[Contribution from the Department of Chemistry of the
University of Buffalo]

STUDIES IN SILICO-ORGANIC COMPOUNDS. V. THE PREPARATION AND PROPERTIES OF CERTAIN POLYETHERS FROM TETRACHLOROSILANE, HEXACHLORODISILANE, AND HEXACHLORODISILOXANE[1]

EDWIN W. ABRAHAMSON, IRVING JOFFE, and HOWARD W. POST

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INTRODUCTION

The purposes of this investigation were twofold. It was desired to determine the general physical properties of silicon polyethers of large organic radicals, and to prepare certain polyethers of tetrachlorosilane, hexachlorodisilane, and hexachlorodisiloxane for comparison of their properties with compounds obtained in another section of the work (1).

Von Ebelman (2) synthesized tetraethoxysilane and tetra-*i*-amoxysilane by treating the anhydrous alcohol with tetrachlorosilane. In 1863, Friedel and Crafts (3) entered the field, using the method of von Ebelman and preparing a mixed polyether, amoxytriethoxysilane, by the successive action of ethyl and amyl alcohols. Two years later these same investigators (4) prepared tetramethoxysilane, isolating in addition a high-boiling product, hexamethoxydisiloxane. A complete bibliography on the subject would include references dated almost to the present time (5, 6).

However, polyethers can sometimes more conveniently be prepared from other polyethers of silicon, preferably those with smaller organic radicals. Thus Friedel and Crafts (3) in 1863 treated tetraethoxysilane with methyl alcohol, obtaining dimethoxydiethoxysilane. Later, Herthorn (7) allowed ethyl alcohol to react with tetraphenoxysilane, obtaining almost quantitative conversion to tetraethoxysilane and phenol. Other work followed (6, 8).

DISCUSSION

In this work, tetrabutoxysilane has been prepared once more, by the action of anhydrous butyl alcohol on tetrachlorosilane. No difficulties were met with.

Methyl Cellosolve was allowed to react with tetrachlorosilane in the molar ratio of 5:1 but even in this proportion, one chlorine atom remained attached to silicon:

$$\text{I.}\quad SiCl_4 + 3\,CH_3OCH_2CH_2OH \rightarrow 3HCl + ClSi(OCH_2CH_2OCH_3)_3$$

The preparation of the tetraethers however was brought about much more satisfactorily by radical interchange between the higher alcohol and a lower tetraether:

$$\text{II.}\quad 4CH_3OCH_2CH_2OH + Si(OC_2H_5)_4 \rightarrow 4C_2H_5OH + Si(OCH_2CH_2OCH_3)_4$$

$$\text{III.}\quad 4C_2H_5OCH_2CH_2OH + Si(OC_2H_5)_4 \rightarrow 4C_2H_5OH + Si(OCH_2CH_2OC_2H_5)_4$$

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These processes presented no especial difficulties and will be described more fully under Experimental Part. The physical properties of the three compounds thus prepared are given in Table I.

Tri-β-methoxyethoxychlorosilane was most susceptible to hydrolysis. This was to be expected, since there remained one chlorine attached to silicon. Although tetra-β-methoxyethoxysilane was somewhat miscible with water, it did not hydrolyze immediately on solution. However, on long standing a gel was formed. In acid solution no hydrolysis was evident, but in caustic media hydrolysis was almost instantaneous. Tetra-β-ethoxyethoxysilane is immiscible in neutral, acid, and caustic media. Hydrolysis was slower than in the case of the methyl homolog described above.

TABLE I

PHYSICAL PROPERTIES

	B.P. °C/MM.	n_D	d	VISCOSITY, POISE
$Si(OC_2H_5)_4$		1.3825(obs.)[a] 1.3821(8.9)[b]		
$ClSi(OCH_2CH_2OCH_3)_3$	289/740 186/9	1.4220[c]	1.0804[e] 1.0756[f]	0.0352[g] .0316[h]
$Si(OCH_2CH_2OCH_3)_4$	292/740 183/9	1.4213[b]	1.0781[e] 1.0680[f]	.0362[d] .0288[h]
$Si(OCH_2CH_2OC_2H_5)_4$	312/740 200/9	1.4226[d]	1.0184[e] 1.0139[f]	.0832[g] .0334[h]

[a] 20.2°.
[b] 20°.
[c] 20.3°.
[d] 20.5°.
[e] $^{20}_{4}$.
[f] $^{25}_{4}$.
[g] 20°.
[h] 25°.

Viscosities were determined by the method of Mack and France (10).

Phenyl Cellosolve reacted with tetraethoxysilane to give tetra-β-phenoxyethoxysilane.

The action of anhydrous alcohols on hexachlorodisiloxane produced variable results. Ethyl alcohol, under the conditions of this work produced almost entirely tetraethoxysilane. Propyl alcohol formed hexapropoxydisiloxane in 27% yield and butyl alcohol produced a 15% yield of hexabutoxydisiloxane. Anhydrous ethyl alcohol reacted with hexachlorodisilane to give a 25% yield of hexaethoxydisilane. The yield of the corresponding propyl compound was 12%.

EXPERIMENTAL PART

Tetrabutoxysilane. Tetrachlorosilane (17 cc., 0.15 mole) was added dropwise to 65 cc., 0.70 mole, of butyl alcohol, anhydrous. After refractionation, the product boiled at 273–277° (760 mm.), d^{25}_4 0.913, found; d^{20}_4 0.899 literature (8); Si 8.91, 8.84, theoretical 8.76.

Methyl Cellosolve and Ethyl Cellosolve (ethylene glycol monomethyl and monoethyl ethers), were made available through the courtesy of Carbide and Carbon Chemicals Corp. Each of these compounds was thoroughly dried over sodium sulfate before use. Their physical properties were satisfactory.

Tri-β-methoxyethoxychlorosilane. Methyl Cellosolve was fed into freshly distilled tetrachlorosilane (150 cc. and 44 cc. respectively) at a rate of three drops per second. The Methyl Cellosolve formed a separate layer on top of the silicon compound. An endothermic reaction set in at the end of ten minutes. Hydrogen chloride was absorbed in a trap containing 50% sodium hydroxide. The reaction mixture was heated to reflux for thirty minutes to drive off the last traces of acid. Fractional distillation yielded 70 g. of product, a yield of 9% based on the tetrachlorosilane used. The product hydrolyzed readily in dilute sodium hydroxide with production of chloride ion (silver nitrate test). The molecular weight was determined by the cryoscopic method, in benzene (11) as 284, theoretical 288.7. This compound was miscible with water, but with slight turbidity indicating hydrolysis. Absolute viscosity was determined with an Ostwald viscosimeter using the method of Mack and France (10) and the formula: $n_1/n_2 = d_1t_1/d_2t_2$, where n is the viscosity in poise units, d the density and t the time of flow in seconds. The reference viscosity used in these determinations was that of water, 0.0088 at 25° and 0.0100 at 20° (10). Physical properties of this and the succeeding two products are listed in Table I.

Tetra-β-methoxyethoxysilane. The method used here was substantially the same as was used in the preparation of the chloro derivative previously described. In 5:1 molar ratio, Methyl Cellosolve and tetraethoxysilane were mixed and subjected to 8 hours reflux, followed by fractional distillation. The product weighed 152 g., 90% yield. Observed molecular weight was 327, theoretical 328.3. This compound was miscible with water but very slow of hydrolysis, save in alkalies.

Tetra-β-ethoxyethoxysilane. Using the same procedure, this compound was obtained in 94% yield, 182 g. Observed molecular weight was 387, theoretical 384.5.

Tetra-β-phenoxyethoxysilane. Phenyl Cellosolve, dried over sodium sulfate, and freshly distilled tetraethoxysilane were refluxed in a 5:1 molar ratio, 200 cc. of the Cellosolve and 70 cc. of tetraethoxysilane. After 6 hours of reflux 65 cc. of ethyl alcohol had been obtained, 92% of theoretical. The mixture became very dark. Excess Phenyl Cellosolve was distilled off whereupon the material remaining in the flask solidified. After recrystallization of the latter from benzene, 10 g. of product was obtained, probably tetra-β-phenoxyethoxysilane, a white crystalline solid m.p. 85–87°. Tetra-β-phenoxyethoxysilane is immiscible in water and sodium hydroxide. A white precipitate was formed with water and acid; Si: 4.95, 4.91, theoretical: 4.86.

Hexachlorodisiloxane and ethyl alcohol. Absolute ethyl alcohol (110 cc., 1.9 moles) was added dropwise to 80 g. (0.28 mole) of hexachlorodisiloxane. The reaction was vigorous, hence addition was slow, but as the addition of alcohol progressed, evolution of hydrogen chloride slowed down. After about one-fourth of the alcohol had been added, a layer began to form on top of the reaction mixture and despite constant shaking, this layer remained to the end. After addition, the system was refluxed at 107° from 5 to 6 hours, then the excess alcohol distilled off. The main product was tetraethoxysilane, b.p. 65–70° (18 mm.), literature 68.5° (18 mm.) (12).

Hexachlorodisiloxane and propyl alcohol. Anhydrous propyl alcohol (50 cc., 0.66 mole) was added dropwise to 20 cc. (0.07 mole) of hexachlorodisiloxane over a period of one hour. After the alcohol had been added, the mixture was heated in an oil-bath at 120° until evolution of hydrogen chloride had ceased. Excess alcohol was distilled off and the remaining liquid distilled at 25 mm. giving:

125–130°	6.0 grams	$Si(OC_3H_7)_4$
150–170°	6.3 grams	intermediates
205–208°	8.0 grams	$(C_3H_7O)_3SiOSi(OC_3H_7)_3$

Hexapropoxydisiloxane is a colorless liquid with a rather sharp odor. It is stable in air but hydrolyzes very slowly in caustic. The yield was 22%. Literature b.p. 190° (20 mm.), 330° (760 mm.) (14), d_4^{25} 0.976 found; d_4^{20} 0.977 literature (14); Si: 13.55, 13.10, theoretical: 13.13.

Hexachlorodisiloxane and butyl alcohol. Anhydrous butyl alcohol (55 cc., 0.59 mole) was added dropwise to 25 g. (0.09 mole) of hexachlorodisiloxane. After addition, the mixture was refluxed until the evolution of hydrogen chloride had ceased. After excess alcohol had distilled off, the remaining liquid was distilled at 20 mm. with the following fractions coming over:

150–160°	7.0 grams	$Si(OC_4H_9)_4$
170–200°	3.7 grams	intermediates
245–250°	7.0 grams	$(C_4H_9O)_3SiOSi(OC_4H_9)_3$

Hexabutoxydisiloxane is a colorless oily liquid stable in air and water but hydrolyzing slowly in caustic. It was prepared in 15.6% yield; Si: 11.20, 10.70, theoretical: 10.95.

Hexachlorodisilane and ethyl alcohol. Absolute ethyl alcohol (120 cc., 2.1 moles) was added dropwise to 82.5 g. (0.306 mole) of hexachlorodisilane. The bulk of the reaction did not take place until the system was refluxed. By the time the temperature had reached 100°, the two separate layers which had formed on addition of the reactants, had merged. Reflux of 6 hours was, however, necessary. The first fraction to distill, after tetraethoxysilane, came over at 132–133° (18 mm.), probably hexaethoxydisilane, literature 140–150° (18 mm.) (13). The yield was 25 g. Hexaethoxydisilane (0.5653 g.), prepared as described, was allowed to react with 10 cc. of 30% potassium hydroxide at room temperature. Hydrogen was immediately evolved, exothermally, and collected by water displacement. Corrected volume of water was 36.9 cc., theoretical 38.83 cc. The reaction is expressed by the following equation:

IV. $(C_2H_5O)_3Si-Si(OC_2H_5)_3 + 3\ HOH + 2\ KOH \rightarrow H_2 + 6C_2H_5OH + O(SiOOK)_2$.

The detailed procedure for this determination will be found in another contribution of this series (1).

Hexachlorodisilane and propyl alcohol. Anhydrous propyl alcohol (45 cc., 0.60 mole) was added dropwise to 20 cc. (0.08 mole) of hexachlorodisilane. After the alcohol had been added, the mixture was heated until no further evolution of hydrogen chloride was noticed. The excess alcohol was distilled off, and the remainder was fractionated at 25 mm. The main fractions were $Si(OC_3H_7)_4$ b.p. 125–130° (25 mm.), intermediate products, and hexapropoxydisilane 4 g., b.p. 190–195° (25 mm.). On treatment with 10 cc. of hot 30% sodium hydroxide, 1.030 g. of hexapropoxydisilane evolved 55.8 cc. of hydrogen (corr.), theoretical 57.5 cc.

SUMMARY

1. Tri-β-methoxyethoxychlorosilane has been prepared by the action of Methyl Cellosolve on tetrachlorosilane. Tetra-β-methoxyethoxysilane and tetra-β-ethoxyethoxysilane have been prepared by the action of Methyl Cellosolve and of Ethyl Cellosolve, respectively, on tetraethoxysilane. A product, probably tetra-β-phenoxyethoxysilane, has been obtained from the action of Phenyl Cellosolve on tetraethoxysilane. The physical properties and certain chemical properties of these compounds have been determined and reported.

2. Hexachlorodisiloxane and absolute ethyl alcohol react with evolution of hydrogen chloride. The main product, under conditions outlined, is tetra-

ethoxysilane. Larger yields of the expected hexaalkoxydisiloxanes have been obtained from the action of anhydrous propyl and butyl alcohols on hexachlorodisiloxane.

3. Hexachlorodisilane reacts with absolute ethyl alcohol and absolute propyl alcohol to form hexaethoxydisilane and hexapropoxydisilane respectively. The determination of the purity and identity of these products is materially aided by a study of their reaction with hot caustic alkali with practically quantitative evolution of hydrogen.

BUFFALO, N. Y.

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