pared and stored in the refrigerator. All transfers of heavy water were made with syringes, previously dried at 200° for five hours, assembled while hot and stored in a desiccator over Drierite. The solutions of sodium deuteroxide were prepared by allowing approximately 0.03 g. of sodium to react with 27 ml. of heavy water under a stream of dry carbon dioxide-free nitrogen gas. The heavy water was aerated with the nitrogen gas for 0.5 hour before the addition of the sodium to ensure the removal of any carbon dioxide which may have been initially present in the liquid. Five ml. of a standard sodium hydroxide solution (or of a standard deuteroxide solution in heavy water) was introduced into a 10-ml. glass-stoppered volumetric flask by means of a 5-ml. pipet. The flask and its contents were placed in a 25° bath, as was approximately 6 ml. of the 2-chloroethanol stock solution. When temperature equilibrium had been attained, 5 ml. of the 2-chloroethanol solution was added to the 10-ml. volumetric flask containing the sodium hydroxide solution by means of a 5-ml. pipet. The solution was rapidly and thoroughly shaken and a stopwatch started. One-ml. pipets were used to transfer samples of the solution into 25-ml. erlenmeyer flasks containing approximately 10-ml. of ice-cold water, three drops of brom thymol blue indicator and a magnetic stirring bar. The flasks were placed in a shallow ice-bath atop a magnetic stirrer and titrated with 0.01 *M* hydrochloric acid from a 5-ml. microburet.

Kinetic Data.—Table II lists the measured second-order rate constants from 21 kinetic runs.

Acknowledgment.—We are grateful to Prof. Richard C. Lord for permission to use the equipment in the Spectroscopy Laboratory and for helpful discussion and criticism. In addition we are indebted to members of Prof. Lord's research group, in particular to Mr. T. J. Porro for his constant aid in obtaining the infrared spectra and Mr. A. Danti who conducted the Raman investigations and provided the necessary calibration data.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF APPLIED CHEMISTRY, FACULTY OF TECHNOLOGY, GUMMA UNIVERSITY]

Preparation of Some Organosilanediols and Phenylsilanetriol by Direct Hydrolysis Using Aniline as Hydrogen Chloride Acceptor[1]

BY TOSHIO TAKIGUCHI

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An improved preparation of unstable silanols involving the hydrolysis of the corresponding chlorosilanes with the theoretical amount of water in ether in the presence of aniline as hydrogen chloride acceptor has been developed. Dimethylsilanediol, diethylsilanediol, diphenylsilanediol and phenylsilanetriol were obtained in pure form by this procedure. Methyltrichlorosilane was also hydrolyzed by the proposed method, but all attempts to obtain a monomeric product have failed.

A striking feature of many organosilanols is their marked tendency to condense to polymeric products. For this reason, direct hydrolytic procedures have only been applied to the preparation of relatively stable silanols, the preparation of diethylsilanediol[2,3] by means of special techniques having been the utmost achievement.

The previous failure to obtain dimethylsilanediol and phenylsilanetriol by direct hydrolysis has been attributed to the extreme instability or rapidity of condensation of these compounds; these silanols, therefore, have heretofore been prepared from the corresponding alkoxysilanes.[4-6]

The general difficulty in preparing unstable silanols by direct hydrolysis from the corresponding chlorosilanes presumably has resulted both from the substantially heterogeneous character of the reaction and from the catalytic effect of hydrogen chloride produced thereby. Without proper precaution, especially against the polymerizing effect of hydrogen chloride, any successful preparation cannot be expected.

Therefore, the hydrolysis of chlorosilanes under carefully controlled mild conditions has generally been the aim of previous investigators.[2-3,7-9]

In the present paper we wish to report an improved method for the preparation of some unstable silanols including both dimethylsilanediol and phenylsilanetriol directly from the corresponding chlorosilanes. Our finding[10] that aniline is an excellent acceptor of hydogen chloride in dry ether, precipitating aniline hydrochloride almost quantitatively, prompted a successful hydrolysis of some chlorosilanes in ether in presence of the theoretical amounts of water and aniline.

When one mole of di- or trichlorosilane (ether solution) was added to an ether solution containing two moles (three moles for trichlorosilane) each of distilled water and aniline, aniline hydrochloride was precipitated and the corresponding silanols were obtained in pure form from the filtrate after evaporation under diminished pressure, the reaction being expressed by the general equation

$$R_nSiCl_{4-n} + (4-n)C_6H_5NH_2 + (4-n)H_2O \longrightarrow R_nSi(OH)_{4-n} + (4-n)C_6H_5NH_3Cl$$

Dimethylsilanediol, diethylsilanediol, diphenylsilanediol and phenylsilanetriol were prepared in good yield by essentially the same procedure although the degree of care required during the preparation varies with the stability of the product.

Dimethylsilanediol, diethylsilanediol, diphenylsilanediol and phenylsilanetriol are colorless

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[1] A brief outline of this method is being submitted in the *J. Chem. Soc. Japan* (*Ind. Chem. Sect.*) as a Short Communication.

[2] P. A. DiGiorgio, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **68**, 344 (1946).

[3] P. D. George, L. H. Sommer and F. C. Whitmore, *ibid.*, **75**, 1585 (1953).

[4] Dimethylsilanediol from dimethyldimethoxysilane; S. W. Kantor, *ibid.*, **75**, 2712 (1953).

[5] Dimethylsilanediol from dimethyldiethoxysilane; J. F. Hyde, *ibid.*, **75**, 2166 (1953).

[6] Phenylsilanetriol from phenyltrimethoxysilane; L. J. Tyler, *ibid.*, **77**, 770 (1955).

[7] J. F. Hyde and R. C. DeLong, *ibid.*, **63**, 1194 (1941).

[8] C. A. Burkhard, *ibid.*, **67**, 2173 (1945).

[9] S. Fukukawa, *Science & Industry, Japan*, **30**, 71 (1956).

[10] T. Takiguchi, *J. Chem. Soc. Japan* (*Ind. Chem. Sect.*), **61**, 1236 (1958).

crystalline solids. All melt with formation of liquid decomposition products.

All efforts to obtain monomeric methylsilanetriol from methyltrichlorosilane were unsuccessful.

Throughout the experiments, with the exception of diphenylsilanediol, acid-rinsed Pyrex or preferably clean quartz equipment was found necessary. Moreover, the isolation of the products in the form of a precipitate at an early stage of the preparation by the use of inert reagents in which the silanol is insoluble was found to be an essential technique.

In determining the hydroxy content, the Karl Fischer titration[11] has been found to be fairly effective.

The melting points measurements must be carried out with acid-rinsed Pyrex capillary tubes heated at 3–5° a minute, the bath being preheated to the appropriate temperatures.

Experimental

Reagents.—Methyl- and phenylchlorosilanes were obtained from the Shin-etsu Chemical Industrial Co. in purified grades; diethyldichlorosilane was synthesized by the Grignard route.[12] All were purified by careful single distillations immediately before use. Aniline was purified by distillation at 58° under 5 mm. after drying over potassium hydroxide, water content 0.10–15%.

Preparation and Properties of Silanols.—A typical procedure is described for dimethylsilanediol.

(a) **Dimethylsilanediol.**—A solution of 30.0 g. (0.23 mole) of dimethyldichlorosilane (freshly distilled) in 300 ml. of ether was added dropwise, with vigorous stirring, to a cooled (0°) solution of 42.8 g. (0.46 mole) of aniline in 700 ml. of ether, 8.3 g. (0.46 mole) of water and enough acetone to render the solution homogeneous. The rate of dropping was 2 ml. per minute at first but 3–5 ml. per minute after the formation of white precipitate became regular, the reaction temperature being maintained below 2° during the addition. Crystal violet[13] (one drop of 1% ethanol solution) which had been added during the addition remained violet during the entire addition. After 10 minutes further stirring, the white precipitate (aniline hydrochloride) was removed by filtration.

The slightly colored filtrate was concentrated to about 100 ml. under reduced pressure and transferred to a clean quartz crystallizing dish containing 100 ml. of warm *n*-hexane. On evaporating the concentrate in a vacuum desiccator, shiny fluffy flakes and a small amount of oily product appeared. When the top layer became semi-solid, it was collected rapidly and rinsed several times with warm *n*-hexane. On drying the flakes in vacuum for several hours, 15.2 g. (71%) of dimethylsilanediol was obtained. The melting point of the diol was 99–100° dec. (rate of heating 5° per minute in a clean Pyrex capillary tube, the bath being preheated to 80°).

Anal. Calcd. for $C_2H_8SiO_2$: C, 27.07; H, 8.75; Si, 30.45; OH/molecule, 2.00. Found: C, 26.6; H, 8.4; Si, 31.1; OH/molecule (Karl Fischer method), 1.97.

Storage of this diol in an acid-rinsed Pyrex ampoule at room temperature did not prevent its condensation. Storage in purified *n*-hexane produced no outward change after two months. Identification was effected by the X-ray powder pattern.[5]

(b) **Diethylsilanediol.**—Diethylsilanediol was prepared by the same method using 22.8 g. (0.1 mole) of diethyldichlorosilane, 18.6 g. (0.2 mole) of aniline and 3.6 g. (0.2 mole) of distilled water. Diethylsilanediol, 14.6 g. (76%), was obtained as a shiny microcrystalline mass. Effective recrystallization was achieved by use of acetone–hexane, ether–hexane and methyl acetate–benzene, the diol separating as shiny elongated platelets melting at 96–97°.

Anal. Calcd. for $C_4H_{12}SiO_2$: C, 39.97; H, 10.07; Si, 23.35; OH/molecule, 2.00. Found: C, 40.2; H, 10.2; Si, 23.1; OH/molecule, 1.98.

This diol is considerably more stable than dimethylsilanediol; no change was observed after four months storage in a tightly stoppered soft glass container.

(c) **Diphenylsilanediol.**—As anticipated, this diol is quite stable; addition of pure diphenyldichlorosilane or a reverse procedure[14] unfailingly gave this diol. A typical procedure was: 25.3 g. (0.1 mole) of diphenyldichlorosilane added to 18.6 g. (0.2 mole) of aniline and 3.6 g. (0.2 mole) of distilled water in ether gave 20.7 g. (90%) of pure diphenylsilanediol. Its density determined indirectly by suspending a clean crystal in aqueous calcium chloride solution of matched density was 1.157.

Anal. Calcd. for $C_{12}H_{12}SiO_2$: C, 66.62; H, 5.59; Si, 12.96; OH/molecule, 2.00; mol. wt., 217. Found: C, 66.3; H, 5.3; Si, 13.3; OH/molecule, 1.97; mol. wt. (glacial acetic acid), 195–207.

The well-known abnormality[7–9,15–17] of this diol in melting point has also been confirmed. Single crystals developed gradually from a large amount of solvent melted at separate temperatures of 133, 148 and 155°, while powdered samples melted in the range of 115–127° with previous softening at 105°, melting being accompanied by decomposition in all cases. But as an approximate rule, acicular crystals obtained at an earlier stage of recrystallization melted at 133° and 155°, prismatic crystals obtained at later stages melted at 148° and 155°. Further investigations on the possible polymorphism or mesomorphism of this compound are being undertaken. The infrared spectra of the diols were quite in accordance with those given by Tatlock and Rochow.[18]

(d) **Phenylsilanetriol.**—Phenyltrichlorosilane (31.7 g., 0.15 mole) dissolved in 350 ml. of dry ether was added to 1000 ml. of ether containing 41.9 g. (0.45 mole) of aniline and 8.1 g. (0.45 mole) of distilled water cooled to 0°; the white precipitate was washed under water vacuum with cold methyl acetate several times. The filtrate was concentrated to about 150 ml. in a vacuum desiccator and 100 ml. of warm *n*-hexane was added. On evaporating the mixture under vacuum in a clean quartz crystallizing dish, there appeared shiny characteristic platelets.

After many rinsings with warm *n*-hexane the platelets were dried in vacuum; 17.3 g. (74%) of shiny platelets was obtained.

Further purification was carried out by rapid recrystallization from methyl acetate–methyl ethyl ketone under vacuum (mean yield 85%) but the runs made at elevated temperature always led to loss of the major part as a resinous sludge. No decrease in melting point was observed after recrystallization under vacuum. Both platelets and powder melted at 130° with decomposition after softening at 128°.

Anal. Calcd. for $C_6H_8SiO_3$: C, 46.13; H, 5.16; Si, 17.98; OH/molecule, 3.00. Found: C, 45.7; H, 5.3; Si, 18.2; OH/molecule, 2.94.

The X-ray powder pattern data obtained by a diffractometer using finely powdered triol are listed in Table I.

The triol was also defined by its infrared absorption spectra.[6]

Hydrolysis of Methyltrichlorosilane.—A 15.0 g. (0.1 mole) sample of methyltrichlorosilane dissolved in 350 ml. of dry ether was added with vigorous stirring to 700 ml. of ether containing 27.9 g. (0.3 mole) of aniline and 5.4 g. (0.3 mole) of distilled water, the flask being cooled below −5° during the addition by a Dry Ice–acetone cooling bath.

The cold filtrate was evaporated under vacuum; the residue was a slightly colored viscous liquid which was soluble in ethanol and insoluble in benzene immediately after preparation, but which was transformed gradually upon standing at room temperature into a yellowish transparent brittle gel. The final product was quite insoluble in a variety of organic solvents.

Gel formation with liberation of water occurred almost instantly on heating the freshly prepared oily liquid. The

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[11] H. Gilman and L. S. Miller, THIS JOURNAL, **73**, 2367 (1951).

[12] E. G. Rochow, U. S. Patent 2,258,220 (1941).

[13] Crystal violet has been found very convenient to indicate the absence of free silanes in this reaction system; *cf.* "Studies on Organochlorosilanes, VI, VII," *J. Chem. Soc. Japan* (*Ind. Chem. Sect.*), in press.

[14] An ether solution containing aniline and water was added to chlorosilane in ether; yield (mean) was 86%; *cf.* ref. 13.

[15] W. Dilthey and F. Eduardoff, *Ber.*, **37**, 1139 (1904).

[16] G. Martin, *ibid.*, **45**, 403 (1912).

[17] F. S. Kipping, *J. Chem. Soc.*, **101**, 2108 (1912).

[18] W. S. Tatlock and E. G. Rochow, *J. Org. Chem.*, **17**, 1555 (1952).

TABLE I

X-RAY POWDER PATTERN DATA[a] FOR PHENYLSILANETRIOL (PRINCIPAL LINES)

d, kX.	I/I_1	d, kX.	I/I_1
4.79	0.11	3.47	0.14
4.67	.21	3.06	.49
4.53	.40	2.55	.28
4.43	.12	2.18	.05
4.23	.06	2.12	.05
4.13	.06	2.03	.07
3.83	1.00	1.91	.07
3.72	0.14		

[a] CuKα radiation filtered by Ni was used to obtain the powder diffraction data; d = interplanar spacing; I/I_1 = relative intensity.

analytical data for the hard brittle gel finally produced supported the formula of methylpolysiloxane. Calcd. for $(CH_3SiO_{1.5})_n$: C, 17.89; H, 4.51; Si, 41.85. Found: C, 17.6; H, 4.3; Si (Parr bomb method[19]), 40.8.

All runs made at low temperature using low concentration of the reactants (3–5%) have failed to yield monomeric methylsilanetriol owing presumably to the condensation during preparation of the initial monomeric or lower polymeric products.

The X-ray powder pattern for the gel showed a broad halo at 4.09 Å.[20] in entire agreement with that of the gel prepared by dropping pure methyltrichlorosilane in water.

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[19] L. Holzapfel and G. Gottschalk, *Z. anal. Chem.*, **142**, 115 (1954).

[20] T. Takiguchi, *J. Org. Chem.*, **23**, 1216 (1958).

KIRYU, JAPAN

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

The Electrochemical Degradation of Quaternary Ammonium Salts[1]

BY MANUEL FINKELSTEIN, RAYMOND C. PETERSEN AND SIDNEY D. ROSS

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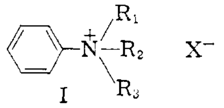
The electrolysis of aqueous solutions of a number of quaternary ammonium salts containing allyl, benzyl, fluorenyl, acenaphthenyl, benzhydryl and cinnamyl groups was found to yield, respectively, propylene, toluene, fluorene, acenaphthene, diphenylmethane and a mixture of allylbenzene and propenylbenzene. Evidence is presented which indicates that the mechanism of electrolysis involves a one-electron transfer to form an intermediate radical.

The electrochemical decomposition of quaternary ammonium salts has received little attention since the work of Emmert[2,3] on the electrolysis of various substituted anilinium salts (I). In aqueous solution at a lead cathode he found that if R_1, R_2 and R_3 were simple alkyl or hydroxyalkyl groups, benzene and the corresponding tertiary amine were obtained. When R_3 was allyl and $R_1 = R_2 = CH_3$ no benzene was formed, but dimethylaniline and propylene were identified as the products.


I

Several quaternary salts containing pyridinium[4,5] and quinolinium[4] groups also have been electrolyzed. The products formed resulted from coupling reactions in the 4-position.

On electrolysis of simple tetraalkylammonium halides in liquid ammonia at −78° Schlubach[6] obtained some evidence for the transitory existence of tetrasubstituted ammonium radicals analogous to sodium and potassium atoms. He found also that the electrolysis of triethylanilinium iodide in liquid ammonia resulted in the formation of diethylaniline at the cathode.

The cleavage of quaternary ammonium salts by sodium amalgam or 30% lead–sodium has been investigated extensively by Emde,[7] Fichter[8] and Robinson.[9] These studies have shown that the electrochemical reactions of Emmert often can be duplicated by chemical means.

Of particular interest to us was the observation of Emmert[3] that propylene was formed in the electrolysis of allyldimethylanilinium iodide. It seemed that quaternary ammonium salts containing other groups possessing structural features that could enhance radical or ion stability might lead to the formation of other hydrocarbon fragments on electrolysis. It thus appeared pertinent to investigate some of the factors influencing the electrochemical cleavage of quaternary ammonium salts to form hydrocarbons and tertiary amines.

The present work is of a descriptive and qualitative nature. The main interest was in determining the nature of the radicals which can be cleaved from a quaternary ammonium ion to form a hydrocarbon. No attempt has been made to find experimental conditions for maximizing the yield.

The work of Emmert on the electrolysis of allyldimethylanilinium iodide was extended to include the use of aluminum and platinum cathodes. Propylene was produced in good yield with either

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[1] This research was performed in part under Contract No. DA-36-039-SC-71186 between the Signal Corps Engineering Laboratories, Department of the Army, and the Sprague Electric Co.

[2] B. Emmert, *Ber.*, **42**, 1507 (1909).

[3] B. Emmert, *ibid.*, **45**, 430 (1912).

[4] B. Emmert, *ibid.*, **42**, 1997 (1909).

[5] E. Ochiai and H. Kataoka, *J. Pharm. Soc. Japan*, **62**, 241 (1942); E. Ochiai and N. Kawagoye, *ibid.*, **63**, 313 (1943).

[6] H. H. Schlubach, *Ber.*, **53B**, 1689 (1920).

[7] For example, H. Emde, *ibid.*, **42**, 2590 (1909); *Ann.*, **391**, 88 (1912).

[8] F. Fichter and H. Stenzl, *Helv. Chim. Acta*, **16**, 571 (1933).

[9] P. Groenewoud and R. Robinson, *J. Chem. Soc.*, 1092 (1934)