

**317.** *Alkyl, Aryl, and Alkoxy-derivatives of Silicon Tetrachloride and Silicochloroform.*

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The compounds *ethylchlorosilane*, *diethylchlorosilane*, *phenylchlorosilane*, *diphenylchlorosilane*, *benzylchlorosilane*, and *dibenzylchlorosilane* have been prepared from silicochloroform by the Grignard reaction. A new method for the preparation of alkyl-alkoxysilanes by the reaction between sodium alkoxide and an alkyl silicon chloride is reported. *Diethyldimethoxysilane* is described. Other known compounds of this type were prepared by the same method and characterised.

THE alkyl, aryl, and alkoxy-derivatives of silicochloroform and silicon tetrachloride are of importance because on hydrolysis they give materials which are known to form resins when heated. The preparation of these resin intermediates from silicochloroform is in fact a useful alternative to their preparation by hydrolysis of the corresponding derivatives of silicon tetrachloride. The only reference in the literature to compounds of the type  $\text{SiRHX}_2$ , where X

is a halogen atom, is in work by Rochow (*J. Amer. Chem. Soc.*, 1945, **67**, 963), who states that if the reaction between methyl chloride and copper-silicon is conducted under conditions such that some pyrolysis of the free hydrocarbon radicals occurs, halogenated products of the type  $\text{SiRHX}_2$  appear in the product. Products in which the chlorine of silicochloroform is completely substituted are, however, known. For example, trimethoxysilane has been prepared from silicochloroform and methyl alcohol (Helferich and Hausen, *Ber.*, 1924, **57**, 795). The corresponding trialkyl compounds have been obtained by the action of zinc alkyls on ethyl orthosilicate (Ladenburg, *Annalen*, 1872, **164**, 301; Pape, *Ber.*, 1881, **14**, 1873), and triphenylsilane has been prepared by various methods (Kipping and Murray, *J.*, 1929, **360**; Reynolds, Bigelow, and Kraus, *J. Amer. Chem. Soc.*, 1929, **51**, 3067; Kraus and Eatough, *ibid.*, 1933, **55**, 5008). The preparations now described are of *ethyl-*, *phenyl-*, and *benzyl-dichlorosilane*, and *di-ethyl-*, *-phenyl-*, and *-benzyl-chlorosilane*, all of which were obtained by using the Grignard reaction. The alkyl-alkoxy-compounds described are related to the derivatives of silicochloroform by the fact that the alkyl (or aryl) groups are in both cases the only ones resistant to hydrolysis.

#### EXPERIMENTAL.

Silicochloroform was prepared by passing hydrogen chloride over powdered silicon at  $380^\circ$  (Booth and Stillwell, *J. Amer. Chem. Soc.*, 1934, **56**, 1529). The product was fractionated through a 16-inch Fenske column, the fraction of b. p.  $31\text{--}34^\circ$  being used in the following preparations.

*Ethylidichlorosilane*.—1.25 G.-mol. of ethylmagnesium bromide in 500 ml. of ether were added slowly to an ice-cooled, mechanically stirred solution of 135.5 g. of silicochloroform in 100 ml. of ether. The reaction mixture was heated under reflux for 4 hours, filtered, and the ethereal solution fractionated through a 16-inch Fenske column fitted with a reflux head, using a reflux ratio of 5 : 1. After removal of the ether, the following four fractions were obtained: (a) b. p.  $<74^\circ$  (8 g.), (b) b. p.  $74.5\text{--}75.5^\circ$  (39 g.), (c) b. p.  $75.6\text{--}95^\circ$  (6 g.), (d) b. p.  $95\text{--}98^\circ$  (5.5 g.). Analysis of fraction (b) gave: Si, 21.6; Cl, 54.7; C, 19.0; H, 4.7. ( $\text{C}_2\text{H}_4\text{Cl}_2\text{Si}$  requires Si, 21.7; Cl, 54.9; C, 18.6; H, 4.7%). A determination of the molecular weight by the Dumas method gave 134.1 (Calc.: 129.1). The vapour-pressure curve of this compound between  $-17^\circ$  and  $70^\circ$  was measured by means of an isoteniscope. The vapour-pressure data are represented by the equation  $\log p = 7.6271 - 1648.2/T$ ; the b. p. was  $74.2^\circ$ , and Trouton's constant 20.4. Fraction (d) was shown by chlorine analysis to be a mixture of the mono- and the di-ethyl compound.

The silicochloroform derivatives described below were prepared by the same method, a suitable proportion of the appropriate Grignard reagent being used. In each case a series of fractions was obtained, one of which preponderated and corresponded to the desired product.

*Diethylchlorosilane*.—A fraction of b. p.  $97\text{--}105^\circ$  was refractionated through a Fenske column and gave this compound, b. p.  $99\text{--}100^\circ$ . The yield of purified product was 19% (Found: Si, 22.9; Cl, 28.9; C, 39.1; H, 9.1; *M*, by Dumas method, 126.8, 128.1.  $\text{SiEt}_2\text{ClH}$  requires Si, 22.9; Cl, 28.9; C, 39.15; H, 9.0%; *M*, 122.7). The equation to the vapour pressure curve for the range  $0\text{--}94^\circ$  was  $\log p = 7.4195 - 1689.5/T$ . The b. p. and Trouton's constant were  $99.2^\circ$  and 19.5, respectively.

*Methylidichlorosilane*.—The Grignard compound used was ethylmagnesium chloride in *n*-butyl ether (Schmalfuss, *J. pr. Chem.*, 1924, **108**, 88). A fraction of b. p.  $40.7^\circ$  was obtained which proved to be the desired compound (Found: Si, 22.9; Cl, 61.9; C, 10.0; H, 4.6.  $\text{SiMeCl}_2\text{H}$  requires Si, 24.4; Cl, 61.7; C, 10.4; H, 3.5%). In this preparation three fractions were collected between  $33^\circ$  and  $40.5^\circ$ , and there was difficulty in obtaining a complete separation.

*Phenylidichlorosilane*.—A fraction of b. p.  $118\text{--}119^\circ/25$  mm. was twice refractionated and gave a fraction, b. p.  $65.0\text{--}65.3^\circ/10$  mm., of *phenylidichlorosilane* (Found: Cl, 40.2; C, 40.8; H, 3.5.  $\text{SiPhCl}_2\text{H}$  requires Cl, 40.0; C, 40.7; H, 3.4%).

*Diphenylchlorosilane*.—A fraction of b. p.  $147\text{--}170^\circ/10$  mm. was refractionated and gave a fraction, b. p.  $140\text{--}145^\circ/7$  mm., of the *chlorosilane* (Found: Si, 12.4; Cl, 16.3; C, 66.3; H, 5.3.  $\text{SiPh}_2\text{ClH}$  requires Si, 12.8; Cl, 16.2; C, 66.0; H, 5.1%).

*Benzylidichlorosilane* had b. p.  $48^\circ/2$  mm. (Found: Si, 14.6; Cl, 37.0; C, 45.8; H, 4.2.  $\text{Si}(\text{CH}_2\text{Ph})\text{Cl}_2\text{H}$  requires Si, 14.7; Cl, 37.0; C, 46.1; H, 4.2%), and *di-benzylchlorosilane* b. p.  $146\text{--}148^\circ/\text{ca. } 1$  mm. (Found: Si, 11.5; Cl, 14.6; C, 67.5; H, 6.2;  $\text{Si}(\text{CH}_2\text{Ph})_2\text{ClH}$  requires Si, 11.4; Cl, 14.4; C, 68.1; H, 6.1%).

*Alkylalkoxysilanes*.—The four compounds of this type prepared were ethyltriethoxy-, diethyldiethoxy-ethyltrimethoxy-, and *diethyl-dimethoxy-silane*. Ladenburg's method of preparation (*Annalen*, 1874, **173**, 143) using the reaction between diethyl zinc and the appropriate silicon ester is not convenient. Reaction between Grignard compounds and esters of orthosilicic acid has been used by Post and Hofrichter (*J. Org. Chem.*, 1939, **4**, 363), and Adrianov (*J. Gen. Chem. U.S.S.R.*, 1938, **8**, 558, 1255; 1939, **9**, 203) has prepared monosubstituted derivatives of the type  $\text{SiR}(\text{OEt})_2$  by forming the Grignard compound *in situ* from the alkyl halide and magnesium in presence of ethyl orthosilicate, with which reaction then occurs. It is not possible by means of the ordinary Grignard reaction to substitute more than one of the alkoxy-groups of an orthosilicic ester.

The direct method of preparing compounds of this type is by reaction of the alkylsilicon chloride with an alcohol. The alcohol must be completely dry or much material of high molecular weight is obtained; *e.g.*, Friedel and Crafts (*Annalen*, 1865, **136**, 203) found that in the reaction between silicon tetrachloride and methanol, two compounds,  $\text{Si}(\text{OMe})_2$  and  $\text{Si}(\text{MeO})_2\text{O}\cdot\text{Si}(\text{OMe})_2$ , were obtained. Our preliminary experiments showed that on refluxing diethylsilicon dichloride and ethyl alcohol together, a considerable quantity of ethyl chloride was formed. This was isolated and characterised by its vapour-pressure curve; it is presumably formed in the secondary reaction between the alcohol and hydrogen chloride,

which yields the alkyl halide and water. Thus, even if the alcohol is initially dry, this water will inevitably lead to the production of more complex products. This difficulty has been overcome by using the sodium derivative of the alcohol in place of the alcohol itself.

The ethylsilicon halides required as intermediates were prepared by means of the Grignard reaction (Kipping, *J.*, 1907, **91**, 209). The sodium alkoxide was prepared by adding sodium in small pieces to an excess of the pure alcohol in a flask fitted with a reflux condenser, boiling off the excess of alcohol at the completion of the reaction, and removing the residual alcohol in an oil-pump vacuum. The product was a fine white powder.

The theoretical quantity of sodium ethoxide covered with ether was placed in a three-necked flask fitted with a mechanical stirrer, reflux condenser, and tap-funnel. The suspension was well stirred, and a solution of the theoretical quantity of ethylsilicon trichloride in an equal volume of ether was added slowly. The product was refluxed for an hour, transferred to a Kon flask and distilled. Ethyltriethoxysilane was collected at 155–160° and redistilled; b. p. 158–160°, yield 40% (Found : Si, 14.73, 14.65. Calc. for  $C_8H_{20}O_3Si$  : Si, 14.60%).

Similar preparations were carried out for diethyldiethoxysilane (b. p. 156–157°, yield, 40%), ethyltrimethoxysilane (b. p. 123°, yield 58%), and *diethylidimethoxysilane* (b. p. 130°, yield 70%) (Found : Si, 18.75, 18.96, 18.78; *M*, by Dumas method, 151.0, 153.3, 152.5.  $C_6H_{16}O_2Si$  requires Si, 18.92%; *M*, 148.3).

The vapour-pressure curves of these compounds were studied by means of an isoteniscope technique, the results being tabulated below.

Compound.	Vapour-pressure relationship.	B. p.	Latent heat, cal./g.-mol.	Trouton's constant.
$SiEt(OEt)_3$ . . . . .	$\log p = 7.4759 - 1980.5/T$	158.9°	9085	21.03
$SiEt_2(OEt)_2$ . . . . .	$\log p = 7.3896 - 1940.5/T$	157.3	8883	20.64
$SiEt(OMe)_3$ . . . . .	$\log p = 7.8760 - 1968.1/T$	120.9	9007	22.86
$SiEt_2(OMe)_2$ . . . . .	$\log p = 7.912 - 2018.5/T$	128.1	9240	23.03

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