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The Use of Hydrogen Fluoride in Preparing Organo-silicon Fluorides

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The replacement of chlorine by fluorine in a molecule is usually accomplished with the aid of metallic fluorides as reagents or catalysts.[1] If, however, the chlorine is sufficiently labile, the use of anhydrous hydrogen fluoride alone is possible.[2] Because of side reactions induced by the metals, yields in the absence of catalysts are generally better, and the purification of the products is simplified. Chlorine attached to silicon enters readily into reactions such as hydrolysis or ammonolysis. We have found the corresponding reaction with hydrogen fluoride to proceed at room temperature or below, producing the fluorides in good yield.

The previous literature on fluorosilanes is limited, with one exception, to the trisubstituted monofluoro compounds. Triethylmonofluorosilane was made from the reaction of ammonium fluoride on a sulfuric acid solution of di-triethylsilyl ether.[3] The addition of SiF_4 to an ether solution of a suitable Grignard reagent resulted in the formation of the corresponding trialkyl and triaryl fluorosilanes.[4,5] The preparation of the di- and tri-fluorosilanes of ethyl and phenyl from the action of zinc fluoride on the corresponding chlorides and by a modification of the procedure used by Flood[3] employing the hydrolyzed polymer is reported in a recent paper.[6]

In the present work the reaction of hydrogen fluoride on the chlorosilanes proceeded rapidly without the addition of any metallic catalyst. Neither silicon tetrafluoride nor hydrocarbons were detected in the reaction products, indicating the complete stability of the carbon–silicon bond to hydrogen fluoride at room temperature.

The chlorosilanes were prepared by the usual procedure[7] from the diethyl ether solution of the appropriate Grignard reagent and silicon tetrachloride. In most cases the mixed chlorosilanes were distilled to obtain the individual chlorides. The methyl compounds, whose boiling points are too similar for convenient separation, and the phenyl compounds, whose boiling points are high, were converted before separation. In all cases the final products were purified by careful fractional distillation.

Since the procedure for conversion was essentially the same for each substance, except for modifications due to the varying boiling points of the products, only the preparation of *di-n*-butyldifluorosilane will be described in detail.

Experimental

Preparation of Di-*n*-butyldifluorosilane.—To 90 g. of anhydrous hydrogen fluoride in a copper pot, cooled in ice, was added 82 g. of di-*n*-butyldichlorosilane. The reaction proceeded slowly with the evolution of hydrogen chloride. About thirty minutes was required for the addition of the chloride, after which time the mixture was allowed to stand overnight, warming to room temperature. The residual hydrogen fluoride was removed by the addition of anhydrous sodium fluoride. After filtration, the solid was rinsed once with benzene. The filtrate and washings were combined and fractionated. At 153.9 to 154.1° (uncor.), 49 g. (70% yield) was obtained. As there was no rise in temperature at the end of the distillation, and as a hold up and residue of 6 g. remained in the column, and also as neither silicon tetrafluoride nor hydrocarbons were detected as reaction products, a significantly higher yield could be expected on using larger quantities.

No systematic study was made to determine optimum conditions. The quantities used were small and the high vapor pressures and reactive nature of the materials resulted in losses. Yields reported below are therefore probably minimum values. The experimentally found yield in the various preparations are: Bu_3SiF, 50%; Bu_2SiF_2, 70%; $BuSiF_3$, 40%; Am_3SiF, 70%; Am_2SiF_2, 80%; $AmSiF_3$, 40%. For the methyl and phenyl compounds a separation of the chlorides was not made prior to the conversion and yields were not calculated but appear to be of about the same magnitude.

Methylfluorosilanes.—In the preparation of the methylfluorosilanes, under these conditions, the products are gases. They were led directly to a tower of anhydrous sodium fluoride in an iron pipe. The heat of absorption raised the temperature to a point where hydrogen chloride and silicon tetrafluoride from the unreacted silicon tetrachloride, as well as hydrogen fluoride, were absorbed. The material passing through the tower was caught in a trap cooled in a Dry Ice-acetone mixture and subsequently fractionated in a low-temperature packed-column.[8]

A summary of the compounds prepared and their properties is given in Table I.

Analysis.—The usual procedures for analysis of organosilicon compounds required modifications before they were successful with the fluorosilanes. The chlorosilanes readily react with an aqueous base, and the liberated acid can be determined by titration. With the fluorosilanes, except for the methyl compounds, quantitative hydrolysis could not be achieved even after prolonged refluxing with a base, as evidenced by high equivalent weights and low fluorine valves. The alternative procedure, the determination of silica from acid oxidation,[9] cannot be applied because of the loss of silicon as the volatile tetrafluoride.

The method adopted was a modification of that of Hahn and Reid.[10] A 0.3–0.4-g. sample was weighed into an ordinary pharmacist's gelatin capsule. The capsule was placed in a Parr bomb with 15 g. of sodium peroxide and 1.0 g. of starch. After ignition, the bomb contents were dissolved in 100 cc. of water and boiled to decompose excess peroxide. The solution was diluted to 400 cc. and

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[1] For a recent review see the article by A. L. Henne in Gilman's "Organic Chemistry," Vol. I, John Wiley and Sons, New York, N. Y., 1943, p. 944.

[2] (a) K. Fredenhagen, *Z. physik. Chem.*, **164**, 190 (1933); (b) J. H. Simons and C. F. Lewis, THIS JOURNAL, **60**, 492 (1938).

[3] E. A. Flood, *ibid.*, **55**, 1735 (1933).

[4] J. A. Gierut, F. J. Sowa and J. A. Nieuwland, *ibid.*, **58**, 897 (1936).

[5] H. V. Medoks, *J. Gen. Chem.* (U. S. S. R.), **8**, 291 (1938); *C. A.*, **32**, 5392 (1939).

[6] H. J. Emeleus and C. J. Wilkins, *J. Chem. Soc.*, 454, (1944).

[7] F. S. Kipping, *Proc. Chem. Soc.*, **20**, 15 (1904).

[8] E. O. Ramler and J. H. Simons, *Ind. Eng. Chem., Anal. Ed.*, **14**, 430 (1942).

[9] J. F. Hyde and R. C. DeLong, THIS JOURNAL, **63**, 1194 (1941).

[10] F. C. Hahn and E. E. Reid, *ibid.*, **46**, 1652 (1924).

TABLE I

PROPERTIES OF ORGANOFLUOROSILANES

Compound	B. p., °C. (uncor.)	Mol. wt. Calcd.	Mol. wt. Found	Si, % Calcd.	Si, % Found	F, % Calcd.	F, % Found	$d^{28.5}_4$
$MeSiF_3$	−28	100.1	97.5 (D)	...	...	33.4[a]	34.2[a]	....
Me_2SiF_2	2	96.1	95.1 (D)	...	...	48.1[a]	50.5[a]	....
n-$BuSiF_3$	50–52	142.1	145.0 (D)	19.75	19.40	40.11	40.35	1.006
n-Bu_2SiF_2	154	180.2	190.0 (V.M.)	15.57	15.03	21.09	21.50	0.9048
n-Bu_3SiF	212–224	218.3	...	12.85	13.09	8.70	8.52	.8465[b]
n-$AmSiF_3$	77	156.1	159.0 (D)	17.97	18.41	36.52	36.13	.9923
n-Am_2SiF_2	193	208.2	224.0 (V.M.)	13.45	13.74	18.25	18.67	.8972
n-Am_3SiF	263–266	260.3	...	10.78	10.98	7.30	7.64	.8415[b]
φSiF_3	101–102	162.1	178 (V.M.)	17.31	17.11	35.16	34.43	1.201[c]
φ_2SiF_2	246–247	220.1	...	12.75	13.26	17.27	17.57	1.155[c]

[a] Equivalent weights determined by titration after hydrolysis. [b] The densities given in ref. 4 are 0.8372 for the tributyl and 0.8389 for the triamyl compounds. [c] The densities given in ref. 6 at 17° are 1.212 for the trifluoride and 1.145 for the difluoride.

freed from metal hydroxides by filtration. The filtrate was made just acid to methyl red with concd. hydrochloric acid, 0.4 g. of sodium carbonate was added, and the solution evaporated to about 150 cc. After standing in the cold for two to three hours, or better overnight, the precipitated silica was collected on an ashless filter paper.

The filtrate and washings were evaporated to 100 cc., and 10 cc. of 20% aqueous calcium chloride was added slowly, with stirring, to the hot solution. The precipitate was coagulated by boiling, then filtered through a weighed Gooch crucible. The precipitate was washed with 20% acetic acid until the filtrate gave no test for calcium ion, and then twice with water. The crucible was dried at 110° for three hours, and then weighed.

It was never possible to remove the silica completely before precipitating the fluoride. The filtrate from the calcium fluoride, on standing for forty-eight hours, deposited a further amount. This was added to the silica previously collected, dried, and ignited to SiO_2.

An attempt was made to determine fluorine from the fusion solution as lead chlorofluoride. In the presence of the high salt concentration little or no precipitate formed.

Densities.—Molecular weights were determined from the vapor density, assuming the perfect gas laws to be applicable. The values in the table initialed (D) were obtained by direct weighing of a known volume of gas; those marked (V. M.) were determined in a modified Victor Meyer apparatus using a vapor displacement method.

Liquid densities were obtained in a 3-cc. pycnometer. There are published values for the series of trialkyl compounds from ethyl to amyl.[4] These values differ considerably from the ones presented here. However, the trend in their values toward higher densities with increasing length of alkyl radical seems at variance with the expected decrease in density for higher hydrocarbon content, which characterizes not only our derivatives but also the homologous series of the known chlorosilanes.[11] The value of Emeleus and Wilkins[6] for the density of phenyl trifluorosilane is confirmed, but there is a significant difference between their value for the diphenyl difluorosilane and that herein reported.

The alkylfluorosilanes are much less reactive toward metathesis than the corresponding chlorosilanes. The trifluoro compounds fume in moist air and are largely hydrolyzed by water. The difluorides do not fume in air and are not readily hydrolyzed by dilute ammonium hydroxide, but they will react with aqueous sodium hydroxide. The higher trialkylmonofluorosilanes are not detectably hydrolyzed by an aqueous base, nor do they react with sodium in liquid ammonia.[4] The variation of activity with the size of the alkyl substituent is demonstrated by the fact that the trimethylfluorosilane can be titrated as an acid.[12]

This same variation is evident in their reaction with the Grignard reagent where the tetraethyl and triethylmonofluorosilanes are formed in about equal amounts,[4] while the propyl, butyl and amyl derivatives do not form the tetraalkylsilane to any appreciable extent under the same conditions.

The thermal stability of the fluorosilanes is remarkable. Even so complex a member as dibutyldifluorosilane can be heated in a sealed glass tube to 300° without evident decomposition. Monomethyltrifluorosilane is quite stable at 400° and decomposes only slowly at 600°.

Summary

1. The reaction of hydrogen fluoride on an organo chlorosilane is employed to produce the corresponding fluorosilane.

2. The fluorosilanes reported for the first time are: monomethyl, dimethyl, mono-*n*-butyl, di-*n*-butyl, mono-*n*-amyl, and di-*n*-amyl.

3. A suitable scheme of analysis is described which consists of a combustion with sodium peroxide, solution, precipitation of silicon as SiO_2, and precipitation of fluorine as CaF_2.

4. Physical properties of the fluorosilanes such as boiling points, vapor densities, and liquid densities are given, and the chemical properties are discussed.

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(11) E. Krause and A. von Grosse, "Die Chemie der metallorganische Verbindungen," Borntraeger, Berlin, 1937.

(12) Private communication from Dr. B. O. Pray.