periodate (5.316 millimoles) and the volume adjusted to 100 ml. Analyses of 10-ml. aliquots at the expiration of eight, twenty-four, thirty-two and forty-eight hours showed that 0.92, 1.03, 1.02, and 1.03 equivalents of oxidant had been consumed, respectively. Titration of aliquot samples with 0.02 *N* sodium hydroxide to methyl red showed no formic acid. No formaldehyde could be detected with a 0.4% dimethyldihydroresorcinol solution according to the procedure of Yoe and Reed.[11] Oxidation of a sample of the original anhydroxylitol with sodium metaperiodate gave similar results, 1.06 equivalents of oxidant being consumed after twenty-four hours.

Oxidation of Anhydroxylitol with Periodic Acid.—To 4.224 g. (0.03149 mole) of anhydroxylitol in 50 ml. of water was added 40 ml. of 0.872 molar periodic acid (0.0349 mole) and the solution was diluted exactly to 250 ml. with water. After thirty-six hours, titration of an aliquot portion for excess periodic acid indicated the consumption of 0.96 equivalent of oxidant. The remainder of the solution was neutralized with hot strontium hydroxide solution to a phenolphthalein end-point. The dialdehyde was obtained as a colorless sirup and was oxidized with bromine water in the presence of strontium carbonate according to the procedure of Jackson and Hudson.[12] After removal of excess bromine by aeration, bromide ion with silver carbonate, silver ion with hydrogen sulfide and hydrogen sulfide by aeration, the solution was concentrated *in vacuo* to about 15 ml. After standing at 0° for several weeks, the solution partly crystallized to yield 2.1 g. of strontium salt. On trituration with 50 ml. of methanol, the mother liquor yielded an additional 4.35 g. The salt was recrystallized twice from 10-ml. portions of water by the addition of 10 ml. of methanol and for analysis it was dried to constant weight at 112° *in vacuo*. The salt had the expected composition and is named strontium D,L-hydroxymethyldiglycolate. *Anal.* of anhydrous salt: Calcd. for $SrC_5H_6O_6$: C, 24.05; H, 2.42; Sr, 35.09. Found: C, 24.1; H, 2.35; Sr, 35.2. Analyses for water on the air-dried or humidified salt gave variable results indicating that a pure distinct hydrate is not easily formed which is in marked contrast to the strontium D-hydroxymethyldiglycolate tetrahydrate obtained by Richtmyer and Hudson[13] from the oxidation of styracitol or polygalitol.

Acknowledgment.—The authors are indebted to Mr. Lawrence White for performing the micro analyses.

Summary

Xylitol has been dehydrated with benzenesulfonic acid or sulfuric acid to yield a mixture of dehydration products from which a pure anhydroxylitol has been isolated in crystalline form.

Anhydroxylitol has been characterized by the preparation of three crystalline derivatives, the tribenzoate, tricarbanilate, and the monotrityl diacetate.

By oxidation with periodic acid and sodium metaperiodate, anhydroxylitol has been shown to contain a 1,4 oxygen ring and is designated as 1,4-anhydro-D,L-xylitol.

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[11] Yoe and Reed, *Ind. Eng. Chem., Anal. Ed.*, **13**, 238 (1941).

[12] Jackson and Hudson, THIS JOURNAL, **59**, 999 (1937).

[13] Richtmyer and Hudson, *ibid.*, **65**, 64 (1943).

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The Preparation and Properties of Some Chloromethylchlorosilanes

BY R. H. KRIEBLE AND J. R. ELLIOTT

The methylchlorosilanes, described by Gilliam, Liebhafsky and Winslow[1] and Gilliam and Sauer,[2] have been shown by Gilliam[3] to undergo both photochemical chlorination at room temperature and vapor phase chlorination at elevated temperatures in the presence of copper gauze to form chloromethylchlorosilane mixtures. The lower chlorination products of trimethylchlorosilane and dimethyldichlorosilane have now been isolated. Tetramethyl-1,3-bis-(chloromethyl)-disiloxane and pentamethylchloromethyldisiloxane have been prepared, respectively, by the hydrolysis of dimethylchloromethylchlorosilane and by the cohydrolysis of this compound with trimethylchlorosilane. The new compounds and their boiling points are listed in Table I.

TABLE I

	Compound	B. p., °C.
I	$(CH_3)_2(CH_2Cl)SiCl$	115
II	$(CH_3)_2(CHCl_2)SiCl$	149
III	$(CH_3)(CH_2Cl)_2SiCl$	172
IV	$(CH_3)(CH_2Cl)SiCl_2$	122
V	$(CH_3)(CHCl_2)SiCl_2$	107 (225 mm.)
VI	$(CH_3)(CCl_3)SiCl_2$	109 (150 mm.)
VII	$[(CH_3)_2(CH_2Cl)Si]_2O$	205
VIII	$(CH_3)_3SiOSi(CH_3)_2CH_2Cl$	152

From the relative yields of the various chlorination products it is apparent that a chloromethyl group is chlorinated in preference to an unsubstituted methyl group. This effect appears to be considerably more marked in the case of trimethylchlorosilane than in the analogous case of *t*-butyl chloride studied by Rogers and Nelson.[4]

Gilliam isolated Cl_3CSiCl_3 and found that on treatment with water, both the Si–Cl and Si–C bonds were hydrolyzed to produce silica, chloroform and hydrochloric acid. It has now been found that chloromethylchlorosilanes containing less than three chlorines in any methyl group are stable toward Si–C fission by acid catalyzed hydrolysis. With alkaline catalysts, however, even monochloromethyl groups undergo Si–C fission with the formation of methyl chloride, the ease of the reaction increasing with the degree of chlorination of the methyl groups. Use has been made of this reaction for the proof of configuration of several of the polychlorinated di- and tri-methyl-

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[1] W. F. Gilliam, H. A. Liebhafsky and A. F. Winslow, THIS JOURNAL, **63**, 801 (1941).

[2] W. F. Gilliam and R. O. Sauer, *ibid.*, **66**, 1793 (1944).

[3] Private communication.

[4] A. O. Rogers and R. E. Nelson, THIS JOURNAL, **58**, 1027 (1936).

chlorosilanes. The configurations of isomeric compounds II and III are established by the fact that on treatment of III with hot aqueous caustic, methyl chloride is liberated, while on similar treatment of II, methylene chloride is formed. Similarly, the configurations of compounds V and VI are established by the formation of methylene chloride and chloroform, respectively, on alkaline hydrolysis.

This cleavage has been found to occur on treatment of pentamethylchloromethyldisiloxane (VIII) with even as mild a base as alcoholic ammonia. The other reaction products have been investigated and will be reported in a later paper. Several other investigators have treated α-chloroalkylsilanes with alkali metal hydroxides but have not observed Si–C fission. Thus, Ushakov and Itenberg[5] have reported that triethyl-α-chloroethylsilane is not affected by boiling alcoholic sodium hydroxide but that in a sealed tube with 10% alcoholic potassium hydroxide at 145° for nine hours, the elements of hydrogen chloride are removed to form triethylvinylsilane in good yield. Sommer, Whitmore, Dorfman and Goldberg[6] have reported that the C–Cl bond in α-chloro-*n*-propyltrichlorosilane is readily hydrolyzed by 1.5 *N* alcoholic potassium hydroxide at 80°. It is therefore apparent that Si–C hydrolysis of α-chloroalkyl groups attached to silicon is not a general reaction. We are undertaking further work to establish the governing structural relations.

Experimental

Chlorination of Trimethylchlorosilane.—One thousand eighty-five grams (10 moles) of trimethylchlorosilane was placed in an ice-jacketed, 2-liter, 3-necked flask provided with a G. E. 4-watt germicidal lamp, a mechanical stirrer, a gas inlet tube and a Dry-Ice cooled reflux condenser, the outlet of which was connected to a water scrubber. After sweeping the apparatus with nitrogen for ten minutes, chlorine was introduced through the gas inlet tube. Hydrogen chloride gas was evolved rapidly. The temperature of the reactants was maintained in the range 24–40°. When titration of the scrubber contents showed the presence of 10.6 *M* of hydrogen chloride, the chlorine was shut off. The product weighed 1451 g., a gain in weight of 366 g., which is equivalent to the substitution of 10.3 g. atoms of chlorine. The product was distilled in a column of about 20 theoretical plates. Besides unchanged starting material, constant boiling distillates were obtained at 115, 149, and 172°. These products will be called I, II and III respectively.

Distillate I was obtained in seven fractions boiling from 115.0 to 115.6° and containing from 24.72 to 24.79% of hydrolyzable chlorine. The mid-fraction was analyzed for hydrolyzable chlorine by titration in an ether–water medium with standard alkali and for total chlorine by combustion with sodium peroxide in a Parr bomb followed by Volhard titration of the liberated chloride ion.[7] From these results I was found to be dimethylchloromethylchlorosilane.

Anal. Calcd. for $(C_3H_8Cl)SiCl$: hydrolyzable Cl, 24.79; total Cl, 49.57. Found: hydrolyzable Cl, 24.77; total Cl, 48.55.

Distillate II was obtained in three fractions boiling from 149.1 to 149.9° and containing from 19.97 to 20.16% hydrolyzable chlorine. It was found to be one of the two possible dichloro derivatives.

Anal. Calcd. for $(C_3H_7Cl_2)SiCl$: hydrolyzable Cl, 19.97; total Cl, 59.92. Found: hydrolyzable Cl, 19.97; total Cl, 59.49.

Five cc. of this material was poured into 20 cc. of water and the oil which formed was warmed with 5 cc. of 40% sodium hydroxide solution. Between 1 and 2 cc. of methylene chloride, b. p. 38.7°, $n^{20}D$ 1.4237, was distilled out. The production of methylene chloride in good yield from the hydrolyzate of a pure dichloro derivative of trimethylchlorosilane demonstrates that both non-hydrolyzable chlorines are attached to the same carbon atom. The chlorosilane is therefore dimethyldichloromethylchlorosilane, $(CH_3)_2(CHCl_2)SiCl$.

Distillate III was obtained in two fractions boiling from 171.1 to 172.8° and containing 19.83 and 20.05% hydrolyzable chlorine. It was found to be the other possible dichloro derivative of trimethylchlorosilane, methyl-bis-(chloromethyl)-chlorosilane, $(CH_3)(CH_2Cl)_2SiCl$.

Anal. Calcd. for $(C_3H_7Cl_2)SiCl$: hydrolyzable Cl, 19.97; total Cl, 59.92. Found: hydrolyzable Cl, 19.83; total Cl, 60.04.

Ten cc. of III was hydrolyzed by shaking with water. The resulting oil was diluted with 20 cc. of 95% ethanol and the solution added slowly to 3 g. of potassium hydroxide pellets. A vigorous reaction started spontaneously and *ca.* 3 cc. (liq.) methyl chloride, b. p. −23.5°, mol. wt. (vapor density method) 48, was evolved and collected in a trap cooled with Dry Ice–acetone.

The composition of the chlorination product is given in Table II.

TABLE II

Component	Composition, wt. %[a]	Mole %, yield[b]	Atoms, C fixed
$(CH_3)_3SiCl$	18.9		
$(CH_3)_2(CH_2Cl)SiCl$	45.4	61.8	4.61
$(CH_3)_2(CHCl_2)SiCl$	20.7	22.7	3.38
$(CH_3)(CH_2Cl)_2SiCl$	7.65	8.5	1.26
Residue (as trichloro derivatives)	7.35	7.0	1.50
	100.00	100.00	10.75

[a] Based on wt. of chlorination product (1451 g.). [b] Based on unrecovered charge.

Preparation of Tetramethyl-1,3-bis-(chloromethyl)-disiloxane (VII).—One hundred grams of dimethylchloromethylchlorosilane was poured into several hundred cc. of water and the mixture was well shaken. An oil phase formed which was separated and dried. The yield was 75.5 g. The oil distilled at constant temperature and constant index of refraction at atmospheric pressure in a Claisen flask. The oil was found to be tetramethyl-1,3-bis-(chloromethyl)-disiloxane, b. p. 204.5°, $n^{20}D$ 1.4390, d^{20}_4 1.045.

Anal. Calcd. for $C_6H_{16}Cl_2OSi_2$: Cl, 30.66. Found: Cl, 31.04.

Five cc. of the oil, 5 g. of potassium hydroxide, and 20 cc. of *n*-butanol were heated to 90° in a flask provided with a water-cooled reflux condenser leading to a liquid air trap. About 1.5 cc. of methyl chloride, m. p. *ca.* −100°, b. p. −23.5°, mol. wt. (vapor density method) 51.7, was distilled out.

Preparation of Pentamethylchloromethyldisiloxane.—One hundred and thirteen grams (0.792 mole) of dimethylchloromethylchlorosilane and 86.0 g. (0.792 mole) of trimethylchlorosilane were mixed and shaken with about 500 cc. of water. After drying over anhydrous sodium carbonate, 137.5 g. of a limpid, colorless oil was distilled in a column of about 15 theoretical plates. Thirty grams

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(5) S. N. Ushakov and A. M. Itenberg, *Zhur. Obshchei Khim.*, **7**, 2495 (1937).

(6) Sommer, Whitmore, Dorfman and Goldberg; paper presented at the New York meeting of the A. C. S.

(7) See W. F. Gilliam, H. A. Liebhafsky and A. F. Winslow, ref. 1.

of hexamethyldisiloxane, b. p. 100.4°, 49 g. of a material, VIII, b. p. 151.6–151.8° and 20.4 g. of tetramethyl-1,3-bis-(chloromethyl)-disiloxane, b. p. 204–204.5°, were obtained in the distillation. VIII was found to be pentamethylchloromethyldisiloxane, n^{20}_{D} 1.4106, d^{20}_{4} 0.9105.

Anal. Calcd. for $C_6H_{17}ClOSi_2$: Cl, 18.02. Found: 18.23.

Chlorination of Dimethyldichlorosilane.—The light source of the apparatus described above was changed to a G. E. H-4 lamp from which the outer glass shell had been removed. The lamp was contained in a quartz test-tube inserted in the neck of the flask and the wattage controlled to 80–100 watts by air cooling during the chlorination. By the procedure outlined above 1290 g. (10 moles) of dimethyldichlorosilane was chlorinated until the scrubber had absorbed 320 g. (8.8 moles) of hydrogen chloride. The reactants increased in weight 308 g., equivalent to the substitution of 8.7 gram atoms of chlorine. The product was fractionally distilled in a column of about 20 theoretical plates. Two fractions were obtained: one (IV) boiling at 122°, and one (V) at 150° besides unchanged starting material and residue (IX). The residue (IX) was distilled at reduced pressure and another fraction (VI) was obtained boiling at 109° (150 mm.).

Fraction IV was redistilled in a column of about 15 theoretical plates. Practically all of it distilled at 121.3°. It was found to be methylchloromethyldichlorosilane.

Anal. Calcd. for $(CH_3)(CH_2Cl)SiCl_2$: hydrolyzable Cl, 43.37; total Cl, 65.05. Found: hydrolyzable Cl, 43.39; total Cl, 65.19.

Five cc. of IV was hydrolyzed by shaking with water and the resulting oil was warmed slightly with 2 g. of solid potassium hydroxide pellets. About 0.5 cc. of methyl chloride, b. p. −24°, mol. wt. (vapor density method) 44, was distilled out.

Fraction V was redistilled at reduced pressure in a column of about 15 theoretical plates. Practically all of the material boiled at 107.2 to 107.8° (225 mm.). This material was found to be one of the two possible dichloro derivatives.

Anal. Calcd. for $(C_2H_4Cl_2)SiCl_2$: hydrolyzable Cl, 35.81; total Cl, 71.64. Found: hydrolyzable Cl, 35.78; total Cl, 71.74.

Five cc. of the compound was hydrolyzed by shaking with 20 cc. of water, and oil formed was mixed with 5 cc. of 40% aqueous potassium hydroxide. The reaction mixture became warm and between 1.5 and 2.0 cc. of methylene chloride, b. p. 39°, n^{20}_{D} 1.4240, mol. wt. (vapor density method) 79, was distilled out. The production of methylene chloride from the hydrolyzate shows that both non-hydrolyzable chlorine atoms are attached to the same carbon atom. Fraction V is therefore methyldichloromethyldichlorosilane.

In the distillation of residue IX from the original atmospheric distillation, indication of a second dichlorinated dimethyldichlorosilane, boiling at 100.5° (155 mm.), was obtained. This compound as yet has not been obtained sufficiently pure for analysis.

Fraction VI was a white crystalline solid, m. p. 99°, b. p. 109° (150 mm.), and was found to be one of the two possible trichloro derivatives.

Anal. Calcd. for $(C_2H_3Cl_3)SiCl_2$: hydrolyzable Cl, 30.50. Found: Cl, 30.53.

Two grams of this material was hydrolyzed by shaking with water, and the oil formed was treated with 5 cc. of 40% aqueous potassium hydroxide. Upon mild heating *ca.* 0.75 cc. of chloroform, b. p. 61°, m. p. *ca.* −70°, n^{20}_{D} 1.4449, was collected. The cleavage of chloroform from the above compound shows that all the non-hydrolyzable chlorines are on the same carbon. Fraction VI is thus methyltrichloromethyldichlorosilane.

The composition of the product is given in Table III.

TABLE III

Component	Composition, wt. %[a]	Mole %, yield[b]
$(CH_3)_2SiCl_2$	25.9	
$(CH_3)(CH_2Cl)SiCl_2$	25.7	36.8
$(CH_3)(CHCl_2)SiCl_2$	32.5	38.3
Intercut b. p. $\frac{88\text{–}106\,°\mathrm{C.}}{150\text{ mm.}}$	7.0	..
$(CH_3)(CCl_3)SiCl_2$	6.4	6.5
Residue	2.5	..
	100.0	81.6

[a] Based on wt. of chlorination product (1598 g.).
[b] Based on unrecovered charge.

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Summary

1. The lower chlorine-substitution products of trimethylchlorosilane and dimethyldichlorosilane have been prepared and identified.

2. In this series of compounds, a chloromethyl group is chlorinated in preference to a methyl group.

3. The chlorine-substituted methyl groups readily undergo hydrolytic fission from silicon in the presence of basic catalysts to form the corresponding chloromethanes. The ease of the reaction increases with the degree of substitution of the methyl group.

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