept at that temperature for some time, a transition appeared to take place. The glasses would shatter with an audible report into a multitude of particles which appeared to possess no regular planes of cleavage. This transition apparently was accompanied by a change in volume as in one case it shattered the freezing point tube and in another instance it cracked it.

Attempts were made to obtain melting points for the glasses and for the products which resulted from the transitions described above, but no breaks in the temperature-time curves could be observed.

Vapor pressures were measured by the static method as described by Booth and Halbedel,[3] and Booth and Suttle.[5] Curves graphed from the vapor pressure data[18] are given in Fig. 1. Expressions of the usual form, $\log p_{(\mathrm{mm.})} = A/T + B$ were derived; the values for A and B are given in Table II.

Physical and Chemical Properties.—n-Butyl trichlorosilane and its three fluorination products are all colorless, mobile liquids. The completely fluorinated compound fumes only slightly on exposure to the atmosphere, undergoing hydrolysis quite slowly. The trichlorosilane and the two chlorofluorosilanes, on the other hand, fume readily in moist air and hydrolyze much more rapidly; so rapidly, in fact, that although they have sweetish odors, these are difficult to detect as they are almost completely masked by the odor of the hydrogen chloride resulting from the hydrolysis. The n-butyl trifluorosilane possesses a sharp, suffocating odor which is distinctly different from those of the other three compounds. It is interesting to note that when the two chlorofluorosilanes are exposed to the atmosphere the only odor which can be detected is that of hydrogen chloride. This would seem to indicate that in these halosilanes the silicon–chlorine bond is more susceptible to hydrolysis than is the silicon–fluorine bond.

Although all four compounds are hydrolyzed without extreme difficulty, they are not soluble in water to any appreciable extent. When they are added to water, two immiscible layers result with the hydrolysis occurring at the interface.

n-Butyl trichlorosilane and its fluorination products are soluble in petroleum ether, benzene, toluene and various

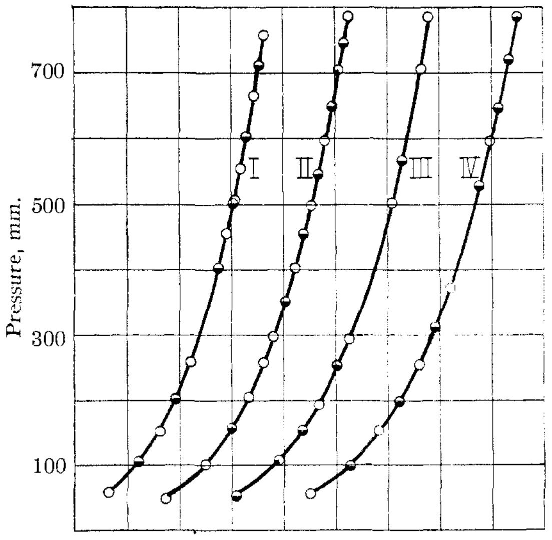

Fig. 1.—Vapor pressure of: I, n-C$_4$H$_9$SiF$_3$; II, n-C$_4$H$_9$SiClF$_2$; III, n-C$_4$H$_9$SiCl$_2$F; IV, n-C$_4$H$_9$SiCl$_3$: sample A, ○; sample B, ●; combined samples, ◐.

---

(12) S. F. Dufton, *J. Soc. Chem. Ind.*, **38**, 45T (1919).

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

(14) W. Siegel, *Z. angew. Chem.*, **42**, 856 (1929).

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

(16) H. S. Booth and F. C. Mericola, THIS JOURNAL, **62**, 640 (1940).

(17) H. S. Booth and D. R. Martin, *ibid.*, **64**, 2198 (1942).

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

TABLE II

Formula		n-$C_4H_9SiCl_3$	n-$C_4H_9SiCl_2F$	n-$C_4H_9SiClF_2$	n-$C_4H_9SiF_3$
Chlorine, %	Calcd.	55.53	40.50	22.35	.....
	Found	55.47 55.38	40.37 40.43	22.30 22.24	.....
Fluorine, %	Calcd.	.....	10.85	23.96	40.09
	Found	.....	10.68 10.76	23.90 23.83	39.98 39.95
Mol. wt.	Calcd.	191.54	175.08	158.63	142.17
	Found	.....	.....	160.4	140.8
Boiling pts., °C.	Swarts' rule	.....	116.7	84.5	....
	obsd.	148.9 ± 0.2	116.1 ± 0.1	84.0 ± 0.1	52.4 ± 0.1
Freezing pt., °C.		.....	.....	.....	−96.9 ± 0.2
Vapn. ht., cal.		9490	8570	8020	7430
Trouton const., cal./deg.		22.5	22.0	22.5	22.8
Vapor pres. constants	A	−2075.1	−1873.3	−1754.4	−1623.4
	B	7.79783	7.69313	7.79298	7.86737
Av. random dev., mm.		±2.1	±1.6	±2.9	±1.4
Maximum dev., mm.		+4.3	+4.1	+5.2	−5.6

chlorinated organic solvents such as carbon tetrachloride, tetrachloroethylene, chlorobenzene, *o*-dichlorobenzene, etc. They also dissolve in ether and ethyl acetate.

In acetone the trifluorosilane gives a perfectly clear solution with no evidence of any reaction. The other three compounds, however, behave peculiarly. They, too, give perfectly clear solutions, but on standing for some time these become pale yellow and gradually darken in color until the liquid is a deep red. The reaction has not been studied further, but the following is probably the explanation of what occurs.[18a]

It is known that if acetone is treated with certain dehydrating agents it undergoes condensation. If, for instance, it is saturated with dry hydrogen chloride and the solution kept for some time, a mixture of mesityl oxide and phorone are obtained.

When the samples of the trichloro- and the two chlorofluorosilanes were added to acetone, there was undoubtedly in each instance enough moisture present in the air space above the liquid and adsorbed on the walls of the container to hydrolyze a small portion of the halosilane. The hydrogen chloride thus liberated very probably brought about the condensation of part of the acetone in the manner just described. The water formed by this reaction then produced further hydrolysis of the halosilane, thus liberating more hydrogen chloride which in turn induced further condensation with the subsequent elimination of still more water. In this manner the cycle was propagated until probably either all of the acetone had undergone condensation or all of the halosilane had been hydrolyzed.

The failure of the *n*-butyl trifluorosilane to react with acetone is probably due to the stability of this compound toward water. There is ample evidence to indicate that the silicon–fluorine bond is much less susceptible to hydrolysis than is the silicon–chlorine bond. It is quite possible, therefore, that the presence of traces of moisture, while sufficient to bring about the hydrolysis of the butylhalosilanes containing chlorine, would have no effect on the completely fluorinated compound.

In methyl, ethyl and *n*-butyl alcohols, as in acetone, there is a marked difference between the reactivity of the trifluorosilane on the one hand and the trichloro- and the two chlorofluorosilanes on the other. The completely fluorinated compound dissolves in each of the three alcohols with no evidence of reaction. The remaining three compounds, on the other hand, undergo alcoholysis more or less readily. The ease of reaction increases with increasing chlorine content of the halosilane and decreasing carbon chain length of the alcohol, with the latter by far the more important factor. In methyl alcohol the reaction is quite violent for all three compounds, and considerable heat is evolved. In *n*-butyl alcohol, on the other hand, alcoholysis proceeds mildly.

As the trifluorosilane appears to undergo no reaction at all with alcohols, it may be that the silicon–fluorine bond is inert toward alcoholysis. It is quite possible, then, that in the case of the two chlorofluorosilanes only partial alcoholysis occurs. If this is true, then it should be possible to use this reaction for the preparation of mixed alkoxyfluorosilanes.

In the absence of moisture *n*-butyl trichlorosilane and its fluorination products appear to be inert to metals. Iron, steel, copper and platinum are unaffected at ordinary temperatures, while mercury and nichrome are not attacked even at the boiling points of the compounds.

As in the case of other alkyl halogeno silanes glassware which has been wet by any of these silanes resists wetting by water, and in such vessels water presents a flat meniscus.

n-Butyl trifluorosilane appears to be somewhat toxic, inhalation of small quantities of the vapor causing headache and nausea. The other three compounds do not seem to be poisonous although they are extremely irritating because of the hydrogen chloride liberated by their hydrolysis.

Discussion

As a result of the study which was made of the fluorination reaction under varying conditions, it appears that there are no practical operating conditions, which will bring about the formation of the two chlorofluorides in really substantial yields. There are, however, several factors tending to increase the production of these compounds: (1) The temperature and pressure should be kept as low as possible, consistent with a smooth yet fairly vigorous reaction. (2) The use of a catalyst is of paramount importance as it lowers considerably the threshold temperature of fluorination. In this particular instance, in fact, the catalyst is absolutely necessary. When it was not used, only traces of the chlorofluorides were obtained. Booth and Swinehart,[8] earlier investigators in this laboratory, found that silicon tetrachloride does not react at all with antimony trifluoride unless a catalyst is used. (3) If appreciable yields of the *n*-butyl chlorofluorosilanes are to be obtained, it is imperative that excessive localized action of the fluorinating agent be prevented. This can be accomplished by rapid stirring of the reaction mixture and by slow addition of the fluorinating agent.

In determining the freezing points of the *n*-butyl trihalosilanes difficulty was encountered because

---

[18a] The authors are indebted to Dr. H. P. Lankelma for suggesting this explanation.

of the tendency of these compounds to vitrify. Of the four compounds only *n*-butyl trifluorosilane gave a definite, reproducible freezing point, and even it showed a tendency to supercool considerably (15°). The other three substances on cooling became more and more viscous, finally forming transparent glasses. As a result of their investigation of the freezing points of several alkyl halides, Turkevich and Smyth[19] have concluded that irregularity of molecular form contributes toward a tendency to vitrification. Furthermore, a small difference in the size of an atom or group in a molecule may make a great difference in this tendency. It is possible that these conclusions may apply in explaining the formation of glasses by the *n*-butyl trihalosilanes.

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

n-Butyl trichlorosilane ($n\text{-}C_4H_9SiCl_3$) was prepared by the reaction of *n*-butylmagnesium bromide with excess silicon tetrachloride. Its fluorination by antimony trifluoride to yield *n*-butyl dichlorofluorosilane ($n\text{-}C_4H_9SiCl_2F$), *n*-butyl chlorodifluorosilane ($n\text{-}C_4H_9SiClF_2$), and *n*-butyl trifluorosilane ($n\text{-}C_4H_9SiF_3$) was studied in the absence and presence of catalyst and under varying conditions of pressure and temperature in order to determine the conditions for optimum production of the two intermediate chlorofluorides. Of the four compounds, only the *n*-butyl trichlorosilane had been reported prior to this work.

A number of the physical constants of the compounds were determined, and a brief study was made of a few of the chemical properties of the four compounds, particularly their solubilities, their action on metals and glass, and their reaction with water and organic compounds containing oxygen.

CLEVELAND, OHIO RECEIVED[20] AUGUST 17, 1946

---

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

[20] Original manuscript received July 18, 1945.

CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1031]

The Polarographic Analysis of Nitrite and of Nitrite–Nitrate Mixtures[1]

BY BERTRAM KEILIN AND JOHN W. OTVOS[2]

A method for the polarographic determination of nitrate in the presence of uranyl ion in acid solution has been described by Kolthoff, Harris and Matsuyama.[3] Since in the earlier methods studied by Tokuoka and Ruzicka[4,5] in which other cations were used as "activators," the reduction potentials for nitrate and nitrite were always found to be identical, it was of interest to us to examine the polarographic behavior of nitrite in the presence of uranyl ion.

At the acid concentrations necessary for suppressing the hydrolysis of uranyl ion, all but a few per cent. of nitrite exists as nitrous acid and the similarity between nitrate and nitrite is thus greatly decreased. Nevertheless the waves for the two substances are very similar in appearance and occur at the same potential.

A method for the separate estimation of nitrate and nitrite in solutions containing both ions is described in this paper. Use is made of the additivity of the waves, and of a simple chemical conversion of nitrite to nitrate without the introduction of new ions which might interfere with the determination.

Experimental

Apparatus and Materials.—A Heyrovsky Type XII Polarograph was used in all experiments. Measurements were made at 25°. Dissolved oxygen was removed by passing nitrogen through the solutions. All chemicals were of reagent grade. The sodium nitrite used in quantitative experiments was standardized against permanganate in acid solution, the primary standard being sodium oxalate.[6]

Decomposition of Nitrous Acid.—It is known that in cold dilute solutions and in the absence of air nitrous acid decomposes to nitric acid and nitric oxide; in the presence of oxygen, nitric acid alone is produced. Because of the instability of nitrous acid, a polarographic procedure for the determination of nitrite in acid solution must involve some error. Experiments performed in connection with this investigation have shown that in air and at concentrations which are of interest in polarography the decomposition of nitrous acid[7,8] is first order and that about six per cent. decomposes in a half hour at room temperature. If the nitrite solution is polarographed as soon as possible after it is acidified, the error arising from nitrous acid decomposition can be kept below 3%.

Comparison of the Nitrous Acid and Nitrate Waves.—Figure 1 shows a nitrous acid wave and a nitrate wave, each obtained with a solution 4×10^{-4} *M* in the nitrous acid[9] or nitrate, $2 \times$

---

[1] This paper is based in whole or in part on work done for the Office of Scientific Research and Development under Contract OEMsr-881 with the California Institute of Technology.

[2] Present address: Shell Development Company, Emeryville, California.

[3] I. M. Kolthoff, W. E. Harris and G. Matsuyama, THIS JOURNAL, **66**, 1782 (1944).

[4] M. Tokuoka, *Coll. Czechoslov. Chem. Comm.*, **4**, 444 (1932).

[5] M. Tokuoka and J. Ruzicka, *ibid.*, **6**, 339 (1934).

[6] J. S. Laird and T. C. Simpson, THIS JOURNAL, **41**, 524 (1919).

[7] Abel, *Z. physik. Chem.*, **148**, 337 (1930).

[8] Bray *et al.*, *Chem. Rev.*, **10**, 161 (1932).

[9] Concentrations of nitrous acid, as given in this paper, include both un-ionized and ionized forms.