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Condensation Products of the Organo-silane Diols

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The hydrolysis of substituted organo-silicon halides is generally accompanied by dehydration to form complex condensation products containing siloxane linkages.^{1,2,3,4} The extent and mode of the condensation is affected by the number of organic groups attached to the silicon. Thus, the mono-substituted compounds can form three-dimensional networks, with possible intermediate stages of dehydration in which thermo-setting properties are in evidence. The condensation of tri-substituted compounds is limited to the formation of dimers or ethers. The di-substituted compounds, on the other hand, should condense with the formation of chain molecules and should yield products having high molecular weights and possible thermoplastic characteristics. Although some polymers are described by Kipping and Murray⁵ which seem to confirm this view, it appears that there is likewise a strong tendency toward the formation of cyclic structures.^{4c} The lack of a clear understanding of the behavior of the substituted organo-silicon compounds and the possibility of producing useful resinous polymers from them led to an investigation of some of the disubstituted compounds, the results of which are described briefly in the present paper.

Discussion of Results

Liquid Hydrolysis Products.—The hydrolysis of the phenylethyl-, diethyl-, phenylmethyl-, dimethyl-, and diphenyl-dichlorosilanes, under mild conditions, results in the formation of relatively low molecular weight products. With one exception these products are liquids. The diphenyl compound forms a crystalline powder. A cyclic trimer appears definitely to be formed upon hydrolysis of the phenylethyldichlorosilane under the conditions described. Cyclic trimeric condensation products also appear to be present in the hydrolysis products of the diethyl and dimethyl compounds.

Resinous Polymers.—The removal of organic groups by hydrolysis or oxidation results in the

formation of additional siloxane linkages which contribute to the formation of higher polymers. When the hydrolysis products of the compounds containing phenyl groups are treated at elevated temperatures with aqueous hydrochloric acid, there is a gradual increase in the viscosity of the product which is accompanied by the evolution of benzene. If this treatment is continued sufficiently long the material reaches an extremely viscous tacky state but is fusible and readily soluble in toluene and other solvents. With still further treatment, gelation occurs and the product becomes infusible and insoluble but remains somewhat resilient. When air is passed through the hydrolysis products of the compounds containing alkyl groups at elevated temperatures, similar changes in viscosity occur and the resinification in this case is accompanied by the formation of aldehydes. Here also insoluble products result on longer treatment.

In the case of the phenylethyl compound, analysis and molecular weight of the polymer resulting from acid treatment just prior to gelation indicate that the cyclic trimeric rings have remained intact but have become joined together by the additional siloxane linkages formed by displacement of the phenyl groups.

The hydrolysis product of the phenylmethyl compound, when brought to a similar physical state by air treatment at elevated temperature, likewise appears to have approximately half of its di-substituted silicon atoms converted to mono-substituted silicon atoms by loss of methyl groups, a fact which is indicated by its increased silica residue. Upon acid treatment of the phenylmethyl hydrolysis product, however, gelation occurs with less loss of organic matter than would be expected from comparison with the behavior of the phenylethyl compound under similar conditions. The cyclic dimethyltrisiloxane, upon resinification, seems to gel when approximately one-fifth of the disubstituted silicon atoms are converted to mono-substituted atoms. In this case complications may be involved in the resinification. The point of gelation may be considerably affected by the compatibility of the polymers present. Opening of the ring may also be involved.

(1) Friedel, *Ann. chim. phys.*, [iv] **9**, 5 (1866).(2) Ladenburg, *Ann.*, **173**, 143 (1874).(3) Diltney, *Ber.*, **38**, 4132 (1905).(4) Kipping and co-workers, (a) *J. Chem. Soc.*, **95**, 302-314 (1909); (b) *ibid.*, **101**, 2108-2166 (1912); (c) *ibid.*, **105**, 484-500, 679-690 (1914); (d) *ibid.*, **107**, 459-468 (1915).(5) Kipping and Murray, *ibid.*, 1427-1431 (1928).

The resinous materials obtained from the sources described vary somewhat in physical properties and the ease with which they are formed. The hydrolysis product of the dimethyl compound, for example, appears to require more drastic treatment for resinification than the hydrolysis product of diethyldichlorosilane. The dialkyl derivatives in general are more rubbery and gel-like than those containing a phenyl group but appear to have less physical strength after curing than the latter. Films formed from solutions of the various resins lose their tackiness and solubility with appropriate baking. They resemble films formed from drying oils, but are superior to the latter in thermal stability.

Crystalline Products.—The diphenylsilane diol was obtained in pure form without difficulty. Attempts to isolate the open chain dimeric and trimeric condensation products described by Kipping were not successful. The data presented by Kipping^{4b} to characterize them appear to be inadequate. The melting point obtained by us for the cyclic diphenyltrisiloxane leads to the belief that Kipping's cyclic tetramer was in reality pure trimer. Thus, his isolation of an open chain tetramer is likewise doubtful. The formation of the cyclic trimer from the diol according to our results, is promoted by the presence of aqueous hydrochloric acid, ammonia, or small amounts of aqueous alkali.

Experimental

Analysis.—The silica determinations were conveniently carried out in "VYCOR" brand test-tubes of ordinary size, by cautiously decomposing the sample with approximately twice its volume of concentrated sulfuric acid and finally igniting to constant weight. To get satisfactory ignition in the case of the aryl compounds, it was necessary to cool and treat with a few drops of concentrated nitric acid several times before completely fuming off the sulfuric acid. The molecular weights were determined cryoscopically. Chlorine was determined by titration of the hydrochloric acid with standard alkali after hydrolysis of the sample.

Preparation of the Di-substituted Silicon Halides.—The usual Grignard reaction was employed. In some instances, butyl ether was used instead of ethyl ether. From butyl ether the removal of magnesium salts was more difficult and heating of the reaction mixture above 40 to 50° resulted in the formation of appreciable amounts of butyl chloride. The desired fractions of the disubstituted silicon halides were selected on the basis of distillation curves. The various boiling points obtained by us were as follows: phenylethyldichlorosilane, 100° (13 mm.); diethyldichlorosilane, 131° (740 mm.); phenylmethyldichlorosilane, 82.5° (13 mm.); dimethyldichlorosilane, 70°

(740 mm.); diphenyldichlorosilane, 160° (10–11 mm.). The phenylmethyldichlorosilane was further identified as follows: 37.30% chlorine, 31.2% silica, d_{25}^{25} 1.1876; (calcd. for $C_6H_5CH_2SiCl_2$, 37.2% chlorine, 31.41% silica).

Liquid Hydrolysis Products.—Three hundred seventy-five grams of phenylethyldichlorosilane added dropwise to 600 cc. of water, with vigorous stirring during three to four hours and with the temperature below 70°, yielded an oily liquid of medium viscosity. Reversing the order of mixing appeared to give the same material. Esterification of the halide with ethyl alcohol followed by hydrolysis seemed to produce the same liquid as did the use of dilute aqueous ammonia in place of water. A 30.8070-g. sample of the halide was hydrolyzed by dropwise addition to three or four times the theoretical amount of water covered with ether to avoid excessive heating. The product was dried to constant weight in vacuum at room temperature. A residue of 21.4030 g. remained, which is 69.4% of the original halide. With complete dehydration the product would theoretically amount to 73.2%. Another sample, converted to the ethyl ester, hydrolyzed and brought to constant weight in vacuum at 100°, likewise indicated that, under relatively mild conditions, dehydration is essentially complete. The product obtained at room temperature gave on analysis: 40.3% silica, molecular weight 445 (0.2366 g. in 2.3513 g. camphor, m. p. 177.5°, $K = 33.2$, $\Delta T = 7.5$), (calcd. for $(C_6H_5SiO)_3$, 40.0% silica, molecular weight 450).

The hydrolysis of diethyldichlorosilane by dropping into excess water resulted in a clear immiscible oil which was somewhat more viscous than water. What appeared to be the same oil was also obtained by dropping a sample of the halide into a dry saturated solution of ammonia in dioxane, adding benzene and washing with water. The other modifications of the hydrolytic conditions mentioned above for the phenylethyl compound gave the same result. Some of the halide was converted to ester, $Et_2Si(OEt)_2$, and a 1.7613-g. sample, after hydrolysis and vacuum treatment at room temperature, gave 1.0322 g. of residue which is 58.5% of the ester (theory for complete hydrolysis and dehydration, 58%). A distillation of the hydrolysis product showed it to be molecularly inhomogeneous. A fraction boiling between 140–148° (17 mm.) gave a molecular weight of 297; (0.3271 g. in 25.5383 g. of benzene, $K = 51.2$; $\Delta T = 0.221^\circ$) (calcd. for a cyclic trimer $(C_2H_5SiO)_3$, 306). For the undistilled product molecular weight values of 519 and 534 were found. The average of Kipping's values for the same material is 601.⁶

A sample of phenylmethyldichlorosilane diluted with three volumes of ether was hydrolyzed by adding water to it dropwise. The hydrolysis product was a colorless viscous liquid. Modification of the hydrolysis conditions seemed to give the same product. Upon decomposition and ignition, a sample of this material gave 43.5% silica (calcd. for the completely dehydrated compound, C_7H_8SiO , 44.1% silica).

Hydrolysis of dimethyldichlorosilane in excess water at room temperature gave a clear mobile liquid. Hydrolysis of the ester, b. p. 112°, from a different source appeared to give the same product. Stock describes a similar material

(6) Martin and Kipping, *J. Chem. Soc.*, **95**, 302–314 (1909).

from hydrolysis of dimethylsilane.⁷ Distillation showed the material to be inhomogeneous. A partially crystalline fraction was obtained. The crystals were hexagonal plates which melted at 45–48°. The molecular weight was 233 (0.0842 g. in 22.6217 g. of benzene, $\Delta T = 0.082^\circ$); ignition gave 81.3% silica (calcd. for a cyclic trimer, $(C_2H_6SiO)_3$, molecular weight 222, silica 81.1%).

Resinous Polymers.—The hydrolysis product of phenylethyldichlorosilane, treated at 190° with a slow stream of air for approximately twenty-four hours, became extremely viscous and tacky. Aldehydes were detected in the exhaust gas. Another sample of the hydrolysis product treated at 190° by dropwise addition of aqueous hydrochloric acid also became extremely viscous and tacky. When either treatment was continued for approximately forty-eight hours a somewhat resilient gel was formed which was insoluble in toluene. A sample of the resin formed by the treatment with aqueous acid and carried to the tacky stage just prior to gelation gave on analysis a residue of 49.6% silica. Its average molecular weight was found to be 1310 (0.1403 g. in 1.1493 g. of camphor, $K = 33.2$, $\Delta T = 3.1^\circ$). These data correspond approximately to an average molecule formed by joining four trimeric rings through siloxane linkages substituted for phenyl groups. Such a compound theoretically would yield 51.9% silica and have a molecular weight of 1386. In a quantitative experiment 67% of the theoretically evolved benzene was collected.

A sample of the hydrolysis product of diethyldichlorosilane, heated at 200–225° under reflux in a stream of carbon dioxide for over thirty hours appeared unchanged. On replacing the carbon dioxide with an oxygen stream and continuing the heating at 160–190°, acetic acid and acetaldehyde were detected in the exhaust gases. There was a corresponding increase in viscosity of the residue. Another sample of the hydrolyzate treated at 200° with an air stream for ten hours became an insoluble rubbery gel.

Air treatment of the liquid hydrolysis product of phenylethyldichlorosilane at 250° formed a soluble, viscous, sticky mass with the evolution of formaldehyde. It gave a residue of 46.4% silica. A sample of the still soluble resin resulting from the acid treatment as above gave a residue of 47.7% silica. The silica residue from a sample of the gelled insoluble material resulting from the acid treatment had increased to 55.6%, thus showing the further removal of phenyl groups.

The hydrolysis products from dimethyldichlorosilane and from the corresponding ethyl ester were resinified by air treatment at elevated temperatures. The cyclic dimethyltrisiloxane likewise became resinified with the same treatment. The rubbery gel resulting from the latter gave on ignition a silica residue of 82.5% indicating an increase in silicon content upon resinification.

On passing a slow stream of moist air through a sample

of diphenyldichlorosilane heated at 170° hydrolysis occurred and a marked increase in viscosity was noted. In a similar experiment the evolution of benzene was also noted by the use of a cooled trap. Dropwise addition of water to the chloride at 170° gave after twenty to thirty minutes an insoluble gel.

Crystalline Products.—The diphenylsilane diol corresponded well with descriptions in the literature. The melting point varied with rate of heating. At 2°/min. it softened at 135° and melted at 155°. A molecular weight of 212 was found; (0.1648 g. in 30.924 g. glacial acetic acid, $K = 39$, $\Delta T = 0.098^\circ$; calcd. 216). It was readily recrystallized by dissolving in a minimum of warm ethyl alcohol and adding benzene. Treatment in hot alcohol solution with small amounts of aqueous ammonia or dilute sodium hydroxide converted it to the condensed cyclic trimer. The trimer was readily recrystallized by dissolving in a minimum of warm benzene and adding alcohol. When pure it melted at 199.5–200°. Its molecular weight was 589 (0.4525 g. in 25.9804 g. of benzene, $K = 51.2$, $\Delta T = 0.151^\circ$) (calcd. for the trimer, $(C_{12}H_{10}SiO)_3$, 594).

When diphenylsilane diol in methyl alcohol solution with a drop of concentrated hydrochloric acid was allowed to stand for two weeks, it yielded material melting at 188–189°, and after one recrystallization using benzene and ethyl alcohol it melted at 197–198°. Repetition of some of Kipping's procedures failed to give us materials corresponding to his chain dimer or trimer.⁴⁶ Finally, some cyclic trimer was separated from the resulting material by fractionally crystallizing it from a benzene and alcohol mixture. A sample of the diol in ethyl alcohol with a few drops of aqueous ammonia after seventeen days became nearly solid with crystals. A fraction of these crystals melted at 161°. Recrystallization did not raise the melting point. A molecular weight of 299 was found which does not correspond to any pure intermediate dehydration products.

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Summary

New resinous products derived from disubstituted silicon compounds are described and the reactions involved in their formation are discussed.

The cyclic diphenyltrisiloxane, melting at 199.5–200°, is the only crystalline condensation product of diphenylsilane diol which appears to be adequately characterized.

Evidence has been found for the presence of cyclic trimeric molecules in the hydrolysis products of diethyl- and dimethyldichlorosilanes.

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(7) A. Stock and C. Somieski, *Ber.*, **52B**, 695–724 (1919); *C. A.*, **13**, 2536 (1919).