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Preparation and Reactions of Dichlorodifluorosilane*

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In view of the differences in behavior of silicon tetrachloride and silicon tetrafluoride toward certain reagents, for example, alcohols, it was of interest to determine whether these differences would manifest themselves in the mixed halide, dichlorodifluorosilane. Selective replacement of the chlorine atoms in the mixed halide should provide a direct synthesis for a number of compounds of the general formula R_2SiF_2 ($R = \text{alkyl, alkylthio, alkoxy, etc.}$) which have hitherto been difficultly accessible.

During the course of this work, a new synthesis for the chlorofluorosilanes was developed. These halides have previously been prepared by the explosive reaction of chlorine with hexafluorodisilane¹ and by the Swarts reaction from silicon tetrachloride and antimony trifluoride.² Since neither method appeared suitable for large-scale laboratory preparation, attention was turned to the redistribution reaction by which the bromochlorides³ and fluoriodides⁴ of silicon, and the chlorofluorides⁵ and bromochlorides of phosphorus⁶ have been obtained by heating a mixture of the corresponding homohalides.

It was found that the chlorofluorosilanes can be conveniently prepared by passing a mixture of silicon tetrachloride and silicon tetrafluoride through a silica tube packed with broken porous plate heated to about 800°. The product normally consists of a mixture of all of the possible mixed halides and of unchanged reactants. However, it was possible to obtain a high conversion to the dichlorodifluorosilane by a combination of fractional condensation and recycling techniques as described in the Experimental section. By a simple low-temperature distillation, pure dichlorodifluorosilane was readily obtained in good yields.

The reaction of dichlorodifluorosilane with alcohols was of particular interest since silicon tetrachloride reacts readily to give esters of the type $(RO)_{4-x}SiCl_x$,⁷ whereas no well-defined products have been reported from silicon tetrafluoride.^{8,9} Esters of the type $(RO)_{4-x}SiF_x$ have been obtained by fluorination of the corresponding chloro compounds¹⁰ or ethyl orthosilicate.¹¹

The reaction of dichlorodifluorosilane with *n*-butyl alcohol in dry ether at -78° gave a mixture of products from which approximately equal amounts of dibutoxydifluorosilane and tributoxy-

fluorosilane, together with traces of butyl silicate, were isolated.¹² In view of the observation of Emelius and Heal¹⁰ on the disproportionation of diethoxydifluorosilane, it appears probable that the primary product of the reaction of dichlorodifluorosilane with *n*-butyl alcohol is dibutoxydifluorosilane and that the other products are formed by disproportionation.

Although it has been reported that mercaptans do not react with silicon tetrachloride,¹³ the thio orthosilicates are obtained when the alkali metal mercaptides are obtained.¹⁴ No reports on the behavior of mercaptans toward silicon tetrafluoride have been noted. With dichlorodifluorosilane, it was found that the alkali metal mercaptides react smoothly in the cold to give good yields of the previously unknown bis-(alkylthio)-difluorosilanes, $(RS)_2SiF_2$. Thus, with sodium ethyl mercaptide, bis-(ethylthio)-difluorosilane and some tris-(ethylthio)-fluorosilane were obtained. These compounds, like the oxygen analogs, are rapidly hydrolyzed by water.

The behavior of dichlorodifluorosilane toward Grignard reagents was also of interest since silicon tetrachloride reacts to give the series $R_{4-x}SiCl_x$,¹⁵ whereas with silicon tetrafluoride the main product is usually of the type R_3SiF .^{16,17} From the reaction of dichlorodifluorosilane in ether with 2 moles of *n*-propylmagnesium bromide at -78°, there was isolated mainly dipropyldifluorosilane, some dipropylchlorofluorosilane, and higher boiling products from which no pure individuals could be isolated. The preponderance of dipropyldifluorosilane in the product indicates that selective reaction of the chlorine atoms does occur.

Experimental

Preparation of Dichlorodifluorosilane.¹⁸—The apparatus is shown in Fig. 1. Silicon tetrafluoride (368 g.) was bubbled through silicon tetrachloride (550 g.) warmed to about 50° and the mixed vapors passed through a silica tube packed with broken porous plate heated to 830° in an electric furnace (A). The exit gases were passed through a vertical condenser (B) maintained at -30 to -35° and the condensate, consisting mainly of trichlorofluorosilane and unchanged silicon tetrachloride, returned directly to the mixing chamber through tube (C) which dipped below the surface of the silicon tetrachloride. The vapors were led to the bottom of a second vertical condenser (D) cooled to -60 to -65°. The condensate (540 g.), which was rich in dichlorodifluorosilane, was collected in the receiver (E) cooled to -60°, and the effluent vapors then led through a spiral trap (F) cooled to -78° to obtain 101 g. of condensate. Exit gases from the trap were vented through a mercury bubbler (G) and the rate of input of silicon tetrafluoride adjusted to keep this loss at a minimum.

At the end of the run, which required 13.5 hours, 169 g.

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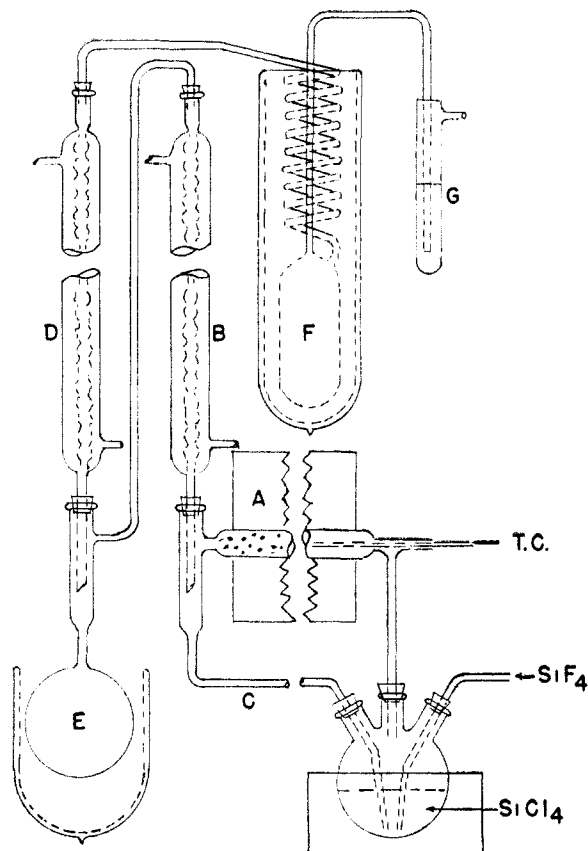


Fig. 1.

of silicon tetrachloride remained in the mixing vessel. The material collected in the receiver (E) was distilled through a 24-in. low temperature column packed with glass helices with the head cooled to -78° to obtain 95 g. of product boiling at -70 to -33° (mainly chlorotrifluorosilane), 378 g. of dichlorodifluorosilane boiling at -33 to -31° and 26 g. of higher boiling residue.

Additional quantities of dichlorodifluorosilane were obtained by recycling the products collected in the spiral trap and the distilled chlorotrifluorosilane with additional silicon tetrachloride. Thus, from 350 g. of silicon tetrachloride and 568 g. of product rich in chlorotrifluorosilane there was obtained 413 g. of product in the receiver (E) after twice more recycling the material collected in the spiral trap. At the end of the run, 264 g. of silicon tetrachloride remained in the mixing chamber. The product from the receiver (E) was distilled as above to obtain 75 g. of chlorotrifluorosilane, 316 g. of dichlorodifluorosilane and 2 g. of higher-boiling residue.

Reaction of Dichlorodifluorosilane with *n*-Butyl Alcohol.—A solution of 37.8 g. of *n*-butyl alcohol in 50 ml. of dry ether was slowly added to a solution of 35 g. of dichlorodifluorosilane in 50 ml. of dry ether cooled to -78° . Precautions were taken throughout this and all succeeding experiments to exclude moisture. The mixture was allowed to warm to room temperature and the ether removed by distillation at atmospheric pressure. The residue was distilled under reduced pressure to obtain 17.5 g., b.p. $58-59^{\circ}$ (13 mm.) (Fraction A), 16.5 g., b.p. $113.5-114.5^{\circ}$ (13 mm.) (Fraction B) and 4.5 g. of higher-boiling residue (Fraction C).

Fraction A was shown by analysis to be the desired dibutoxydifluorosilane.¹⁹

Anal. Calcd. for $C_8H_{18}F_2O_2Si$: C, 45.28; H, 8.49; F, 17.92; Si, 13.20. Found: C, 44.30; H, 8.69; F, 17.45; Si, 12.60.

(19) Considerable difficulty was experienced in the analysis of compounds containing silicon and fluorine. Others have commented on similar difficulties. See, for example, Pearson, Brice and Simons. *This Journal*, **67**, 1769 (1945).

Fraction B corresponds to the tributoxyfluorosilane, b.p. 134° (32 mm.), obtained by Peppard, Brown and Johnson¹¹ by ester interchange between triethoxyfluorosilane and *n*-butyl alcohol.

Anal. Calcd. for $C_{12}H_{27}FO_3Si$: C, 54.13; H, 10.15; F, 7.14; Si, 10.51. Found: C, 54.66; H, 10.69; F, 6.50; Si, 10.40.

Distillation of Fraction C gave an easily hydrolyzed product boiling at $140-145^{\circ}$ (2 mm.), which serves to identify it as butyl orthosilicate.

Reaction of Dichlorodifluorosilane with Sodium Ethyl Mercaptide.—A solution of 36 g. of dichlorodifluorosilane in 175 ml. of dry ether was placed in a three-necked flask equipped with stirrer, condenser and device for adding a solid reagent. The flask and contents were cooled to -78° and 40 g. of dry sodium ethyl mercaptide was added portionwise with stirring. When the addition was complete, the mixture was allowed to warm to room temperature and filtered to remove solid salts. The ether was removed by distillation, leaving 40 g. of liquid product which was distilled to obtain 24 g. of product boiling at $163-164^{\circ}$ (Fraction A). Continued distillation under reduced pressure gave 6 g. of product boiling at $114-115^{\circ}$ (10 mm.) (Fraction B) and 3 g. of higher-boiling residue.

Anal. Fraction A. Calcd. for $C_4H_{10}F_2S_2Si$: C, 25.53; H, 5.32; F, 20.21; S, 34.04; Si, 14.89. Found: C, 27.38; H, 5.64; F, 21.55; S, 32.37; Si, 15.70.

Anal. Fraction B. Calcd. for $C_6H_{14}FS_2Si$: F, 8.26; S, 41.34; Si, 12.17. Found: F, 10.75; S, 40.34; Si, 12.50.

These results served to identify Products A and B as bis-(ethylthio)-difluorosilane and tris-(ethylthio)-fluorosilane, respectively. Both compounds are rapidly hydrolyzed by water to give white, gelatinous precipitates and a strong odor of ethyl mercaptan.

Reaction of Dichlorodifluorosilane with *n*-Propylmagnesium Bromide.—*n*-Propylmagnesium bromide was prepared from 82 g. of *n*-propyl bromide and 18 g. of magnesium turnings in 360 ml. of dry ether. The Grignard reagent was added slowly with stirring to a solution of 50 g. of dichlorodifluorosilane in 200 ml. of dry ether cooled to -78° . The mixture was allowed to warm to room temperature, heated to reflux for 1 hour and filtered. Two such runs were combined and the ether was evaporated on a steam-bath to obtain 60 g. of product. Repeated distillation gave 25 g. of product boiling at $111-113^{\circ}$ (Product A), 11 g. distilling at $140-144^{\circ}$ (Product B), and 11 g. of higher-boiling residue from which no pure compounds could be isolated.

Anal. Fraction A. Calcd. for $C_6H_{14}F_2Si$: C, 47.37; H, 9.22; F, 25.00; Si, 18.42. Found: C, 47.19; H, 9.37; F, 24.00; Si, 18.09.

Anal. Fraction B. Calcd. for $C_8H_{14}ClFSi$: C, 42.73; H, 8.32; Cl, 21.06; F, 11.28; Si, 16.62. Found: C, 42.14; H, 8.35; Cl, 18.61; F, 12.67; Si, 16.66.

These results served to identify Products A and B as di-*n*-propyldifluorosilane and di-*n*-propylchlorofluorosilane, respectively.

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Summary

1. Chlorofluorosilanes are readily obtained by passing a mixture of silicon tetrafluoride and silicon tetrachloride through a silica tube packed with broken porous plate heated to about 800° .

2. Dibutoxydifluorosilane and tributoxyfluorosilane have been obtained by the reaction of dichlorodifluorosilane with *n*-butyl alcohol. The monofluoro derivative is believed to arise from disproportionation of the difluoro compound during distillation.

3. Bis-(ethylthio)-difluorosilane and tris-(ethylthio)-fluorosilane have been prepared from dichlorodifluorosilane and sodium ethyl mercap-

tide. They represent a new class of silicon compounds.

4. Dichlorodifluorosilane reacts with *n*-propyl-

magnesium bromide to yield mainly dipropyl-difluorosilane and some dipropylchlorofluorosilane.

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The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms

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Introduction

This paper describes a technique for estimating the volume and area of porous adsorbents available to molecules of various sizes. This technique was developed to deal with relatively coarsely porous adsorbents exhibiting a wide range of pore sizes, but the procedure to be described appears to be applicable to porous solids of any nature.

Wheeler¹ proposed a theory which is a composite of BET multilayer adsorption and capillary condensation viewpoints. This theory can be summarized by the equation

$$V_s - V = \pi \int_{r_{pn}}^{\infty} (r - t)^2 L(r) dr \quad (1)$$

where V_s is the volume of gas adsorbed at saturation pressure, V is the volume of gas adsorbed at pressure p , $L(r)dr$ is the total length of pores whose radii fall between r and $r + dr$. r_{pn} is the critical radius, that is, the radius of the largest pore still completely filled with liquid adsorbate at any particular pressure and t is the multilayer thickness which is normally built up at pressure p .

Wheeler considered the radius of the pore to be equal to the sum of the multilayer thickness as calculated from the BET theory and the radius normally calculated from the simple Kelvin equation. He also suggested that the pore size distribution, $L(r)$, may be approximated by a simple Maxwellian or Gaussian distribution.

Shull² pointed out that the BET thicknesses become much larger than experimental thicknesses for flat surfaces in the high pressure region. Shull proposes the use of experimental data^{3,4} taken from nitrogen isotherms for crystalline materials, for the determination of the multilayer thickness, t , in the Wheeler theory. He then developed a simplified method for fitting the experimental data to Maxwellian or Gaussian distribution functions.

Almost simultaneously Oulton⁵ proposed a method for determining the pore distribution from the isotherm without the necessity of assuming a definite form for the distribution. He corrects for physical adsorption on the walls of pores empty of capillary condensed adsorbate, hereafter termed capillary condensate, by assuming that the thickness of the physically adsorbed layer is constant and equal to that of the statistical number of

monolayers at the relative pressure of the hysteresis point.

This paper will show that the assumption of a simple Gaussian or Maxwellian distribution of pore sizes is inadequate for many adsorbents. It will also show that Oulton's assumption of constant thickness for the physically adsorbed layer, while adequate for a finely porous material such as that to which he applied it (a cracking catalyst with a pore area maximum at radius 26.5 Å.), is inadequate to deal with more coarsely porous adsorbents. A formal analysis of the relationship between nitrogen desorption isotherms at liquid nitrogen temperatures and the distribution of pore volume and area with respect to pore radius will be made on the assumption that equilibrium between the gas phase and the adsorbed phase during desorption is determined by two mechanisms: (1) physical adsorption on the pore walls (which would occur to the same extent whether the area involved constituted walls of pores or a flat surface impenetrable to nitrogen), and (2) capillary condensation in what Oulton⁵ has called the "inner capillary volume." Results of the analysis will be applied to several adsorbents utilizing the experimental data used by Shull² to provide a functional relationship between thickness of physically adsorbed layer and relative pressure, and utilizing the classical Kelvin equation, relating vapor pressure depression to capillary radius, to define the relationship between volume of capillary condensate and relative pressure.

Analysis of Desorption

Consider a system of open ended, cylindrical pores (Fig. 1) such that all pores of equal radius can be regarded as responding in the same way with respect to changes of relative pressure of the adsorbate. Assume that the relative pressure $(P/P_0)_1$, differs infinitesimally from unity so that substantially all pores are filled with liquid. The largest pore⁶ has a radius r_{p1} . Upon its surface is a physically adsorbed layer of molecules of statistical thickness t_1 . Within this physically adsorbed layer is the inner capillary with radius r_k , from which evaporation occurs as P/P_0 is lowered.

Under the equilibrium conditions specified, the relationship between the pore volume, V_{p1} , and the inner capillary volume, V_k , is

$$V_{p1} = V_k r_{p1}^2 / r_k^2 \quad (2)$$

(6) For simplicity all pores of equal radius, or whose radii fall within chosen limits, will be referred to as if they were one pore.

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