TABLE I

OLEFIN AND HYDROCHLOROSILANE ADDITION PRODUCTS

Compound	Olefin	B. p., °C.	% Hydrolyzable Cl Calcd.	% Hydrolyzable Cl Found	Yield,[a] %	Conversion,[b] %	Molar[c] ratio	Residue, g.
1-Pentyltrichlorosilane[d]	1-Pentene[e]	166–169	51.9	51.7	73	44	17[i]	8.0
Cyclohexyltrichlorosilane[f]	Cyclohexene[e]	199	48.9	48.4	64	30	8.8[i]	14.9
Isobutyltrichlorosilane[g]	Isobutylene[e]	136	55.5	55.5	..	10	4[j]	..
1-Pentylmethyldichlorosilane	1-Pentene[h]	164–168	38.4	38.3	37	10	3.3[i]	7.0
2-Pentylmethyldichlorosilane	2-Pentene[h]	100[m]	38.4	38.0	71	21	6.2[i]	14.5
1,2-Bis-(trichlorosilyl)-ethane[l]	Vinyltrichlorosilane[e]	199	71.6	70.9	19	19	3.2[i]	5.8
1,3-Bis-(trichlorosilyl)-propane	Allyltrichlorosilane[e]	111[n]	68.5	68.3	83	33	13[i]	..
1,2-Bis-(trichlorosilyl)-ethane[l]	Acetylene[e]	202	71.6	71.2	3	3	[k]	1.0

[a] Yield, based on the unrecovered olefin. [b] Yield, based on olefin charged. [c] Yield, in moles of adduct per mole of peroxide. [d] 1-Pentyltrichlorosilane has been reported by Whitmore, *et al.* [THIS JOURNAL, **68**, 475 (1946)], and 2-pentyltrichlorosilane by Bygden [Inaug. Diss. Uppsala (1916)], and Melzer [*Ber.*, **41**, 3390 (1908)]. [e] With trichlorosilane. [f] Palmer and Kipping [*J. Chem. Soc.*, 1020 (1930)], prepared this silane by the Grignard reaction. [g] Bygden, *Ber.*, **44B**, 2640 (1911); Inaug. Diss., Uppsala, 1916. [h] With methyldichlorosilane. [i] 30% Diacetyl peroxide in dimethyl phthalate. [j] *t*-Butyl perbenzoate. [k] Benzoyl peroxide. [l] This compound has been characterized by Patnode and Schiessler [U. S. Patent 2,381,000 (Aug. 7, 1945)], m. p. 27–28°. [m] Pressure 100 mm. [n] Pressure 20 mm.

carbon bonds had been formed. *Anal.* Found: Si, 1.9; Cl, 4.9.

Acknowledgment.—The authors wish to thank Mr. L. B. Bronk and Miss M. Clarke for analytical data.

Summary

1. Isobutyl-, 1-pentyl and cyclohexyltrichlorosilane and 1-, and 2-pentylmethyldichlorosilane have been prepared by the peroxide-catalyzed addition of trichlorosilane or methyldichlorosilane to the corresponding olefin.

2. 1,2-bis-(Trichlorosilyl)-ethane and 1,3-bis-(trichlorosilyl)-propane have been prepared by the addition of trichlorosilane to vinyl- and allyltrichlorosilane, respectively.

3. 1,2-bis-(Trichlorosilyl)-ethane has been prepared by the addition of trichlorosilane to acetylene.

SCHENECTADY, N. Y. RECEIVED APRIL 11, 1947

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC CO.]

Cyclic Dimethylpolymethylenedioxysilanes

BY R. H. KRIEBLE AND C. A. BURKHARD

An investigation of the reactions of organohalogenosilanes and organoalkoxysilanes with glycols has been made. Several of the dimethylpolymethylenedioxysilanes have been isolated and characterized. These compounds are the silicon analogs of the cyclic acetals and ketals.

The acetals derived from glycols constitute a typical bifunctional system, in which either cyclic or polymeric forms are obtained depending on the number of atoms in the possible ring structure. The formals have been studied by Hill and Carothers,[1] who found that trimethylene and tetramethylene formals, prepared by acetal interchange from the glycols and dibutyl formal, were largely in the form of the cyclic monomers of six and seven membered rings, respectively. The formals of glycols bearing more widely separated hydroxyls were all polymeric, and on pyrolysis gave cyclic monomer in only trace amounts (with the exception of the polyformal of triethylene glycol which on pyrolysis gave in good yield the cyclic monomer of eleven ring atoms). Similar ring-chain relations are found in the acetals[2] and benzals[3] of glycols. There is less information concerning the polymethylene ketals of acetone. The cyclic ethylene ketal is readily formed in the presence of acid catalysts, the equilibrium constant of formation being 0.14.[4] The cyclic trimethylene ketal is formed only with difficulty due to an unfavorable equilibrium constant.[5] No mention is made of polymeric products in either case. The cyclic tetramethylene ketal apparently has not been reported.

A striking difference between the dimethylpolymethylenedioxysilanes and the formally analogous carbon compounds discussed above is the ease with which the silanes are prepared in the form of cyclic compounds even though the ring size is as large as eleven atoms. The new ring compounds are listed in Table I.

All the compounds but V have been prepared by

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[1] Hill and Carothers, THIS JOURNAL, **57**, 925 (1935).

[2] Hill and Hibbert, *ibid.*, **45**, 3124 (1923).

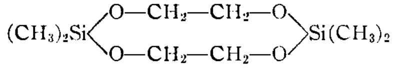
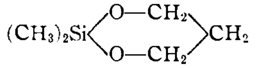
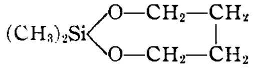
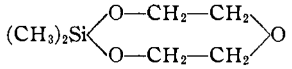
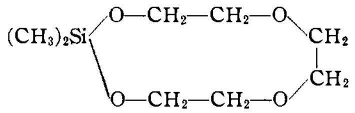
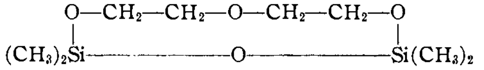
[3] Franke and Gigerl, *Monatsh.*, **49**, 8 (1938).

[4] Böeseken and Hermans, *Rec. trav. chim.*, **40**, 525 (1921).

[5a] Böeseken and Hermans, *Ber.*, **55B**, 3758 (1922).

[5b] Salmi and Rannikko, *ibid.*, **72B**, 600 (1939).

Table I

Cpd. no.	Name	Structure
I	Dimeric dimethylethylenedioxysilane	
II	Dimethyl-(trimethylene-1,3-dioxy)-silane	
III	Dimethyl-(tetramethylene-1,4-dioxy)-silane	
IV	Dimethyl-(2,2′-oxydiethoxy)-silane	
V	Dimethyl-(2,2′-ethylenedioxydiethoxy)-silane	
VI	Tetramethyl-1,3-(2,2′-oxydiethoxy)-disiloxane	

alcoholysis of dimethyldiethoxysilane, or tetramethyl-1,3-diethoxydisiloxane by the appropriate glycol, usually in the presence of small amounts of *p*-toluenesulfonic acid as catalyst. The theoretical amount of ethanol is readily distilled out of the reaction mixture, leaving in all cases a limpid liquid product from which the cyclic silane is obtained in good yield by distillation.

The hydrolysis and alkoxy interchange reactions of alkoxysilanes appear to involve reaction at the silicon–oxygen bond and not at the carbon–oxygen bond, since the configuration of an alkyl group, asymmetric at the point of attachment, survives the reaction unchanged. Dimethyldi-*d*-2-butoxysilane was prepared from dimethyldichlorosilane and *d*-2-butanol. A sample was hydrolyzed by shaking with very dilute acid. The 2-butanol thereby recovered was found to have maintained its original activity without change. Similarly the dimethylethoxy-2-butoxysilane formed by alkoxy interchange between dimethyldiethoxysilane and dimethyldi-*d*-2-butoxysilane was found to have a specific rotation of the same sign and approximately half the value of the original dimethyldi-*d*-2-butoxysilane. Compounds I, IV and V were also made by the reaction of dimethyldichlorosilane with the appropriate glycol. The preparation of II and III by this method was unsuccessful because of side reactions.

It is remarkable that dimethylethylenedioxysilane could not be prepared as the monomeric 5-membered ring[6] while the dimeric 10-membered ring forms so readily, and the analogous acetone ethylene ketal is known only in the monomeric state. This difference between the silane and the methane cannot be ascribed to the greater size of the silicon atom, since a model of the former, based on 1.7 Å. for the silicon–oxygen bond and tetrahedral angles for carbon, silicon and oxygen is readily constructed if the ring be puckered slightly.

The unusual ease of formation of large rings, noted in the dimethylsilicone series,[7] is in evidence to a lesser degree in the polymethylenedioxysilanes. A relatively straight angle in the Si–O–Si linkage[8] and to a lesser extent in the Si–O–C linkage would be consistent with these facts. The probability of the ends of a chain finding themselves in a position for ring closure decreases as the number of units in the chain increases above 5. Making the bond angle of one of the ring atoms a straight angle, effectively reduces the number of units by one, and therefore makes ring closure more probable. However, in II the *maximum* valence angle for oxygen consistent with the normal bond lengths (Si–O = 1.7 Å.) and tetrahedral carbon and silicon is about 120° compared to about 106° in the hypothetical monomeric ethylenedioxysilane. Therefore, all that can be concluded is that if in fact the normal angle of an Si–O–C linkage does approach a straight angle, it can easily be deformed to a value in the vicinity of the tetrahedral angle.

Dimethylhexamethylenedioxysilane is obtained only in the form of a viscous oil which does not distil, even in the presence of an acid catalyst at 250° and 4 mm. and is presumably therefore a linear polymer. On the other hand, the 2,2′-oxydiethyoxysilane and the 2,2′-ethylenedioxydiethoxysilane are both readily obtained as monomeric ring compounds. This appears to be an example of the Carothers[9] oxygen effect. Stollé and Stollé–Comté[10] have shown that in 8- to 15-membered polymethylene rings strain is introduced by the compression of external domain of hydrogen which necessarily occurs on ring closure, if tetrahedral valence angles are maintained. Carothers has pointed out that the replacement of an annular methylene group by oxygen reduces strain by relieving the congestion of peripheral

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(6) Kipping and Abrams, [*J. Chem. Soc.*, 81 (1944)] have recently reported bis-(tetraphenylethylenedioxy)-silane.

(7) Patnode and Wilcock, This Journal, **68**, 358 (1946).

(8) Sauer and Mead, *ibid.*, **68**, 1794 (1946).

(9) Carothers and Hill, *ibid.*, **55**, 5043 (1933).

(10) Stollé and Stollé-Comte, *Helv. Chim. Acta*, **13**, 1185 (1930).

TABLE II

	Compound	Method of prep.	M. p., °C.	B. p., °C.	d^{20}_4	n^{20}_D	MR_D Calcd.[a]	MR_D Obs.	$[\alpha]^{20}_D$	Silicon, % Calcd.	Silicon, % Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
I	Dimeric dimethylethylenedioxysilane	A, B	55	178	1.0585	1.4388	59.05[b]	58.6[b]	.....	...	..	40.63	40.8	8.53	8.68
II	Dimethyl-(trimethylene-1,3-dioxy)-silane	B	..	121.7	0.9703	1.4120	34.2[c]	34.1[c]	.....	...	...	45.39	45.4	9.08	9.20
III	Dimethyl-(tetramethylene-1,4-dioxy)-silane	B	..	142	....	1.4218	....	...	.....	...	...	49.28	48.9	9.65	9.3
IV	Dimethyl-(2,2′-oxydiethoxy)-silane	A, B	..	90 (50 mm.)	1.0452	1.4331	40.4[d]	40.3[d]	.....	...	...	44.39	44.5	8.70	8.75
V	Dimethyl-(2,2′-ethylenedioxydiethoxy)-silane	A	..	96 (9 mm.)	1.0704	1.4487	51.3[e]	51.6[e]	.....	13.60	14.0	...	..	..	..
VI	Tetramethyl-1,3-(2,2′-oxydiethoxy)-disiloxane	B	..	*ca.* 110 (50 mm.)	1.0452	1.4275	58.9[c]	58.1[c]	.....	...	...	40.63	40.5	8.57	8.50
VII	Dimethyl-1-butoxyethoxysilane	B	..	155	0.8426	1.3949	50.3	50.2	.....	15.92	15.4	...	..	..	..
VIII	Dimethyldi-*d*-2-butoxysilane	A	..	173.6	0.8339	1.4014	59.5	59.7	+24.9°	13.73	13.2	...	..	..	..
IX	Dimethyl-*d*-2-butoxyethoxysilane	..	..	144.6	0.8328	1.3930	50.3	50.5	+13.7°	15.92	15.2	...	..	..	..
X	Tetramethyl-1,3-diethoxydisiloxane	..	..	158	0.8831	1.3880	59.6	59.5	.....	25.25	25.7	...	..	..	..
XI	Dimethyldi-*dl*-2-butoxysilane	A	..	174	0.8332	1.4014	59.5	59.5	.....	13.73	13.2	...	..	..	..
XII	Dimethyl-*dl*-2-butoxyethoxysilane	..	..	144.6	0.8432	1.3932	50.3	49.9	.....	15.92	15.2	...	..	..	..

[a] Calculated values of MR_D using method of Sauer [THIS JOURNAL, **68,** 954 (1946)]. [b] Calculated assuming the monomer molecular weight, 118. Molecular weight of freshly prepared crystals in cyclohexane 243, calcd. 236. [c] MR_D calculated assuming a monomer molecular weight. [d] MR_D calculated assuming monomer molecular weight. Molecular weight of freshly distilled compound in cyclohexane 171, calcd. 162. [e] MR_D calculated assuming monomer molecular weight. Molecular weight of freshly distilled compound in cyclohexane 243, calcd. 206.

hydrogens and by providing an easily deformable valence angle.

Compound I undergoes a reversible polymerization of remarkable ease. Thus the neutral crystalline dimer of melting point 55° soon liquefies on standing at room temperature in well-stoppered bottles and after several days cryoscopic molecular weights indicate an average degree of polymerization of about nine. Further standing causes no further change. The liquid polymer on the other hand may be readily reconverted to crystalline dimer by heating to temperatures as low as 130–150° in a still at 20-mm. pressure. The polymerization is apparently associated with a small amount of hydrolysis since the polymeric mixture shows absorption in the infrared at 2.9 μ which is characteristic of the hydroxyl group. Compounds IV and V show a similar behavior.

Experimental

The new compounds and their properties are shown in Table II. They were prepared by two general methods.

Reaction of Dimethyldichlorosilane with Alcohols—Method A.—Dimethyldichlorosilane was added dropwise to an equimolar amount of the alcohol or glycol at a temperature of 55°. On completion of the addition, the product was refluxed briefly to expel the remaining hydrogen chloride and distilled through a fractionating column of about 20 theoretical plates, usually under reduced pressure.

In the case of ethanol, hydrogen chloride evolution ceased when the product still contained several per cent. of hydrolyzable chlorine, presumably as dimethylethoxychlorosilane. At the reflux temperature, slow decomposition into ethyl chloride (b. p. 12°) and tetramethyl-1,3-diethoxydisiloxane (X) occurred. By neutralizing with a small excess of trimethylamine before distillation a good yield of pure dimethyldiethoxysilane was obtained: b. p. 113.5°, n^{20}_D 1.3810, d^{20}_4 0.838, MR^{20}_D calcd. 41.0,[11] found 41.1. The previously reported constants,[12] which give an MR^{20}_D of 38.96, appear to be in error.

The method failed in the preparation of II and III, trimethylene glycol giving an as yet unidentified chlorine containing distillate, and tetramethylene glycol giving tetrahydrofuran: n^{20}_D 1.4049, d^{20}_4 0.844, b. p. 64.5°, MR^{20}_D calcd. 20.11, found 20.0.

Reaction of Dimethyldiethoxysilane with Alcohols—Method B.—Equivalent amounts of dimethyldiethoxysilane and the alcohol or glycol plus a few tenths of 1% of *p*-toluenesulfonic acid monohydrate were boiled under reflux in a small still. Ethanol formed rapidly and was distilled out at 78° in azeotropic admixture[13] with a small amount of dimethyldiethoxysilane. The product in all cases was a limpid liquid. A slight excess of triethylamine was added to neutralize the catalyst and the product was distilled. In spite of this precaution to avoid depolymerization, the crude products in the preparation of II, III and IV distilled without showing the usual indications of cracking to give excellent yields of cyclic monomer.

In the preparation of I the column head temperature was erratic and the distillate was a mixture of crystals (m. p. 55°, after washing with cold ligroin) and oil. The properties of the oily distillate were constant throughout a distillation: n^{20}_D 1.4388 ± 0.0002; d^{20}_4 1.0585, MR^{20}_D calcd. for dimethylethylenedioxysilane 59.05, found 58.6. The crystals liquefied on standing to an oil of identical properties. The oil on redistillation, again gave a largely

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(11) Sauer, THIS JOURNAL, **68,** 954 (1946).

(12) Post and Hofrichter, *J. Org. Chem.*, **5,** 572 (1940).

(13) The ethanol distills as an azeotropic mixture with dimethyldiethoxysilane, consisting of 79% ethanol, n^{20}_D 1.3662.

crystalline distillate, which again liquefied on standing. Carbon and hydrogen analyses (see Table II) of the oil are in good agreement with a dimethylethylenedioxysilane formula and it is evident that the crystal-oil transformation represents some kind of labile polymerization. The cryoscopic molecular weight, in cyclohexane, of the washed crystals was found to be 243 (theory for dimer 236). Both the molecular weight and the boiling point are therefore in good agreement with a dimeric structure. The oil, on the other hand, has an average molecular weight of 1164, which is 9.9 times that of the monomeric structure. All attempts to distil the unpolymerized dimer out of the oil at low pressures and temperatures resulted in depolymerization, substantially all of the oil distilling over as crystalline dimer. The average degree of polymerization of the polymer itself is therefore not known.

The infrared absorption of a solution of 114 mg. of freshly prepared crystalline dimeric dimethylethylenedioxysilane in 1.14 cc. of dioxane was measured in the region of 3 μ. A very small absorption (almost too small to be noticeable) was found at 2.9 μ. A second portion of these same crystals was allowed to stand in a well-stoppered bottle for a period of one week during which time it polymerized to an oil. A solution of 113 mg. of this oil in 1.13 cc. of dioxane was prepared and a moderately strong bond was observed at 2.9 μ. A sample of liquid polymeric dimethylethylenedioxysilane of molecular weight 1164, that had stood at room temperature for a period of about three and one-half months, likewise showed absorption at 2.9 μ with an intensity about equal to that of the sample that had stood for only one week. The region in which this absorption has been observed is characteristic of the hydroxyl groups.

In the preparation of VI, X was substituted for dimethyldiethoxysilane. About half the crude product could be distilled up to a pot temperature of 250°. The distillate was almost entirely cyclic monomer. The residue was a thick oil.

Hexamethylene glycol and dimethyldiethoxysilane were allowed to react by method B. The product was a viscous oil which did not depolymerize to volatile products at 250° and 4 mm.

Hydrolysis and Alkoxyl Interchange with Dimethyldi-*d*-2-butoxysilane.—A mixture of 27 g. of VIII, $[\alpha]^{20}\text{D}$ +24.9°, 20 g. of dimethyldiethoxysilane and 0.50 g. of *p*-toluenesulfonic acid was allowed to stand at room temperature for one week, after which it was separated into dimethyl-*d*-2-butoxyethoxysilane, $[\alpha]^{20}\text{D}$ +13.7°, dimethyldi-*d*-2-butoxysilane, $[\alpha]^{20}\text{D}$ +19.8° (in $CHCl_3$), and dimethyldiethoxysilane. Dimethyl-1-butoxyethoxysilane and dimethyl-*dl*-2-butoxyethoxysilane were likewise prepared by equilibration of the corresponding dimethyldialkoxysilanes with *p*-toluenesulfonic acid as the catalyst.

A sample of VIII was shaken with water acidified with a trace of *p*-toluenesulfonic acid. The aqueous layer was separated and found to contain 3.33 g. of 2-butanol per 100 g. of solution by comparing its refractive index with those of synthetic mixtures. From the observed $\alpha^{20}\text{D}$ of +0.4° an $[\alpha]^{20}\text{D}$ of +12° is calculated for the pure 2-butanol. $[\alpha]^{20}\text{D}$ for the original *d*-2-butanol from which VIII was made was +11.5°.

Acknowledgment.—The authors wish to acknowledge the help given by Dr. M. M. Sprung for consultation, Dr. E. W. Balis and Mr. L. B. Bronk for analyses, Dr. D. J. Mead for infrared data, and Dr. C. B. Hurd of Union College for use of the polarimeter.

Summary

1. Cyclic polymethylenedioxydimethylsilanes, of six to eleven annular atoms, have been prepared and characterized. Several of these compounds are found to polymerize and their polymers to depolymerize with great ease.

2. Dimethyldi-*d*-2-butoxysilane was prepared and equilibrated with dimethyldiethoxysilane to give dimethylethoxy-*d*-2-butoxysilane. . Dimethylethoxy-1-butoxysilane was prepared in a similar manner using the corresponding dibutoxysilane.

3. The hydrolysis and alkoxy interchange reactions of the alkoxysilanes appear to involve reaction at the silicon–oxygen bond, since the configuration of an alkyl group asymmetric at the point of attachment through oxygen to silicon survives the reactions unchanged.

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RECEIVED MAY 13, 1947

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

The Preparation and Some Properties of Hydrides of Elements of the Fourth Group of the Periodic System and of their Organic Derivatives

BY A. E. FINHOLT, A. C. BOND, JR., K. E. WILZBACH AND H. I. SCHLESINGER[1]

Although the hydrides of silicon, of germanium and of tin have been known for some time, their preparation has been difficult. The most satisfactory method for the silicon and germanium compounds has been the treatment of magnesium silicide or germanide with acidic reagents. In the earlier work, aqueous hydrochloric acid was employed to liberate silane[2] or germane[3]; the substitution of ammonium bromide in liquid ammonia for the aqueous acids constituted a marked improvement in the preparation of these hydrides.[4] But even these improved procedures are troublesome. The preparation of the magnesium compounds has to be carried out under rigid conditions; the hydrides are likely to contain impurities which must be removed by low temperature fractionations or by a series of chemical treatments, and the use of liquid ammonia as a solvent requires special techniques. Furthermore, these methods are not applicable to the preparation of the alkyl or aryl derivatives of the hydrides; for

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(1) Present address of A. E. Finholt: Metal Hydrides, Inc. Beverly, Mass., of A. C. Bond, Jr.: University of Michigan, Ann Arbor, Mich., of K. E. Wilzbach: U. S. Rubber Co., Passaic, New Jersey.

(2) Stock and Somieski, *Ber.*, **49**, 111 (1916).

(3) Dennis, Corey and Moore, THIS JOURNAL, **46**, 657 (1924).

(4) Kraus and Carney, *ibid.*, **56**, 765 (1934), for germane, and Johnson and Isenberg, *ibid.*, **57**, 1349 (1935), for silane.