

Chemistry of Several Tetrasilylmethanes

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The attempted conversion of tetrakis(dimethylsilyl)methane to the corresponding tetraalkoxy derivative under alkaline alcoholysis conditions resulted in extensive cleavage of the central silicon-carbon bonds. Alcoholysis of tetrakis(dimethylsilyl)methane under acidic conditions employing chloroplatinic acid catalysis gave moderate to good yields of the tetraalkoxy derivatives. Three new compounds are reported: tetrakis(dimethylmethoxysilyl)methane, tris(dimethylmethoxysilyl)methane, and tetrakis(dimethylethoxysilyl)methane.

Compounds having two silicon atoms bound to the same carbon atom have been known for some time² and the synthesis of organosilicon compounds in which one carbon atom is bonded to three or four silicon atoms has been described more recently.³ From the products of the reactions of carbon tetrachloride or chloroform with silicon metal catalyzed by copper, Müller and Seitz have isolated small amounts of tetrakis(trichlorosilyl)methane and tris(trichlorosilyl)methane. The use of these compounds as intermediates to prepare reasonable yields of derivatives retaining one functional group on each silicon atom is not an attractive possibility. Using an *in situ* technique developed in this laboratory,⁴ however, a variety of tetrasilylmethanes and trisilylmethanes can now be prepared by Grignard synthesis from carbon tetra- or trihalides and appropriate organochlorosilanes.

Such compounds provide a means for studying the effect of tri- and tetrasilicon substitution on the chemical properties of the silicon to carbon bond. Studies of the reactions of some tetrasilylmethanes and trisilylmethanes under alkaline and mildly acidic conditions are described in this paper.

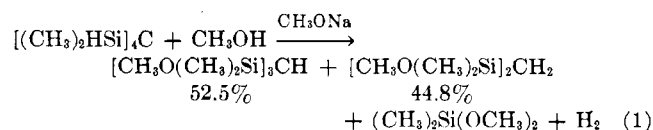
The stability of the silicon-carbon bond in alkylsilanes and substituted alkylsilanes in which the carbon atom is connected to one silicon atom has been studied in detail. The cleavage of unsubstituted tetraalkylsilanes by nucleophilic agents has not been reported. However, silicon-carbon bonds are cleaved in compounds in which the susceptibility of the silicon atom to nucleophilic attack has been increased by replacement of an alkyl group by a more highly electronegative configuration. Hexamethyldisiloxane⁵ in a sealed tube at temperatures over 100° is cleaved by aqueous sodium or potassium hydroxide to methane and hydroxypentamethyldisiloxane. Chlorination of an alkyl group also increases the tendency toward cleavage. It has been reported⁶ that no cleavage is detected in the reaction of chloromethyltrimethylsilane with sodium methoxide in methanol, but reaction with sodium ethoxide in ethanol resulted in a moderate amount of cleavage, presumably due to a higher reaction temperature, changed structure, or a combination of these.

The silicon-carbon bond is also broken by electrophilic attack upon the carbon. Methane is formed when the methyl-silicon bond of β -trimethylsilylpropionic acid⁷ is attacked by concentrated sulfuric acid.

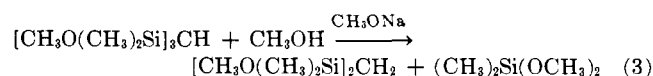
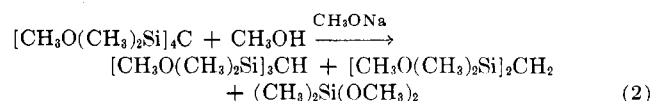
Methane is also the product of the cleavage of tetramethylsilane⁸ by a hydrogen halide in the presence of aluminum chloride.

Discussion and Results

Both tetrakis(trimethylsilyl)methane and (tristri-methylsilyl)methane were found to be quite resistant to cleavage by nucleophilic reagents. As can be seen from the results summarized in Table I, tetrakis(trimethylsilyl)methane is unaffected even after prolonged reflux in methyl alcohol plus sodium methoxide or 1-propanol containing sodium *n*-propoxide; tris(trimethylsilyl)methane remains unchanged during prolonged reflux in methyl alcohol with sodium methoxide. The attempted conversion of tetrakis(dimethylsilyl)methane through reaction with methanol containing sodium methoxide to the corresponding tetraalkoxy derivative resulted in extensive cleavage of central silicon-carbon bonds.



Replacement of hydrogen on silicon by methoxy on silicon in reaction 1 is essentially quantitative. Under reaction conditions identical to those prevailing in reaction 1, it has been shown that tetrakis(dimethylmethoxysilyl)methane (see equation 2 and Table I) is cleaved to tris(dimethylmethoxysilyl)methane and bis(dimethylmethoxysilyl)methane and that tris(dimethylmethoxysilyl)methane (see equation 3 and Table I) is cleaved to bis(dimethylmethoxysilyl)methane.



In view of these facts the most reasonable reaction course for 1 appears to be alkoxylation followed by cleavage of central silicon-carbon bonds in one or more of the possible alkoxyated intermediates. Base-catalyzed cleavage reactions, such as those of β -halogenated organosilicon compounds, are usually characterized by β elimination. That such elimination did not occur in the cleavage of $[\text{CH}_3\text{O}(\text{CH}_3)_2\text{Si}]_4\text{C}$ to produce $[\text{CH}_3\text{O}(\text{CH}_3)_2\text{Si}]_2\text{C}=\text{Si}(\text{CH}_3)_2$ is not surprising not only because of the stability of the silicon-oxygen

(1) Multiple Fellowship on Silicones sustained by Dow Corning Corporation and Corning Glass Works.

(2) L. Sommer, *et al.*, *J. Am. Chem. Soc.*, **69**, 980 (1947).

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(6) J. Speier, *ibid.*, **70**, 4142 (1948).

(7) L. H. Sommer, *ibid.*, **75**, 3765 (1953).

(8) P. D. George, U. S. Patent 2,802,852 (1957).

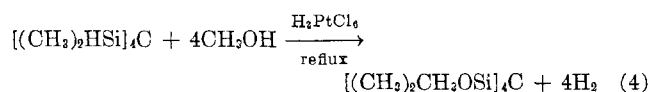
TABLE I
 ALCOHOLYSIS AND CLEAVAGE OF TETRASILYLMETHANES

Substituted methane	Alcohol	Catalyst	Reflux time, hr.	Products	
				Structure	Yield, ^a %
[(CH ₃) ₃ Si] ₄ C	CH ₃ OH	CH ₃ ONa	24	[(CH ₃) ₃ Si] ₄ C recovered unchanged	
	CH ₃ (CH ₂) ₂ OH	CH ₃ (CH ₂) ₂ ONa			
[(CH ₃) ₂ Si] ₃ CH	CH ₃ OH	CH ₃ ONa	8	[(CH ₃) ₂ Si] ₃ CH recovered unchanged	
	[H(CH ₃) ₂ Si] ₄ C	CH ₃ OH	8	[CH ₃ O(CH ₂) ₂ Si] ₃ CH ^b	52.5
				[CH ₃ O(CH ₂) ₂ Si] ₂ CH ₂	44.8
				(CH ₃) ₂ Si(OCH ₃) ₂	...
[CH ₃ O(CH ₂) ₂ Si] ₄ C	CH ₃ OH	CH ₃ ONa	3	[CH ₃ O(CH ₂) ₂ Si] ₃ CH	67.1
				[CH ₃ O(CH ₂) ₂ Si] ₂ CH ₂	16.7
[CH ₃ O(CH ₂) ₂ Si] ₃ CH	CH ₃ OH	CH ₃ ONa	7	[CH ₃ O(CH ₂) ₂ Si] ₂ CH ₂	45.3
				[CH ₃ O(CH ₂) ₂ Si] ₂ CH ₂	43.1
[H(CH ₃) ₂ Si] ₄ C	CH ₃ OH	H ₂ PtCl ₆	6	[CH ₃ O(CH ₂) ₂ Si] ₃ CSi(CH ₃) ₂ H ^c	99.0
[H(CH ₃) ₂ Si] ₄ C	CH ₃ OH	H ₂ PtCl ₆	19	[CH ₃ O(CH ₂) ₂ Si] ₄ C ^b	68.3
[H(CH ₃) ₂ Si] ₄ C	CH ₃ CH ₂ OH	H ₂ PtCl ₆	8	[CH ₃ CH ₂ O(CH ₂) ₂ Si] ₄ C ^b	44

^a Based on starting substituted methane. ^b Compounds here reported for first time. ^c Empirical formula indicated by analysis of reaction products; probably a mixture of two or more compounds.

bond, but also because no compound containing a silicon to carbon double bond has ever been isolated.

The successful conversion of tetrakis(dimethylsilyl)methane to either tetrakis(dimethylmethoxysilyl)methane or tetrakis(dimethylethoxysilyl)methane was achieved by direct reaction with methanol or ethanol catalyzed by chloroplatinic acid.⁹



While isolation of all products leading to a complete material balance for the chloroplatinic acid-catalyzed reactions has not been attempted, the yields of tetrakisalkoxy compounds are high enough to indicate that under these conditions the silicon-carbon bond in such compounds is fairly resistant to cleavage.

Experimental

Materials.—Tetrakis(trimethylsilyl)methane and tetrakis(dimethylsilyl)methane were prepared from CBr₄ by methods previously described.⁴ Reagent grade absolute alcohols were used. The chloroplatinic acid catalyst solution in *n*-propyl alcohol was 0.1 *M*.

Analysis.—All structures were confirmed by H¹ n.m.r. analysis. All carbon and hydrogen analyses and the silicon analysis of tetrakis(dimethylmethoxysilyl)methane were performed by Galbraith Laboratories, Knoxville, Tennessee. Melting points are uncorrected. All yields are based on the starting substituted silylmethanes.

Reactions Employing Base Catalysis. A. Tetrakis(dimethylsilyl)methane.—In a flask equipped with a condenser and gas collection apparatus, 15 g. (0.061 mole) of tetrakis(dimethylsilyl)methane and 68 ml. of absolute methanol, to which 0.2 g. of sodium had been added, were refluxed for 8 hr. During this time a quantitative volume of gas was evolved. The reaction mixture was neutralized with glacial acetic acid and distilled. The precut, largely methanol-(CH₃)₂Si(OCH₃)₂ azeotrope and methanol, was washed with an excess of water which contained a few drops of hydrochloric acid. Upon standing, an organic phase, 3.9 g., separated, *n*_D²⁵ 1.3943, *d*₄²⁵ 0.952; for octamethylcyclotetrasiloxane, lit.¹⁰ *n*_D²⁵ 1.3935, *d*₄²⁵ 0.9497. The remainder of the reaction mixture was fractionated at reduced pressures yielding two products. Bis(dimethylmethoxysilyl)methane, 5.2 g. (44.8%), had b.p. 81° (40 mm.), *d*₄²⁵ 0.872, *n*_D²⁵ 1.4125, *R*_D

found 0.2855, *R*_D calcd. 0.2875; lit.¹¹ b.p. 61–63° (20 mm.), *d* 0.869, *n*_D²⁵ 1.4111.

Anal. Calcd. for C₇H₂₀O₂Si₂: Si, 29.20. Found: Si, 29.09. Tris(dimethylmethoxysilyl)methane, 8.85 g. (52.5%), had b.p. 130° (40 mm.), *d*₄²⁵ 0.932, *n*_D²⁵ 1.4385, *R*_D found 0.2820, *R*_D calcd. 0.2837.

Anal. Calcd. for C₁₀H₂₈Si₃O₃: C, 42.79; H, 10.05; Si, 30.03. Found: C, 43.07; H, 10.21; Si, 30.56.

B. Tetrakis(dimethylmethoxysilyl)methane.—In 30 ml. of absolute methanol to which 0.1 g. of sodium had been added, 10 g. (0.027 mole) of tetrakis(dimethylmethoxysilyl)methane was refluxed for 3 hr. After neutralizing the mixture with glacial acetic acid the methanol-(CH₃)₂Si(OCH₃)₂ azeotrope and methanol were distilled at atmospheric pressure. This distillate was washed with acidified water and a second phase developed which was identified as octamethylcyclotetrasiloxane as in paragraph A. Two products were separated from the remaining material by fractional distillation: 5.2 g. (16.7%) of bis(dimethylmethoxysilyl)methane and 7.6 g. (67.1%) of tris(dimethylmethoxysilyl)methane, both characterized as outlined in paragraph A.

C. Tris(dimethylmethoxysilyl)methane.—As described in paragraph B, 7.4 g. (0.026 mole) of tris(dimethylmethoxysilyl)methane and 30 ml. of absolute methanol which contained 0.1 g. of sodium were refluxed for 7 hr., neutralized with glacial acetic acid, and distilled. A yield of 2.18 g. (43.1%) of bis(dimethylmethoxysilyl)methane was obtained; 3.35 g. (45.3%) of tris(dimethylmethoxysilyl)methane was recovered unchanged.

D. Tetrakis(trimethylsilyl)methane.—A solution of 18.4 g. (0.061 mole) of tetrakis(trimethylsilyl)methane in 68 ml. of methanol to which had been added 0.2 g. of sodium was refluxed 16 hr. The mixture was cooled in an ice bath, then filtered. The tetrakis(trimethylsilyl)methane was recovered unchanged. The same result was obtained when this procedure was repeated substituting *n*-propyl alcohol, a better solvent for tetrakis(trimethylsilyl)methane than methanol.

E. Tris(trimethylsilyl)methane.—As outlined in D, 10.1 g. of tris(trimethylsilyl)methane, 50 ml. of absolute methanol, and 0.2 g. of sodium were refluxed for 8 hr. The reaction mixture was diluted with ether and washed with water. The ether was evaporated leaving the unchanged tris(trimethylsilyl)methane.

Reactions with Chloroplatinic Acid Catalysis. A. Methanolysis of Tetrakis(dimethylsilyl)methane.—A mixture of 23.6 g. (0.095 mole) of tetrakis(dimethylsilyl)methane, 5 drops of chloroplatinic acid catalyst solution, and 100 ml. of absolute methanol was refluxed for 6 hr. The mixture was cooled in an ice-water bath and filtered, 17.6 g. of precipitate. Five drops more of chloroplatinic acid solution was added to the filtrate and after 2-hr. reflux, part of the methanol was distilled from the mixture. The additional precipitate, 7 g., which had appeared was filtered and the filtrate distilled. After the methanol had been removed, no other distillable materials were obtained. The solid residue, 7.4 g., was combined with the earlier precipitates

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(11) M. Kumada, A. Habuoki, *J. Inst. Polytech., Osaka City Univ.*, Sec. No. C, **3**, 65 (1952).

(32.2 g. crude products) and recrystallized from absolute methanol, melting point, sublimes.

Anal. Calcd. for $C_{12}H_{14}Si_4O_3$: Si, 33.18; mol. wt., 338.8. Found: Si, 33.38; mol. wt. (cryoscopic), 334.

The analytical results suggest that this material is tris(dimethylmethoxysilyl)dimethylsilyl methane. However, this structure cannot be assigned to this product until careful fractional crystallization has been carried out, since it conceivably could have been a mixture of tetrakis(dimethylmethoxysilyl)methane and dimethylsilylmethanes of lower degrees of methoxylation.

This preparation was then repeated using a flask equipped with a reflux condenser and gas collection apparatus, 20 g. of tetrakis(dimethylsilyl)methane, 100 ml. of absolute methanol, and 10 drops of chloroplatinic acid solution. During a 19-hr. reflux period 25 drops of additional catalyst solution was added and the theoretical volume of hydrogen was collected. The reaction mixture was then treated as before; the crude product was recrystallized from absolute methanol; 20.3 g. (68.3%) of tetrakis(dimethylmethoxysilyl)methane was obtained; melting point, sublimes.

Anal. Calcd. for $C_{13}H_{36}Si_4O_4$: C, 42.33; H, 9.84; Si, 30.47; mol. wt., 368.8. Found: C, 42.53; H, 9.86; Si, 30.33; mol. wt. (cryoscopic), 351.

B. Ethanolysis of Tetrakis(dimethylsilyl)methane. In the usual way, 13.3 g. (0.054 mole) of tetrakis(dimethylsilyl)methane, 56 ml. of absolute ethanol, and 3 drops of chloroplatinic acid solution were refluxed for 8 hr. During this time an additional 6 drops of the catalyst solution was added. The mixture was cooled in a Dry Ice-acetone bath and filtered; the precipitate recrystallized from absolute ethanol; 10 g. (44%) of tetrakis(dimethylethoxysilyl)methane, m.p. 114–115°, was obtained.

Anal. Calcd. for $C_{17}H_{44}Si_4O_4$: C, 48.06; H, 10.44; Si, 26.45. Found: C, 48.11; H, 10.37; Si, 26.37.

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Substituted Quinodimethans. VII. Substituent and Structural Effects in Cyano-Substituted Quinodimethans

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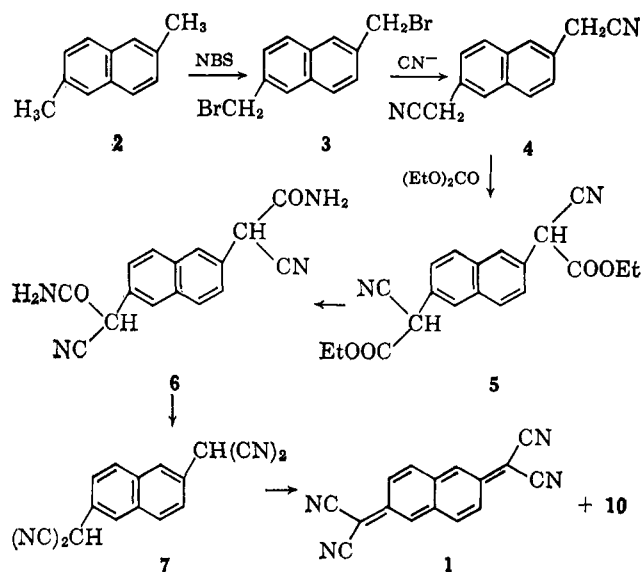
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The stable quinodimethans 11,11,12,12-tetracyano-2,6-naphthoquinodimethan, methyl-7,7,8-tetracyano-*p*-quinodimethan, *n*-propyl-7,7,8-tetracyano-*p*-quinodimethan, and 2,5-dimethyl-7,7,8-tetracyano-*p*-quinodimethan undergo one-electron reduction to give stable anion-radicals. The properties of these quinodimethans and anion-radicals are compared with those of other stable quinodimethans.

The recent synthesis in this laboratory of 7,7,8,8-tetracyanoquinodimethan¹ (TCNQ) led to the discovery that TCNQ forms a variety of stable, crystalline, paramagnetic anion-radical salts, some of which exhibit unusually low electrical resistivities. A detailed description of these stable anion-radical salts is given in paper II of this series.² Because of the unusual stability and electrical properties of TCNQ anion-radical salts, it seemed desirable to investigate the steric and electromeric effects of ring substituents on TCNQ and its anion-radical and to search for new quinodimethan π -acid systems. The present paper reports the results of these studies.

A. 11,11,12,12-Tetracyanonaphtho-2,6-quinodimethan (TNAP) Synthesis.—To study the effect of a lengthened, conjugated system on the properties of negatively substituted quinodimethans and their anion-radicals, the synthesis of 11,11,12,12-tetracyano-2,6-naphthoquinodimethan (TNAP, 1) was undertaken. 2,6-Dimethylnaphthalene (2) was chosen as the starting material because of its ready availability. Bromination of 2 with two equivalents of *N*-bromosuccinimide (NBS) gave 2,6-bis(bromomethyl)naphthalene (3). The structure of 3 was confirmed by nuclear magnetic resonance which showed the presence of two methylene groups and the absence of a methyl group, which would result from the introduction of the two bromine atoms on the same carbon atom. Treatment of the dibromide 3 with cyanide ion gave 2,6-naphthalenediacetonitrile (4) which was treated with ethyl

carbonate and base to give diethyl 2,6-naphthalenedicyanoacetate (5). Treatment of the cyano ester 5 with aqueous ammonia gave 2,6-naphthalenedicyanoacetamide (6) which was dehydrated with phosphorus oxychloride to give 2,6-naphthalenedimalononitrile (7). The final step in the synthesis was the oxidation of the dimalononitrile 7 with *N*-bromo-, *N*-chloro-, or *N*-iodosuccinimide to give TNAP (1) along with some highly insoluble substance (10).



Properties of TNAP.—TNAP was isolated as stable, high-melting, purple crystals having a metallic sheen. Solutions of TNAP in organic solvents are red, and the ultraviolet spectrum of an acetonitrile solution of TNAP

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