By W. D. English,² A. Taurins, and R. V. V. Nicholls

ABSTRACT

By passing appropriate dichloroalkanes, e.g. 1,1-dichloroethane, over a mixture of silicon and copper at elevated temperature, the new compounds 1,1-bis-trichlorosilylethane, 1,2-bis-trichlorosilylpropane, and 1,4-bis-trichlorosilylbutane and the previously reported *bis*-trichlorosilylmethane, dichlorosilyltrichlorosilyl-methane, and 1,2-*bis*-trichlorosilylethane were synthesized. Trichloromethane yielded perchlorodisilane; 2-chloropropane gave propene.

By causing the chlorosilylalkanes to react with lithium aluminum hydride, disilylmethane, 1,1-disilylethane, 1,2-disilylethane, and 1,2-disilylpropane were synthesized.

Several physical constants of the compounds were measured.

INTRODUCTION

Few organo-silicon compounds have been prepared which contain more than one silicon atom with each silicon having only one silicon-carbon bond. Of compounds with the structure $(SiX_3)_2R$ where X is halogen, only those where R represents methylene (11,18), dimethylene (3,11), and trimethylene (3) have been described, while no compound of the type $(SiH_3)_2R$ has been reported.

The Rochow synthesis of organo-silicon compounds (15,16,17) extended to the use of polyhaloalkanes by Patnode and Schiessler (11,12) provides a simple method for the introduction of two silicon atoms into a molecule. The process developed by Finholt et al. (5,6) using lithium aluminum hydride is suitable for the replacement of chlorine with hydrogen.

In this investigation dichloromethane, 1,1- and 1,2-dichloroethane, 1,2-dichloropropane, and 1,4-dichlorobutane were used as sources of the corresponding bis-trichlorosilylalkanes. Trichloromethane did not form tris-trichlorosilylmethane, nor did 2-chloropropane give 2-trichlorosilylpropane. Reduction of the bis-trichlorosilyl derivatives of methane, ethane, and propane yielded the corresponding disilylalkanes.

EXPERIMENTAL³

The silicon used in this research contained iron, 0.89%; aluminum, 0.78%; calcium, 0.2%; manganese, 0.03%. The various haloalkanes were used as received. Cylinder nitrogen was deoxygenated in the manner described by Uhrig, Roberts, and Levin (21).

Reaction tubes of stainless steel or Pyrex were employed. They were heated in electric furnaces controlled by autotransformers.

The condensing system consisted of three sections. The first was a trap maintained above the boiling point of the reactant but below that of the product. Then a condenser and flask kept at 0°C., and finally a trap cooled by Dry Ice. Uncondensed gases passed out through a calcium chloride drying tube.

Vapor pressures were measured dynamically in an apparatus similar to that

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Melting and boiling points are corrected.

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to F Q	F1~:/	%	Chlorine	%	Silicon	Mol	. wt.
rroauce	riein,	Calc.	Found	Calc.	Found	Calc.	Found
Cl ₃ SiCH ₂ SiCl ₃	8	75.2	75.8, 75.1	18.8	18.7	283	291
(Cl₂HSiCH₂SiCl₃	ŝ	71.2	69.7	22.5	20.0	249	260
Cl ₃ SiCH(CH ₃)SiCl ₃	∞.	71.7	71.8, 70.3 70.2, 71.1	18.9	18.7, 19.0 18.9		I
Cl ₃ SiCH ₂ CH ₂ SiCl ₃	1	71.7	71.8	18.9	19.0	297	299
Cl _a SiCH ₂ CH(CH ₃)SiCl ₃	1.6	68.5	68.5, 67.2 67.0	18.1	18.5, 18.0 19.2	<u>į</u> 1	11
Cl ₃ Si(CH ₂) ₄ SiCl ₃	0.01	65.6	65.5	17.2	17.2	1	I
Cl ₃ SiSiCl ₃	0.3	i	1	I	1	1	ł

TABLE I The Rochow reaction

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Reactant	Flow rate, gm./hr.	Furnace temperature, °C.	Product	Yield, %	
Dichloromethane	21	350-390	ClaSiCH2SiCl3 Cl2HSiCH2SiCl3	∞ m	
1,1-Dichloroethane	30	360-380	Cl ₃ SiCH(CH ₃)SiCl ₃	. 00	
1,2-Dichloroethane 1,2-Dichloropropane	120	> 330 300-320 (\$ 360)	Cl ₃ SiCH ₂ CH ₂ SiCl ₃ Cl ₃ SiCH ₂ CH(CH ₃)SiCl ₃	1.6	

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Identified as dibromide

 $CH_{3}CH = CH_{2}$ Cl₃SiSiCl₃

0.312

330-360 340 - 360360-410

73 83 45

1,4-Dichlorobutane Trichloromethane 2-Chloropropane 647

described by Mack and France (10). Densities were determined with a Fisher-Davidson gravitometer. Molecular weights were determined cryoscopically in benzene.

Refractive indices were measured with an Abbé refractometer. Although precautions were taken, after only 10 measurements with *bis*-trichlorosilylmethane, enough polymerization had taken place on the prisms to render the instrument useless. The prisms had to be reground. Dr. M. C. Hunter advised us (8) that no compound containing more than three silicon-halogen bonds should be placed in a prism refractometer.

A mixture was made of silicon and copper powders, 9:1 by weight, both powders -50, +100 mesh. Enough powder was placed in the reaction tube to half fill it. Nitrogen was passed through the tube while the temperature was raised. Then the alkyl halide was added at such a rate that its vapor formed a 1:1 mixture with the nitrogen. After all the alkyl halide was added the temperature was raised to 500°C, with the nitrogen still flowing to sweep out the reactor.

Table I contains a summary of the best conditions found for each reactant, the products formed, and analyses of the products. Chlorosilyl compounds were analyzed by the method of Hyde and DeLong (9). Hydrogen attached to silicon was determined by Stock's method (20), and the resulting solution was then analyzed for silicon.

Reaction of Chloroform with Copper-Silicon

When 360 gm. of chloroform was passed over heated copper-silicon (340-360°C.), 100 gm. was recovered. Aside from a large quantity of silicon tetrachloride, the only product identified was 1.2 gm. boiling at 140-150°C. Perchlorodisilane boils at 145°C. (7).

Reaction of 2-Chloropropane with Copper-Silicon

When 210 gm. of 2-chloropropane was passed through the heated copper-silicon (360-410°C.) a large amount of liquid condensed in the Dry-Ice-cooled trap. At room temperature this evolved a gas which decolorized bromine in carbon tetra-chloride. 1,2-Dibromopropane (63 gm.) was obtained by fractionation. This boiled at 138-142°C.; d, 1.938; $n_{\rm p}^{20}$, 1.5195. The literature (7) gives the following constants: b.p., 140°C.; d, 1.933; $n_{\rm p}^{20}$, 1.5203.

The reactions between chlorosilanes and lithium aluminum hydride were carried out in round-bottomed five-necked flasks. A dropping funnel, an indented West condenser for refluxing, a nitrogen inlet, and a thermometer were connected to the flask. There was a connection between the flask and the top of the dropping funnel to equalize pressure. To the upper end of the reflux condenser was attached a trap cooled in Dry Ice. The trap opened to the atmosphere through a calcium chloride drying tube. In Table II are listed the disilyl alkanes synthesized and the analytical results.

Synthesis of Disilylmethane

Reduction of 32 gm. of dichlorosilyltrichlorosilylmethane in 50 ml. ether by the addition of 24 gm. of lithium aluminum hydride in 250 ml. ether, followed by fractional distillation of the solution, yielded 5 gm. (52%) disilylmethane,

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		Analysis						
Compound	Yield, %	%	Silicon	% Hydrogen attached to silicon				
		Calc.	Found	Calc.	Found			
Disilylmethane 1,1-Disilylethane 1,2-Disilylethane 1,2-Disilylpropane	0-80 . 8 5 Produc	73.4 62.2 t not com	73.6 62.3,62.6 pletely pure*	7.9 6.7 _	4.0* 6.6 -			

TABLE II Disti vi al kanes

*See text.

boiling at 26–27°C. This was a colorless, mobile liquid whose vapor ignited spontaneously in air. Once, while some of the vapor was being transferred, it was accidentally mixed with a small quantity of air and then slightly warmed ($> 35^{\circ}$ C.). The apparatus was completely shattered in the resulting explosion.

A sample weighing 0.0219 gm. was analyzed. The amount of hydrogen that should have been released was 38.6 ml. The amount actually released was 19.5 ml. or 0.504 of the theoretical amount. When the solution was acidified a further quantity of gas was evolved. This observation was not repeated as the rest of the disilylmethane was lost in the explosion described.

No product was obtained when excess lithium aluminum hydride solution was added to *bis*-trichlorosilylmethane. When the chlorosilane was added to the hydride an 80% yield was obtained.

Synthesis of 1,2-Disilylpropane

1,2-bis-Trichlorosilylpropane, 0.8 gm., was hydrogenated. Fractionation did not yield pure 1,2-disilylpropane. However, the fraction boiling where predicted by the Egloff equation, 94°C., contained more silicon than the fractions on either side (Table III). It is believed that the compound synthesized was 1,2-disilylpropane.

FRACTIO	NATION OF 1	,2-DISILY	LPROPANE
Boiling range (corrected), °C.	Weight, gm.	% Si	Weight Si gm.
92-94 94-96 96-98	$0.2 \\ 0.3 \\ 0.7$	$3.9 \\ 8.6 \\ 1.7$	$\begin{array}{c} 0.008 \\ 0.026 \\ 0.012 \end{array}$

DISCUSSION OF RESULTS

The Rochow synthesis was found to be simple but yields were low. Temperature control was usually not critical in the range 300-400°C. as long as at least 300°C. was maintained. Preheating the copper-silicon mixture with hydrogen at 1000°C. did not affect the yields, nor did the rate of addition of the dichlo roalkane. These findings are similar to those reported by Riccoboni and Zotta (1 4). The relative positions of the chlorine atoms influenced the yields. 1,1-Dichloro compounds gave 8% yields, 1,2- compounds gave *ca*. 1% yields, and 1,4-dichlorobutane gave only a trace (0.01%) of 1,4-*bis*-trichlorosilylbutane.

In all experiments more silicon tetrachloride and silicon chloroform were produced than desired products and there were low boiling substances which did not contain silicon or labile chlorine. In the experiments with 1,2-dichloropropane the by-product decolorized a solution of bromine in acetic acid but no brominated substance could be isolated. When 2-chloropropane was the starting material an unsaturated substance was identified as propene from the dibromide. The low boiling by-products from experiments with dichloromethane and 1,1-dichloroethane did not decolorize bromine solutions. From these properties, it is likely that the by-products were hydrocarbons. These have previously been reported from the Rochow reaction (19).

The presence of silicon-hydrogen bonds in the products, e.g. dichlorosilyltrichlorosilylmethane from dichloromethane, the large quantities of chlorosilanes and hydrocarbons produced, and the low yields of the desired products all point to extensive decomposition of the dichloroalkanes. This could not be avoided, as, at temperatures causing less decomposition, less of the desired products were obtained.

An interesting point is that no products were identified in which only one of the original chlorine atoms had reacted to yield a chloroalkyltrichlorosilane.

The reaction of trichloromethane with copper-silicon to produce perchlorodisilane was similar to the synthesis of that compound from carbon tetrachloride (2, 12).

The physical properties of the compounds synthesized are summarized in Table IV.

All compounds were colorless when pure but the chlorine-containing ones decomposed to colored substances on standing. *bis*-Trichlorosilylmethane exhibited a blue fluorescence in ultraviolet light. A similar fluorescence was noted by Challenger and Kipping (4) with some of their alkylchlorosilanes. The completely hydrogenated substances had a musty odor, the lower chlorine-containing ones had the odor of hydrogen chloride, and the higher ones had a musty yet sharp odor.

Vapor pressures at several temperatures were measured for most of the compounds. Graphs were plotted of vapor pressure vs. temperature and log vapor pressure vs. reciprocal of absolute temperature. The former were smooth curves, the latter straight lines. The equations of the straight lines were calculated and are given in Table IV. The latent heats of evaporation and Trouton's constants were calculated from the slopes of the log p vs. T^{-1} plots. The Trouton values indicated that the chlorine-containing compounds were associated, while disilylmethane was not. This is similar to previous findings (1,6).

The only reference to dichlorosilyltrichlorosilylmethane in the literature (11) gives just one datum, $b.p._{10} = 51.0-52.5^{\circ}$ C. In this work the boiling point measured at atmospheric pressure was 167–168°C. Using the Ramsay-Young

PHYSICAL PI	ROPERTIES O	F ORGANIC	COMPOU	UNDS CONTA	INING TW	O SILICON /	ATOMS		
· · · · · · · · · · · · · · · · · · ·	}			Vapor pressure equation					
	B.p., °C.	Density	l,	Const	tants	Range.	Error.	Lv(calc.),	Trouton's
Compound	at 760 mm.	gm./ml.	· · C.	A	В	°K.	±°K.	cal./mol.	cal./mol./°K.
bis-Trichlorosilylmethane ² (Cl ₃ SiCH ₂ SiCl ₃)	1803	1.545 1.521	17	- 2380	8.1397	328-453	1.5	10,900	24.0
Dichlorosilyltrichlorosilylmethane (Cl2HSiCH2SiCl3)	167–1684	1.464	27.5	-	-	-	-	-	-
1,1-bis-Trichlorosilylethane (Cl ₃ SiCH(CH ₃)SiCl ₃)	191	1.454	27.5	- 2425	8.1089	363-468	1.2	11,900	23.7
1,2-bis-Trichlorosilylethane (Cl ₃ SiCH ₂ CH ₂ SiCl ₃)	198 ⁵ 85(25mm.)	1.467	28	- 2440	8.059	401-474	1.2	11,180	23.6
1,2-bis-Trichlorosilylpropane (Cl ₃ SiCH ₂ CH(CH ₃)SiCl ₃)	175-180 (80 mm.)	-	-	-	-	<u> </u>	-	-	-
1,4-bis-Trichlorosilylbutane (Cl ₂ Si(CH ₂) ₄ SiCl ₃)	97-99 (5 mm.)] -	-	-	- 1	-		-	-
Disilylmethane (H ₃ SiCH ₂ SiH ₃)	28	0.754	20	- 1370	7.4190	247-299	0.7	6240	20.8
$\begin{array}{l} 1,1\text{-}Disilyle thane (H_{3}SiCH(CH_{3})SiH_{3}) \\ 1,2\text{-}Disilyle thane (H_{3}SiCH_{2}CH_{2}SiH_{3}) \\ 1,2\text{-}Disilyl propane (H_{3}SiCH_{2}CH(CH_{3})SiH_{3}) \end{array}$	$\begin{array}{r} 56-57\\67.0-68.5\\94-96\end{array}$	M.p. — M.p. —	50°C. 15°C. t	o – 14°C.					
$\frac{1}{1} \log h_{m} = A T^{-1} + B$	i	<u> </u>			·				

TABLE IV

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¹ $log p_{mm} = A I^{-1} + B.$ ² $n_{22}^{22} = 1.471 \pm 0.001.$ ³ $B.p_{.164} = 184 - 185^{\circ}C.$ (11), $b.p. = 185.1 - 185.5^{\circ}C.$ (18). ⁴ $B.p_{.16} = 51.0 - 52.5^{\circ}C.$ (11). ⁵ $B.p. = 202^{\circ}C.$ (2), $b.p_{.25} = 92.5 - 93^{\circ}C.$ (11).

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formula (13) with bis-trichlorosilylmethane as the reference substance, the boiling point of dichlorosilyltrichlorosilylmethane was calculated to be 51°C, at 10 mm. pressure.

All compounds hydrolyzed very rapidly in alkali, forming curdy, brittle gels; those containing chlorine hydrolyzed slightly more rapidly than those without. The chlorinated compounds fumed in air. Glass apparatus dried at 110°C. for several hours still retained sufficient moisture to cause formation of polymer films.

Why disilylmethane evolved only 50% of the theoretical quantity of hydrogen when decomposed with alkali cannot be explained. The further evolution of gas when the solution was neutralized may indicate that a complex formed in the concentrated solution. Stock (20) used 30% sodium hydroxide while 60% potassium hydroxide was used in our work.

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