[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Properties of the Silicon–Hydroxyl Bond in Trialkylsilanols[1]

BY L. H. SOMMER, E. W. PIETRUSZA[2] AND F. C. WHITMORE

In 1872 Ladenburg[3] reported several methods for the preparation of the first trialkylsilanol, triethylsilanol. The best of these were the preparations from triethylchlorosilane, by addition to cold, dilute ammonium hydroxide, and from triethylsilyl acetate (prepared from triethylethoxysilane and acetic anhydride in a sealed tube) by heating with sodium carbonate solution. Ladenburg found that triethylsilanol can be condensed to hexaethyldisiloxane by phosphorus pentoxide or sulfuric acid, and that sodium reacts readily to give sodium triethylsilanolate on warming or addition of dry ether.[4] Sauer[5] reports the preparation and ease of intermolecular dehydration of trimethylsilanol at room temperature with potassium carbonate, alumina and even on prolonged refluxing.

The silicon–hydroxyl bond in trialkylsilanols is interesting from both theoretical and practical standpoints. The similarities and differences between this bond and the carbon–hydroxyl bond in tertiary alcohols are of interest. Practically, the intermolecular dehydration of these compounds is important because a similar dehydration of dialkyl- and monoalkyl-hydroxysilanes is responsible for the formation of valuable silicone polymers.[6] The present paper reports a study of the silicon–hydroxyl bond in triethylsilanol and trimethylsilanol.

Experimental

Triethylsilyl Sulfate.[7]—Hexaethyldisiloxane, 99 g. (0.4 mole) was added to 56 g. of fuming sulfuric acid (20% SO_3) maintained at 0–20° during one-half hour. After stirring for two hours at room temperature, 40 g. of ammonium sulfate was added and stirring was continued for two hours. The upper layer was then decanted and treated with a second 40-g. portion of ammonium sulfate, followed by extraction with three 100-cc. portions of dry pentane. The pentane was removed under reduced pressure. Since previous runs had shown that triethylsilyl sulfate decomposes somewhat on slow distillation under reduced pressure, the product was rapidly distilled at 12 mm. from a Claisen flask. There was obtained 65.2 g. of triethylsilyl sulfate, b. p. 170° (12 mm.), n^{20}D 1.4442, a yield of 50%.

Anal. Calcd. for $C_{12}H_{30}SiSO_4$: Si, 17.2; SO_4, 29.4; neut. equiv., 163. Found: Si, 17.2; SO_4, 29.5; neut. equiv., 166.

A similar run was made using 0.2 mole of the disiloxane 0.6 mole of concentrated sulfuric acid and 0.44 mole of ammonium sulfate. Yield of triethylsilyl sulfate was 43%.

Triethylsilanol.—Triethylchlorosilane,[8] 151 g. (1 mole), was added to 600 cc. of dry ether and the solution was cooled by a salt–ice-bath. This solution was then titrated with 1 *N* sodium hydroxide during one-half hour at 0° with vigorous stirring to the neutral point (phenolphthalein). The ether layer was separated and the aqueous layer extracted with three 100-cc. portions of ether. Drying of the ether solution with potassium carbonate was followed by fractional distillation to give 125 g., a yield of 95%, triethylsilanol, b. p. 77.5° (28 mm.), n^{20}D 1.4329, d^{20} 0.8638.[9]

Anal. Calcd. for $C_6H_{16}SiO$: Si, 21.2. Found: Si, 20.99, 21.05.

A similar procedure using triethylsilyl sulfate instead of triethylchlorosilane gave a 75% yield.

In larger runs, triethylsilanol was prepared from hexaethyldisiloxane *via* the sulfate and from ethyl orthosilicate *via* triethylchlorosilane in 73 and 71% yield, respectively. In these preparations the sulfate and the chlorosilane were not distilled prior to hydrolysis.

Trimethylsilaneol.—Sauer[5] reported that the hydrolysis of trimethylchlorosilane gave hexamethyldisiloxane or azeotropic hexamethyldisiloxane–trimethylsilanol. However, treatment of the chlorosilane with ammonia to give hexamethyldisilazane followed by acid hydrolysis, gave a 30% over-all yield of trimethylsilanol. Dimethyl silicone with methyl Grignard gave a product which on hydrolysis gave trimethylsilanol. We are able to prepare trimethylsilanol in 70% yield from hexamethyldisiloxane.

To 196 g. (2.0 moles) of concentrated sulfuric acid in a 1-liter three-necked flask fitted with a stirrer there was added 81 g. (0.5 mole) of hexamethyldisiloxane[10] with stirring. The flask was cooled in an ice-bath during the addition. One of the necks of the flask was then connected to a 3-liter three-necked flask containing 300 cc. of dry ether, which in turn was connected to a trap cooled in Dry Ice and acetone. The third neck was connected by Gooch rubber tubing to an Erlenmeyer flask containing 48.1 g. (1.3 moles) of ammonium fluoride. This was added without exposure to air during one hour. The ice-bath was then removed and the flask was heated with warm water in order to distil the trimethylfluorosilane[11] into the second flask, which was cooled in a salt–ice-bath. The cold ether solution of trimethylfluorosilane was titrated to the neutral point (phenolphthalein) with about 1 liter of 1 *N* sodium hydroxide. By slow addition of the alkali (one hour) with vigorous stirring it was possible to keep the reaction mixture neutral during most of the addition. The organic layer was then separated, the aqueous layer extracted twice with 100 cc. ether, and the

---

[1] Paper VIII in a series on organosilicon compounds. See Sommer, Bailey, Strong and Whitmore, THIS JOURNAL, **68**, 1881 (1946) (Paper 7).

[2] Allied Chemical and Dye Corporation Fellow, 1945–1946.

[3] Ladenburg, *Ann.*, **164**, 320 (1872).

[4] (a) Other workers have prepared triethylsilanol by different methods. Grüttner and Cauer, *Ber.*, **51**, 1288 (1918), used hydrochloric acid and *p*-triethylsilylphenylmethylcarbinol; Kraus and Nelson, THIS JOURNAL, **56**, 195 (1934), hydrolyzed ethyltriethylsilylamine to triethylsilanol; (b) Pape, *Ann.*, **222**, 367 (1884), prepared tri-*n*-propylsilanol and reported that it reacts with sodium; Taurke, *Ber.*, **38**, 1666 (1905), prepared tri-isoamylsilanol.

[5] Sauer, THIS JOURNAL, **66**, 1707 (1944).

[6] For an excellent treatment of these polymers see Rochow, "The Organosilicon Polymers," *Chem. Eng. News*, **23**, 612 (1945).

[7] Sommer, Pietrusza, Kerr and Whitmore, THIS JOURNAL, **68**, 156 (1946).

[8] Prepared from tetraethyl orthosilicate in 71% yield by the method of DiGiorgio, Strong, Sommer and Whitmore, THIS JOURNAL, **68**, 1380 (1946), Paper 6.

[9] Ladenburg[4] reported: b. p. 154° at 760 mm. and 70.5° at 16.5 mm., $n^{16.6}$D 1.4364, d^{20} 0.8647.

[10] (a) Prepared from ethyl orthosilicate and methylmagnesium bromide. Details will be reported later; (b) for the first preparation of this compound see ref. 6.

[11] (a) The characterization and properties of the trimethylfluorosilane will be reported in a later paper; (b) for the preparation of triethylfluorosilane by a similar method see Flood, THIS JOURNAL, **55**, 1735 (1933).

ether solution of the product dried over anhydrous potassium carbonate (30 g.) for one and one-half hours. After removal of the ether by rapid distillation through a stripping column, the residue was fractionally distilled in a glass-helix packed column of 15 theoretical plates. There was obtained 63.0 g. of trimethylsilanol, b. p. 99° (734 mm.), n^{20}D 1.3888, d^{20} 0.8141, a yield of 70% based on the hexamethyldisiloxane. The high purity of the trimethylsilanol is shown by the fact that a weighed sample gave the theoretical volume of hydrogen on slight warming with sodium and dry xylene.

Reactions of Triethylsilanol

Despite the ease of hydrolysis of triethylchlorosilane (it can be titrated as an acid with 0.1 *N* alkali) it was found that triethylsilanol gives triethylchlorosilane in 77% yield on treatment with concentrated (38%) hydrochloric acid.

$$(C_2H_5)_3SiOH + HCl \longrightarrow (C_2H_5)_3SiCl + H_2O$$

Treatment with 34 and 47% hydrobromic acid gave hexaethyldisiloxane. Heating of a mixture of triethylsilanol and acetic anhydride gave triethylsilyl acetate. Triethylsilanol and fuming sulfuric acid gave triethylsilyl sulfate.

Reaction with Hydrochloric Acid.—In a 1-liter flask, equipped with an efficient stirrer, there was placed 450 cc. of concentrated hydrochloric acid and the flask was cooled in an ice-bath. Triethylsilanol, 66 g. (0.5 mole) was added with vigorous stirring during one hour. The mixture was then stirred for an additional hour. The flask was stoppered, removed from the ice-bath and allowed to come to room temperature while the flask was shaken. The upper layer was separated and dried over anhydrous zinc chloride for two hours. Fractional distillation gave 58.1 g. of triethylchlorosilane, b. p. 145° (729 mm.), n^{20}D 1.4311, a yield of 77%. Titration of a weighed sample with standard alkali gave 23.45% hydrolyzable chlorine (calcd., 23.6%). Treatment with methylmagnesium bromide gave methyltriethylsilane,[12] b. p. 126°, n^{20}D 1.4150.

Similar treatment of trimethylsilanol gave hexamethyldisiboxane.

Reaction with Acetic Anhydride.—A solution of triethylsilanol, 26.4 g. (0.2 mole), and 20.4 g. (0.2 mole) of acetic anhydride was heated on the steam-bath for twelve hours. Fractional distillation gave 26.2 g. (0.15 mole) of triethylsilyl acetate,[3] b. p. 167° (726 mm.), neutral equivalent 180 (calcd. 174), a yield of 76%.

Reaction with Sulfuric Acid.—To 49 g. of concentrated sulfuric acid was added 66 g. (0.5 mole) of triethylsilanol. After standing for two hours, two layers formed. Fuming sulfuric acid (62 g.) was then added and a homogeneous solution resulted. Ammonium sulfate (87 g.) was added and the mixture was allowed to stand for five hours. The upper layer was decanted, treated with more ammonium sulfate (44 g.) and fractionated. There was obtained 43.2 g. of triethylsilyl sulfate, b. p. 128° (2 mm.), a yield of 50%. The neutral equivalent was 4% low due to slowness of distillation (see above).

Confirming Ladenburg's observation, it was found that triethylsilanol reacts rapidly with sodium to give hydrogen and sodium triethylsilanolate. A comparison of the relative reactivity of triethylsilanol and triethylcarbinol with sodium gave the following results: $(C_2H_5)_3SiOH$ gave hydrogen quantitatively; $(C_2H_5)_3COH$ gave no hydrogen.

Carefully cleaned sodium was added to a weighed sample of triethylsilanol dissolved in dry xylene. Measurement of the evolved hydrogen by means of a gas buret showed that 99% of the theoretical volume was evolved after twenty minutes of refluxing. When the experiment was repeated with triethylcarbinol no hydrogen was evolved during two hours of refluxing.

In another run, triethylsilanol was stirred with an equivalent amount of finely divided sodium in the absence of a solvent. Warming gave a vigorous evolution of hydrogen. Reaction was complete in one-half hour as shown by the complete solubility of the solid product in anhydrous ethyl ether. In a parallel study, triethylcarbinol gave very little reaction, even after three hours of heating with sodium.

Triethylsilanol was fractionated at atmospheric pressure during a six-hour period without any appreciable dehydration. Heating with approximately equal volumes of distilled water, 0.01 *N* hydrochloric acid, or 0.01 *N* alkali, for eleven hours gave better than 90% recoveries of the silanol. This is in contrast to the behavior of trimethylsilanol.[6] Heating with a few drops of concentrated hydrochloric acid for the same period of time gave about 50% dehydration to the disiloxane. Parallel treatment with 12 *N* alkali gave very little dehydration. Refluxing with twice its volume of 20 or 70% sulfuric acid for four hours gave 75 and 85% yields of the disiloxane, respectively.

Refluxing triethylsilanol with anhydrous copper sulfate for three hours gave 31% conversion to the disiloxane. Iodine is much more effective, complete dehydration taking place on heating for one-half hour. Triethylsilanol passed over activated alumina at 360° gave only 8% dehydration.

Reactions of Trimethylsilanol

With Sodium.—A weighed sample of trimethylsilanol was dissolved in carefully dried xylene. Warming with clean sodium for fifteen minutes and measurement of the evolved hydrogen by means of a gas buret gave as equivalent weights, 90.4 and 92.0; theoretical for trimethylsilanol is 90.0.

With Aqueous Sodium Hydroxide.—Addition of trimethylsilanol to 12 *N* sodium hydroxide gives a white precipitate of sodium trimethylsilanolate.

$$(CH_3)_3SiOH + NaOH \longrightarrow (CH_3)_3SiONa + H_2O$$

This surprising behavior of trimethylsilanol as an acid toward alkali, the activity of both silanols with sodium, and the formation in good yield of triethylsilyl acetate from the silanol and acetic anhydride, are evidence that *the H of the hydroxyl in trialkylsilanols is much more reactive than that in tertiary alcohols.*

In a 200-cc. flask, fitted with a mechanical stirrer, was placed 25 cc. of 12 *N* sodium hydroxide. Upon adding a small amount of trimethylsilanol, a white precipitate formed and heat was evolved. The flask was cooled with cold tap water and 8.14 g. (0.09 mole) of trimethylsilanol was slowly added. A mushy, white solid formed. This was shaken and stirred with three 100-cc. portions of anhydrous ether. The solid was insoluble in the ether, but by vigorous stirring, it was suspended in the ether so that by several quick decantations most of it was separated from the aqueous layer. The product was allowed to settle and the ether was decanted. The solid was then washed twice with 50 cc. of anhydrous ether and dried in a vacuum desiccator over phosphorus pentoxide at 20 mm. pressure for twenty-four hours. The yield of product was 8.7 g., 87% of the theoretical.

A 0.5-g. sample was dried in an Abderhalden apparatus at 2 mm. pressure for two hours, dissolved in 25 cc. of water and excess standard acid, and back-titrated with standard base using phenolphthalein. The neutral equivalent thus obtained was 128; calcd. value is 112.

Five grams of the crude product was treated with 50 cc. of warm acetone. A milky suspension formed. This was filtered by suction and 100 cc. of anhydrous ether was added to the filtrate with stirring. The solution was cooled in the ice-box for twelve hours. A flaky white solid crystallized out. This was filtered and dried in an Abderhalden apparatus for three hours at 2 mm. pressure. There was obtained 0.88 g. of sodium trimethylsilanolate, a 16% yield.

Anal. Calcd. for C_3H_9SiONa: Si, 25.0; C, 32.1; neut. equiv., 112. Found: Si, 25.0; C, 32.1; neut. equiv., 108.

Sodium trimethylsilanolate melts with decomposition at 147–50°. Acid hydrolysis gave hexamethyldisiloxane, b. p. 100°, n^{20}D 1.3772.

---

[12] Whitmore, *et al.*, THIS JOURNAL, **68**, 475 (1946).

Acknowledgments.—We are indebted to the Minnesota Mining and Manufacturing Co. and The Miner Laboratories for a research grant which made this work possible. We thank R. N. Walter of this Laboratory for the analyses.

Summary

1. Triethylsilanol was prepared in good yield from triethylsilyl sulfate and from triethylchlorosilane.
2. Hydrolysis of trimethylfluorosilane gave trimethylsilanol in excellent yield.
3. Reactions of triethylsilanol and trimethylsilanol have been studied.
4. Formation of the sodium salt from trimethylsilanol and aqueous alkali, and the activity of both silanols with sodium, indicate that the hydrogen of the silicon-hydroxyl group is more reactive than that of the carbon-hydroxyl in tertiary alcohols.

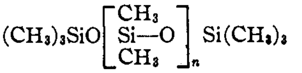
STATE COLLEGE, PA. RECEIVED MARCH 29, 1946

[CONTRIBUTION FROM DOW CORNING CORPORATION]

Organosilicon Polymers. II. The Open Chain Dimethylsiloxanes with Trimethylsiloxy End Groups[1]

BY M. J. HUNTER,[2] E. L. WARRICK,[3] J. F. HYDE[4] AND C. C. CURRIE[2]

In a recent paper[5] the preparation and properties of a series of low polymer cyclic dimethylsiloxanes were described. It was indicated that other series of open chain polymers would be reported at a later date. This paper will describe the series of open chain dimethylsiloxanes with trimethylsiloxy end groups represented by Formula I



$$(CH_3)_3SiO\left[\begin{matrix}CH_3\\ Si—O\\ CH_3\end{matrix}\right]_n Si(CH_3)_3 \qquad (I)$$

where *n* may vary from one to a very large number.

At the time this paper was completed and ready for submission, several articles by Patnode and Wilcock,[6] Hurd,[7] and Wilcock[8] appeared describing polymers of this series and showing some of the interesting physicochemical properties of these materials.

Open chain silicon-oxygen-silicon polymers are well known in mineral silicate chemistry[9] where they form the skeletal structures of such materials as pyroxenes and amphiboles. These silicon-oxygen-silicon open chains are substituted with metal oxide ions on the two remaining positions of each silicon in the chain.

Other inorganic low polymer siloxane chains have been described by Schumb and Holloway,[10] who isolated chains containing six and seven silicon atoms separated by alternate oxygen atoms with chlorine groups satisfying all the remaining silicon valences.

Organo-silicon open chain polymers were first described by Kipping,[11] who isolated a series of polydiphenylsiloxane low polymer units with hydroxyl end groups. Due to the relative instability of the hydroxyl groups, these linear polymers are readily converted into other diphenylsiloxane configurations.

Low Polymer Open Chain Siloxanes

Low polymer disubstituted siloxanes may be divided into three classes: (1) the cyclic members, similar to those previously described,[5,6] (2) open chain polymers with temporary or reactive end groups similar to the hydroxyl terminated polymers described by Kipping,[11] and (3) linear polymers with permanent end groups which show a high relative stability to both heat and moisture. Copolymer chains of dimethylsiloxane units with trimethylsiloxy end groups fall into this third class of polymers.

The methyl polysiloxanes of Formula I may be prepared by cohydrolyzing a mixture of ethoxytrimethylsilane[12] and diethoxydimethylsilane.[13] The condensation products from this reaction, when equal molar mixtures of the two silane intermediates are employed, form a water-white fluid which is approximately 95% distillable. Somewhat similar copolymer mixtures may be obtained from the cohydrolysis of chlorotrimethylsilane[14] and dichlorodimethylsilane[15] which was also pointed out by Patnode and Wilcock.[7] A third method for preparing these compounds is that described by the above authors[7] who isolated them from the rearrangement products of hexamethyldisiloxane and octamethylcyclotetrasiloxane, after treatment with sulfuric acid.

---

(1) Presented in large part before the High Polymer Conference at Gibson Island, June 25, 1945, by E. L. Warrick.

(2) Dow Corning Corporation, Midland, Michigan.

(3) Mellon Institute, Pittsburgh, Pennsylvania.

(4) Corning Glass Works, Corning, New York.

(5) Hunter, Hyde, Warrick and Fletcher, THIS JOURNAL, **68**, 667 (1946).

(6) Patnode and Wilcock, THIS JOURNAL, **68**, 358 (1946).

(7) Hurd, *ibid.*, **68**, 364 (1946).

(8) Wilcock, *ibid.*, **68**, 691 (1946).

(9) Bragg, "Atomic Structure of Minerals," Cornell University Press, Ithaca, N. Y., 1937, pp. 139–146.

(10) Schumb and Holloway, THIS JOURNAL, **63**, 2753 (1941).

(11) Kipping, *J. Chem. Soc.*, **101**, 2108–2125 (1912).

(12) Daudt, U. S. Patent 2,390,518, Dec. 11, 1945.

(13) McGregor and Warrick, U. S. Patent 2,380,057, July 10, 1945.

(14) (a) Taylor and Walden, THIS JOURNAL, **68**, 842 (1944); (b) Gilliam and Sauer, *ibid.*, **66**, 1793 (1944); (c) McGregor and Warrick, U. S. Patent 2,386,488, Oct. 9, 1945.

(15) (a) Gilliam, Liebhafsky and Winslow, THIS JOURNAL, **63**, 801 (1941); (b) Rochow, U. S. Patent 2,286,793, June 16, 1942.