tion with alkyl halides in the presence of a suitable metal at elevated temperatures.

2. A similar reaction whereby chlorosilanes may be hydrogenated with hydrogen gas or hydrogen chloride to form silicon–hydrogen compounds also has been found. It has been possible, in effect, to produce SiH_4 from $SiCl_4$.

3. The mechanism of the alkylation and hydrogenation reactions has been discussed.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Derivatives of the Methylchlorosilanes. II. 2-Chloroethoxysilanes

BY ROBERT O. SAUER AND WINTON PATNODE

The usual method of converting halogenosilanes to their alkoxy derivatives, namely, alcoholysis, possesses several obvious disadvantages, most of which attend the concomitant and vigorous evolution of hydrogen halide. In the hope of eliminating this corrosive, volatile by-product we have undertaken a study of the etherification of halogenosilanes by various epoxides. In the present paper the reaction products of several chlorosilanes with ethylene oxide[1] are described (eq. 1: R = H—, CH_3—, C_6H_5—).

$$R_NSiCl_{4-N} + (4\text{-}N)\underbrace{CH_2CH_2O}_{} \longrightarrow R_NSi(OCH_2CH_2Cl)_{4-N} \quad (1)$$

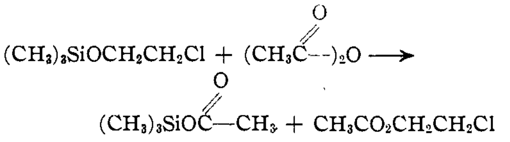
Etherification with this reagent presumably occurs in two steps, the first and perhaps rate-determining one being the addition of hydrogen chloride (generally present in chlorosilanes in at least traces) to the ethylene oxide (eq. 2).

$$\underbrace{CH_2CH_2O}_{} + HCl \longrightarrow HOCH_2CH_2Cl \quad (2)$$

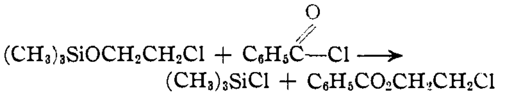
The second step is then the normal alcoholysis reaction accompanied by the regeneration of the hydrogen chloride.

In support of this hypothesis we have noted an unmistakable increase in the reaction rate when hydrogen chloride is added. We are presently unable to state, however, whether or not a chlorosilane will react at all with anhydrous ethylene oxide. This point is of interest in view of the statement[2] that silicon tetrachloride is without effect on ethylene oxide at room temperature.

To demonstrate unequivocally the structure of the ethers obtained in the reactions of equation 1 we have shown that the products from silicon tetrachloride and either ethylene chlorohydrin or ethylene oxide are identical. The chlorine atoms in the latter product have been replaced by piperidino groups yielding, after treatment with hydrogen chloride, the known 2-piperidinoethanol hydrochloride. Acetic anhydride and benzoyl chloride reacted with the chloroethoxy ether from trimethylchlorosilane according to equations 3 and 4, respectively



$$(CH_3)_3SiOCH_2CH_2Cl + (CH_3\overset{O}{\overset{\diagup\!\!\diagup}{C}}\text{--})_2O \longrightarrow (CH_3)_3SiO\overset{O}{\overset{\diagup\!\!\diagup}{C}}—CH_3 + CH_3CO_2CH_2CH_2Cl \quad (3)$$



$$(CH_3)_3SiOCH_2CH_2Cl + C_6H_5\overset{O}{\overset{\diagup\!\!\diagup}{C}}—Cl \longrightarrow (CH_3)_3SiCl + C_6H_5CO_2CH_2CH_2Cl \quad (4)$$

indicating again that the chlorine atom is in the 2-position and further that no rearrangement of the methyl groups attached to silicon has occurred during etherification.

Experimental

Preparations.—Two general methods were used in this work. In the first (A) ethylene oxide gas was bubbled slowly through the boiling or heated chlorosilane at pressures a few millimeters above atmospheric, relying on a water-cooled reflux condenser to return the vaporized reaction mixture to the heating flask. As the reactions were generally exothermic little heating was required. In the second method (B) the ethylene oxide under pressure (maximum, 12–14 lb. gage) was brought into contact with the chlorosilane in a pressure bottle. In a few cases the rate of addition of ethylene oxide had to be controlled to prevent too great a rise in temperature; in general, the latter was kept at or below 60°. The products were purified by fractional distillation, usually at reduced pressure. The yields were generally 80–95% of the theoretical based on the chlorosilanes.

Table I lists the compounds prepared, their physical properties, the method of synthesis and the yields obtained.

Analyses.—The chlorine analyses recorded in Table I were made by three different methods. In Methods I and II the samples were digested in Pyrex test-tubes with concentrated aqueous (I) or ethanolic (II) potassium hydroxide solution for one and one-half to three hours. The chloride ion was then determined volumetrically by a Volhard titration. In weighing out the samples a variety of techniques were used depending upon the volatility of the sample. Method III utilized the regular semi-micro Parr bomb technique (combustion with sodium peroxide and sugar) followed by a Volhard titration. Blanks in all these procedures were found to be negligible.

Because instability of the ethers containing silicon–hydrogen bonds was anticipated, these substances were also analyzed for carbon, hydrogen and silicon (see footnotes to Table I).

Proof of Structure.—Tetrakis-2-chloroethyl silicate was prepared by treating silicon tetrachloride with four moles of ethylene chlorohydrin.[3] The product (n^{20}D 1.4640;

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[1] Compare the analogous reaction with the phosphorus halides [I. G. Farbenind. A.-G., British Patent 338,981, Aug. 31, 1929; *C. A.*, **25**, 2437 (1931)].

[2] Staudinger and Schweitzer, *Ber.*, **62**, 2011 (1929).

[3] Dearing and Reed [THIS JOURNAL, **50**, 3058 (1928)] report this reaction, but state that they could not distill the product without decomposition, even at reduced pressures. Taurke [*Ber.*, **38**, 1661 (1905); *Ann.*, **143**, 217 (1905)] first prepared tetrakis-2-chloroethyl silicate from silicon tetrachloride and ethylene glycol.

TABLE I

SOME 2-CHLOROETHOXYSILANES: $R_NSi(OCH_2CH_2Cl)_{4-N}$

Formula	B. p., °C.	B. p., mm.	$n^{20}D$	d^{20}_4 (vac.)	Method of prepn.	Yield, %	% Cl Calcd.	% Cl Found	Method of anal.
$Si(OCH_2CH_2Cl)_4$	153–154	2	1.4641	1.344	A	78–87	40.98	40.7	I
	184	7							
$HSi(OCH_2CH_2Cl)_3$[a]	117–118	2	1.4577	1.2886	B	...[c]	39.75	39.6, 39.7	I
$CH_3Si(OCH_2CH_2Cl)_3$	137	6	1.4562	1.257	A	87	37.77	37.7	II
								37.7	III
$C_6H_5Si(OCH_2CH_2Cl)_3$	158	1	1.5077	1.2680	B	68	30.95	30.8	I
								30.3, 31.1	III
$CH_3SiH(OCH_2CH_2Cl)_2$[b]	95–97	18[d]	1.4431	1.1643	B	...[c]	34.91	34.8, 34.7	I
$(CH_3)_2Si(OCH_2CH_2Cl)_2$	213	758	1.4420	1.135	A	96	32.66	32.6	II
								32.4	III
$(C_6H_5)_2Si(OCH_2CH_2Cl)_2$	142–146	0.1	1.5510	1.2027	B	89	20.78	20.8, 20.7	II
$(CH_3)_3SiOCH_2CH_2Cl$[e,f]	134.3	760	1.4140	0.9443	A	80	23.23	23.2	II[g]
					B	81		22.9, 22.8	III

[a] *Anal.* Calcd. for $C_6H_{13}SiO_3Cl_3$: C, 26.32; H, 4.90; Si, 10.49. Found: C, 26.6, 26.8; H, 4.6, 4.6; Si, 10.8, 10.9. [b] *Anal.* Calcd. for $C_5H_{12}SiO_2Cl_2$: C, 29.56; H, 5.96; Si, 13.81. Found: C, 29.3, 29.0; H, 5.4, 5.5; Si, 14.0, 13.8. [c] Isolated from the reaction product obtained by treating a mixture of $HSiCl_3$ and CH_3SiHCl_2 with ethylene oxide. [d] Appears to decompose when distilled at atmospheric pressure. [e] Appears to form a minimum boiling azeotrope with ethylene chlorohydrin, $n^{20}D$ 1.426 ± 0.001, b. p. 120–122°. [f] *Anal.* Calcd. for $C_5H_{13}SiOCl$: mol. wt., 152.7. Found (cryoscopic in cyclohexane): mol. wt., 153. [g] Two samples by Method I gave 5.8 and 6.0% Cl. Appreciable volatilization of the sample had apparently occurred prior to hydrolysis.

d^{20}_4 (vac.) 1.343; % Cl by Method III, 40.5, 41.1, 41.0) was identical with that from silicon tetrachloride and ethylene oxide (see Table I). In addition 33.6 g. of the product from ethylene oxide was treated with 68.5 g. of piperidine in 250 ml. of benzene for ten hours at reflux temperature. Piperidine hydrochloride, m. p. 247.5° (cor.), 33.6 g. (69%), was removed by filtration and the filtrate saturated with hydrogen chloride. After recrystallization from ethanol the crude 2-piperidinoethanol hydrochloride thus formed weighed 33.8 g. (46%). The purified salt, m. p. 125.4–125.8° (cor.), and a sample of 2-piperidinoethanol hydrochloride, m. p. 125.5–126.0° (cor.), prepared in an analogous fashion from ethylene chlorohydrin and piperidine[4] gave a mixed melting point of 125.2–125.5° (cor.). Since melting points of 120°[5] and 64–65°[6] have been reported for the compound in question, our sample was analyzed for ionic chlorine by titration with 0.1 *N* silver nitrate solution using fluorescein indicator.

Anal. Calcd. for $C_7H_{16}NOCl$: Cl, 21.40. Found: Cl, 21.2.

Further evidence for the structures assigned is indicated in the reactions described below.

Trimethylacetoxysilane (eq. 3).—From a mixture of 86.4 g. (0.58 mole) of trimethyl-2-chloroethoxysilane and 74.4 g. (0.73 mole) of acetic anhydride there was slowly distilled during a ten-hour period 66.5 g. of material, b. p. 95–110°. By fractional distillation in a column of 20 theoretical plates the following fractions were obtained from this impure distillate: A, b. p. 56.0–96.8°, 3.7 g.; B, b. p. 98.6–101.9°, 18.3 g.; C, b. p. 101.9–102.9°, 9.0 g.; D, b. p. 102.9–103.3°, 9.0 g.; E, b. p. 103.3–103.5°, 12.0 g.; F, b. p. 103.5–106.0°, 4.5 g. Fraction A had the odor of acetyl chloride and gave a white precipitate with silver nitrate solution. A trace of chlorine was also indicated in fraction B but the others gave no precipitate in this test for chlorine. Upon washing with water fractions A and B yielded 17.2 g. of hexamethyldisiloxane.

Fraction E was analyzed for acetoxy groups by titration with aqueous 0.5 *N* sodium hydroxide solution to the phenophthalein end-point.

Anal. Calcd. for $C_5H_{12}O_2Si$: acetyl, 32.56. Found: acetyl, 33.0.

From the residue in the reaction flask there was obtained 55.7 g. (79%) of 2-chloroethyl acetate, b. p. 144–145°, $n^{20}D$ 1.4240. Accepted values[7] of $n^{20}D$ for 1-chloro- and 2-chloro-ethyl acetate are 1.4118 and 1.4247, respectively.

Cleavage of Trimethyl-2-chloroethoxysilane by Benzoyl Chloride (eq. 4).—A mixture of 61.0 g. (0.40 mole) of trimethyl-2-chloroethoxysilane, 60.0 g. (0.43 mole) of benzoyl chloride and 1 ml. of pyridine was heated at 130–140° for four hours under a fractionating column. The distillate collected (45 ml.) was fractionally distilled giving 28.9 g. (67%) of trimethylchlorosilane, b. p. 57.3–57.5° (757 mm.), 32.6% Cl (calcd., 32.64% Cl).

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Summary

Ethylene oxide reacts with chlorosilanes to give good yields of the corresponding 2-chloroethoxysilanes. Seven new ethers of this type have been prepared and characterized.

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(4) Ladenburg, *Ber.*, **14**, 1877 (1881).

(5) Roithner, *Monatsh.*, **15**, 667 (1894).

(6) Basileiados, *Bull. soc. chim.*, [5] **4**, 1131 (1937); *C. A.*, **32**, 167 (1938).

(7) "International Critical Tables," Vol. 1, p. 276.