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Chlorides and Other Derivatives of Tetramethylsilane

BY JOHN L. SPEIER AND B. F. DAUBERT

Chloromethyltrimethylsilane has been prepared^{1,2} and some compounds derived from it have been studied.^{3,4}

In this paper the study of compounds derived from chloromethyltrimethylsilane is continued and broadened to include two new chlorides of tetramethylsilane with some of their reactions and derivatives. The new chlorides are dichloromethyltrimethylsilane and bis-(chloromethyl)-dimethylsilane.

Trimethylsilylmethylmagnesium chloride^{1,4} was found to react vigorously with phenyl isocyanate in absolute ether, but hydrolysis of the addition compound resulted in the formation of acetanilide rather than of α -trimethylsilylacetanilide, thus showing again that a carbonyl group in a position *beta* to silicon decidedly facilitates cleavage of the group.⁴ This result perhaps may explain the findings of Kipping⁵ who attempted unsuccessfully to prepare benzylethylpropylsilylacetic acid from the appropriate chlorosilane and sodioacetoacetic ester. No silicon-containing acid derivative could be isolated from the hydrolyzed products of the reaction. The reaction products of Gilman and Clark⁶ obtained by a similar procedure might be another example of this phenomenon as pointed out by Whitmore, *et al.*,⁴ who reported the hydrolytic instability of other *beta* oxygenated organosilicon compounds.

Dichloromethyltrimethylsilane in absolute alcoholic sodium ethoxide rapidly formed methylene chloride and ethoxytrimethylsilane with the liberation of a large amount of heat. Cleavage of the dichloromethyl group from silicon was also brought about by potassium acetate in glacial acetic acid at elevated temperatures. These findings extend those of Krieble and Elliott,⁷ who showed that alkaline reagents caused cleavage of chlorinated methyl groups from siloxane structures and that the ease of cleavage increased with the degree of substitution upon the methyl group.

Potassium acetate in glacial acetic acid was found to convert bis-(chloromethyl)-dimethylsilane into the corresponding diacetate ester in good yield. The diacetate yielded the dialcohol, dimethylsilylenedimethanol, [bis - (hydroxymethyl)-dimethylsilane] when subjected to methanolysis in the presence of hydrochloric acid. Chloromethyltrimethylsilane treated in essentially the same manner yielded trimethylsilylmethanol.³

(1) Whitmore and Sommer, *THIS JOURNAL*, **68**, 481 (1946).

(2) Whitmore, Sommer and Gold, *ibid.*, **69**, 1976 (1947).

(3) Speier, Daubert and McGregor, *ibid.*, **70**, 1117 (1948).

(4) Whitmore, Sommer, Gold and Van Strien, *ibid.*, **69**, 1551 (1947).

(5) Kipping, *J. Chem. Soc.*, **91**, 717 (1907).

(6) Gilman and Clark, *THIS JOURNAL*, **69**, 967 (1947).

(7) Krieble and Elliott, *ibid.*, **67**, 1810 (1945).

Experimental Part

Preparation of Dichloromethyltrimethylsilane and bis-(Chloromethyl)-dimethylsilane.—Chloro-(dichloromethyl)-dimethylsilane⁷ and (chloro)-bis-(chloromethyl)-methylsilane⁷ were each found to react smoothly with a slight excess of methylmagnesium bromide in ether to yield the expected dichloromethyltrimethylsilane (70% yield) and bis-(chloromethyl)-dimethylsilane (63% yield), respectively. These compounds were found to possess the following properties: dichloromethyltrimethylsilane, b. p. 133° at 730 mm., n_D^{25} 1.4430, d_4^{25} 1.0395. Molar Refraction: Calcd.⁸ for $\text{Cl}_2\text{CHSiMe}_3$: 39.96. Found: 40.04. *Anal.* Calcd. for $\text{C}_4\text{H}_{10}\text{SiCl}_2$: Cl, 45.2. Found: Cl, 44.9, 45.1. bis-(Chloromethyl)-dimethylsilane, b. p. 160° at 724 mm., n_D^{25} 1.4579, d_4^{25} 1.075. Molar refraction: Calcd.⁸ for $(\text{ClCH}_2)_2\text{SiMe}_2$: 39.96. Found: 39.87. *Anal.* Calcd. for $\text{C}_4\text{H}_{10}\text{SiCl}_2$: Cl, 45.2. Found: Cl, 45.0, 44.8.

The synthesis of chloromethyltrimethylsilane by the above method has been described.²

Formation of Acetanilide from Trimethylsilylmethylmagnesium Chloride.—To an ethereal solution of about 0.014 mole of trimethylsilylmethylmagnesium chloride^{1,4} was added an excess of phenyl isocyanate. A vigorous reaction occurred and the mixture set to a gelatinous mass. After twenty-four hours the mass was stirred with water and filtered with suction. The solids collected were stirred with 95% ethanol and filtered. To the ethanolic solution thus obtained, dilute aqueous sodium carbonate was added and the mixture was heated to boiling and quickly filtered free of the precipitate that formed. The filtrate on becoming cool yielded carbanilide, m. p. 225–235°. After the removal of this compound, most of the alcohol was driven from the solution by evaporation. When the essentially aqueous solution thus obtained was cooled, acetanilide precipitated, m. p. 110–111°. Further evaporation of the mother liquor yielded a second crop of acetanilide, m. p. 111–112°. These crops were combined and recrystallized from water to yield a product, m. p. 111–112°, (approx. 80%) which showed no change of melting point when mixed with an authentic sample of acetanilide, m. p. 112°, and which contained only a trace of silicon.

Cleavage Reactions of Dichloromethyltrimethylsilane.—Dichloromethyltrimethylsilane (154 g., 0.98 mole) was added to absolute ethanol (350 ml.) at room temperature into which sodium (25 g.) had been dissolved. A vigorous boiling ensued immediately. Before the apparatus could be assembled for distillation through a one-foot Vigreux column, a certain amount of material was lost. Distillate boiling over a range from 40 to 78° was collected. This distillate was washed with dilute hydrochloric acid to remove the ethanol and to hydrolyze any ethoxytrimethylsilane that might be present. The washed product was distilled and found to consist only of methylene chloride (60 g., 71%) b. p. 40–41°, n_D^{25} 1.4217, d_4^{25} 1.310, and of hexamethylsiloxane (57 g., 73%), b. p. 99°, n_D^{25} 1.3749.

Dichloromethyltrimethylsilane (14 g.) was sealed into a glass tube with anhydrous potassium acetate (22 g.) and glacial acetic acid (11 ml.) and heated at 200° for three hours. A large amount of potassium chloride formed. The tube was opened and its contents washed with water. A dark liquid was thus obtained which smelled strongly of formaldehyde. A portion of this liquid was treated with 2,4-dinitrophenylhydrazine in acidified ethanol solution and yielded the 2,4-dinitrophenylhydrazone of formaldehyde, m. p. 159°, which

(8) Warrick, *ibid.*, **68**, 2455 (1946).

showed no depression of melting point when mixed with an authentic sample of the derivative of formaldehyde, m. p. 165°. The derivative contained only a trace of silicon. At 150° a similar mixture after nineteen hours showed no signs of having reacted in any way.

Preparation of bis-(Acetoxymethyl)-dimethylsilane (Dimethylsilylenedimethanol Diacetate).—bis-(Chloromethyl)-dimethylsilane (292 g., 1.85 moles), potassium acetate (412 g., 4.2 moles) and glacial acetic acid (300 ml.) were heated together and shaken in a stainless steel autoclave at 118–130° for four hours and at 148–160° for sixteen hours. The contents of the autoclave were then washed once with water to remove the salts and most of the acid present. The water insoluble liquid was distilled. The only compound found, other than acetic acid, was bis-(acetoxymethyl)-dimethylsilane (339 g., 90%), b. p. 124° at 27 mm., 223° at 739 mm., n_D^{25} 1.4309–1.4310, d_4^{25} 1.0135. Molar refraction: Calcd.⁸ for (AcOCH₂)₂-SiMe₂: 52.34. Found: 52.17. Anal. Sap. equiv. Calcd. for (AcOCH₂)₂SiMe₂: 102.2. Found: 102.6, 102.1.

bis-(Acetoxymethyl)-dimethylsilane (110 g.) was dissolved in a ten-fold excess of dry methanol and acidified with three drops of concentrated hydrochloric acid. Periodically during three weeks methyl acetate was removed by distillation. Each time methanol was added to restore the solution to its original volume and the solution was permitted to stand at room temperature for several days before more methyl acetate was removed. The solution was distilled, after no further amount of methyl acetate appeared to form. bis-(Hydroxymethyl)-dimeth-

ylsilane (dimethylsilylenedimethanol) was obtained as a colorless, odorless, viscous liquid, completely soluble in water; b. p. 130° at 27 mm., n_D^{25} 1.4611, d_4^{11} 0.993. Molar refraction: Calcd.⁸ for (HOCH₂)₂SiMe₂: 33.38. Found: 33.20. Saponification number, 12.7. Anal. Calcd. for C₄H₁₂O₂Si: Si, 23.3. Found: Si, 23.2, 23.3.

Summary

Some of the reactions of the chlorides of tetramethylsilane have been studied. These compounds showed a tendency, under certain conditions, toward cleavage of the substituted methyl group from the silicon atom. The dichloromethyl group was found to be more easily cleaved than the chloromethyl group. Hydrolysis of the addition product of trimethylsilylmethylmagnesium chloride and phenyl isocyanate was shown to result in the formation of acetanilide, thus revealing the ease of cleavage of *beta* carbonyl silicon compounds.

The new compounds, bis-(chloromethyl)-dimethylsilane, dimethylsilylenedimethanol diacetate, dimethylsilylenedimethanol, and dichloromethyltrimethylsilane were prepared and characterized during the investigation.

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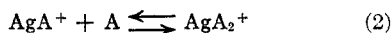
The Basic Strengths of Amines as Measured by the Stabilities of Their Complexes with Silver Ions

BY RICHARD J. BRUEHLMAN¹ AND FRANK H. VERHOEK

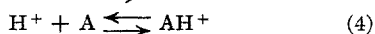
The relationship of the basic strengths of amines as determined by the stability of their ammonium ions to their strengths as measured by the stability of their complexes with silver ion has been discussed repeatedly. It has been stated that a parallelism between the two measures exists² and that a parallelism does not exist.^{3,4} Except for the last paper cited,⁴ the conclusions have commonly been based on a consideration of the instability or association constants for the over-all reaction



where A represents the amine. It was pointed out,⁵ however, that each such constant contains an equilibrium constant for the reaction



in which the ion reacting with the amine is different for each amine considered, and that a more just comparison is that between the two reactions



(1) Present address, Argonne National Laboratory, Chicago, Illinois.

(2) Larsson, *Z. physik. Chem.*, **A169**, 215 (1934).

(3) Britton and Williams, *J. Chem. Soc.*, 796 (1935).

(4) Vosburgh and Cogswell, *THIS JOURNAL*, **65**, 2412 (1943).

(5) Carlson, McReynolds and Verhoek, *ibid.*, **67**, 1334 (1945).

Accordingly the equilibrium constants of reactions (3) have been measured for several amines and compared with those for reactions (4) measured in similar systems. The equilibrium constants of reactions (2) were also measured.

The equilibrium constants were determined by means of *pH* measurements on solutions of amine, silver ion, acid and neutral salt according to the method of Bjerrum,⁶ on selected groups of primary, secondary, and tertiary amines of varied basic strength. The selection was severely limited by the requirements that the amine be reasonably soluble in water, that it form complexes in such a *pH* range that silver oxide would not precipitate out, that it have a basic strength different from other members of the group, and that the complex formed be sufficiently soluble that a solid phase did not form. This paper reports equilibrium constants for the formation of amines of silver ion with five primary amines, three secondary amines, and four pyridines. In order to estimate the validity of the comparison of equilibrium constants for equations (3) and (4) at a single temperature, temperature coefficients over a ten-degree temperature interval were determined in most cases.

In addition, equilibrium constants were deter-

(6) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1941.