distilled at 99.6° (750 mm.); n^{20}_D 1.3910. It was assumed to be an azeotrope between M_2 (b. p. 100.4°) and toluene (b. p. 110.8°). After the excess toluene was removed, the next fraction (10 g., 0.036 mole) was distilled at about 250°, leaving as a residue a low viscosity oil, which was assumed to consist of linear compounds of the type $M_2D'_x$. The 250° fraction was redistilled; b. p. 95° (5.0 mm.), n^{20}_D 1.4468, d^{20}_4 0.9080, R_D 0.2941, R_D (calcd.) 0.2929.

Anal. Calcd. for $C_{13}H_{26}Si_3O_2$ (M_2D'): C, 52.30; H, 8.78. Found: C, 52.8, 52.6; H, 8.9, 8.7.

Acknowledgment.—The author is indebted to Miss Mary L. Caldwell, who carried out the microanalyses for carbon and hydrogen.

Summary

1. Two stereoisomeric cyclic trimers and a cyclic tetramer have been obtained by the hydrolysis of methylphenyldichlorosilane.

2. Linear methylphenylpolysiloxanes have been prepared from the cyclic ones by means of hexamethyldisiloxane or tetramethyl-1,3-diphenyldisiloxane and an alkaline catalyst.

3. Evidence for an equilibrium between siloxanes, silanols and silyl ethers has been found.

SCHENECTADY, NEW YORK RECEIVED OCTOBER 3, 1947

[CONTRIBUTION FROM MELLON INSTITUTE AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Preparation and Properties of Trimethylsilylmethanol

BY JOHN L. SPEIER, B. F. DAUBERT AND R. R. MCGREGOR

Organo-silicon compounds containing organic functional groups such as the carbinol group are not readily prepared by the usual methods of synthesis of organo-silicon compounds. The literature records the preparation of only two compounds in which this group is contained. The first is triethylsilylethanol of uncertain structure[1] obtained by the chlorination of tetraethylsilane, conversion of the chloride to the acetate and hydrolysis of the acetate. The second is 1-trimethylsilyl-2-propanol prepared from trimethylsilylmethylmagnesium chloride and acetaldehyde.[2]

Since it was desired to investigate the properties of an α-hydroxyalkylsilane, trimethylsilylmethanol was synthesized in good yield through the sequence of reactions:

$$\mathrm{Me_3SiCH_2Cl}^{3} \xrightarrow[190\,^{\circ}\mathrm{C.}]{\substack{\mathrm{KOAc}\\ \mathrm{HOAc}}}$$

$$\mathrm{Me_3SiCH_2OAc} \xrightarrow[\mathrm{H_2SO_4}]{\mathrm{MeOH}} \mathrm{Me_3SiCH_2OH}$$

The trimethylsilylmethanol so prepared was found to be approximately six times as reactive in forming a phenylurethan as its carbon analog, neopentyl alcohol, and approximately three times as reactive as methanol in the same reaction.

Experimental

Preparation of Trimethylsilylmethyl Acetate.—Chloromethyltrimethylsilane[4] (3.1 moles), potassium acetate (3.8 moles), and glacial acetic acid (420 ml.) were charged into a stainless steel high-pressure reactor and shaken at 190–192° for eighteen hours. The contents of the reactor were then washed thoroughly with distilled water. The water-insoluble liquid, after drying over anhydrous sodium carbonate, was slightly amber in color and weighed 416.5 g. (92%). The mixture was distilled through a three-foot Stedman column and was found to boil entirely between the temperatures of 136.2–136.8° at 748 mm., all but 5 ml. distilling at the higher temperature. The ester has the following constants: b. p. 136.8° at 748 mm., $[n]^{25}_D$ 1.4060, $[d]^{25}_4$ 0.8667. Molar refraction: Calcd.[5] for Me_3SiCH_2OAc, 41.31. Found: 41.37. Sapn. equiv.: Calcd., 146.2. Found: 146.5, 146.6. *Anal.* Calcd. for $C_6H_{14}O_2Si$: Si, 19.2. Found: Si, 19.3, 19.1.

Preparation of Trimethylsilylmethanol.—Trimethylsilylmethyl acetate (420 ml., 2.5 moles) was dissolved in absolute methanol (9 moles) and acidified with 10 drops of concentrated sulfuric acid. After standing at room temperature for two days, 165 ml. of the azeotropic mixture of methanol and methyl acetate was removed by distillation. The charge was then diluted with methanol (4 moles) and permitted to stand four days at room temperature before fractionation to yield 268 ml. (80%) of constant boiling trimethylsilylmethanol, b. p. 121.6° at 729 mm. The alcohol redistilled from lime had the following properties: b. p. 121.7–121.9° at 751 mm., $[n]^{25}_D$ 1.4169, $[d]^{25}_4$ 0.8261. Molar refraction: Calcd.[5] for Me_3SiCH_2OH, 31.83. Found, 31.71. The alcohol has a strong odor resembling that of menthol.

Preparation of Trimethylsilylmethyl 3,5-Dinitrobenzoate.—Trimethylsilylmethanol (1.1 g.) was added dropwise to 3,5-dinitrobenzoyl chloride (2.5 g.) and heated to 90° until no more hydrogen chloride was evolved. The mixture was cooled, and ground into a fine powder in the presence of two portions of warm 5–6% sodium carbonate solution. It was heated with a third portion of sodium carbonate solution until it fused. On stirring vigorously as it cooled, solidification occurred. The solids were washed with water in a suction filter, dissolved in boiling 95% ethanol, and filtered while hot. On cooling to room temperature, 2.3 g. of crystalline product was obtained which melted at 69.5–70°. The mother liquor was heated to boiling and diluted with water to the point of incipient turbidity. Again on cooling, 0.9 g. of crystalline product formed, m. p. 68.5–70°. The two crops of crystals were combined and recrystallized once from 95% ethanol. The recrystallized product melted at 70–70.5°. Further recrystallizations did not change this melting point.

Anal. Calcd. for $C_{11}H_{14}O_6N_2Si$: C, 44.26; H, 4.73; N, 9.33; Si, 9.41. Found: C, 44.04; H, 4.41; N, 9.33; Si, 9.47, 9.45.

Preparation of (Trimethylsilylmethoxy)-trimethylsilane.—Trimethylsilylmethanol (19.7 g.) dissolved in dry

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(1) Friedel and Crafts, *Compt. rend.*, **61**, 792 (1865).

(2) Whitmore, Sommer, Gold and Van Strien, THIS JOURNAL, **69**, 1551 (1947).

(3) Whitmore and Sommer, *ibid.*, **68**, 481 (1946), first prepared chloromethyltrimethylsilane and showed that it reacted with potassium acetate in glacial acetic acid.

(4) Chloromethyltrimethylsilane was prepared for use in this work by the method of Whitmore, Sommer and Gold, *ibid.*, **69**, 1976 (1947).

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

chloroform–quinoline solution was treated with an equivalent amount of trimethylchlorosilane. The mixture, which was kept cool during the addition of the trimethylchlorosilane, separated into two layers. After the addition was complete, the mixture was shaken vigorously for fifteen minutes and then diluted with absolute ether (250 ml.). The quinoline hydrochloride was removed by filtration. The filtrate was distilled to yield a fraction (36 ml., 84%) boiling at 129.8° at 738 mm. which was found to be (trimethylsilylmethoxy)-trimethylsilane of the following properties: b. p. 129.8° at 738 mm., $[n]^{25}\text{D}$ 1.3971, $[d]^{25}_4$ 0.7781. Molar refraction: Calcd.[5] for $Me_3SiCH_2OSiMe_3$, 54.00. Found, 53.91. *Anal.* Calcd. for $C_7H_{20}OSi_2$: Si, 31.81; C, 47.71; H, 11.42. Found: Si, 31.4, 31.4; C, 47.86; H, 11.61.

Reactivity of Trimethylsilylmethanol with Phenyl Isocyanate Relative to Other Alcohols.—The method of Davis and Farnum[6] for comparing the relative reaction rate constants of alcohols by means of the competitive reaction of one equivalent of each of two alcohols for one equivalent of phenyl isocyanate in benzene solution was adapted for use in studying the reactivity of trimethylsilylmethanol. These authors showed that the reaction of alcohols with phenyl isocyanate to form the phenylurethans is rapid, essentially irreversible, complete, and free from side reactions. Also, the products can be isolated quantitatively free from solvent and excess alcohol.

The methyl, ethyl, neopentyl and trimethylsilylmethyl alcohols used in this study were all carefully dried and purified. Commercial absolute methanol was refluxed over magnesium shavings and distilled. Commercial absolute ethanol was refluxed two days over amalgamated aluminum foil and distilled. The neopentyl alcohol[7] was prepared from *t*-butylmagnesium chloride and formaldehyde. Only the portion of the product distilled from lime boiling at 111.1° at 737 mm., m. p. 50–53° was used. The phenyl isocyanate was freshly distilled *in vacuo* immediately before use to ensure its being free of carbanilide.

An equivalent of phenyl isocyanate (*ca.* 1 g.) reacted with two equivalents of trimethylsilylmethanol in dry benzene (10 ml.) in a vial closed with a well-fitted ground-glass stopper. The vial was permitted to stand twenty-four hours at approximately 25°. The benzene and excess alcohol were then evaporated in a stream of filtered air with final drying under high vacuum for twenty-four hours. The product so obtained had a melting point of 80–80.5°. Repeated recrystallization from several solvents caused no change in this melting point. *Anal.* Calcd. for $C_{11}H_{17}O_2NSi$: Si, 12.57; C, 59.23; H, 7.68; N, 6.28. Found: Si, 12.59, 12.61; C, 58.89, 59.10; H, 7.37, 7.46; N, 6.15, 6.07.

The same technique was applied to a sample of neopentyl alcohol to produce a derivative melting sharply at 113°. Recrystallization from several solvents did not change this melting point. The phenylurethan of neopentyl alcohol is reported as melting at 114°.[8,9]

Trimethylsilylmethanol was made to compete with the alcohols mentioned essentially by the method of Davis and Farnum.[6] A dry benzene solution containing exactly equimolar amounts of trimethylsilylmethanol and neopentyl alcohol was prepared. From a buret there was added an amount of this solution calculated to contain exactly enough of each alcohol to react with 1.096 g. of phenyl isocyanate delivered from a carefully calibrated pipet into a glass-stoppered vial. The solution was quickly and thoroughly mixed and permitted to stand at least twenty-four hours at approximately 25°. In the same fashion solutions of trimethylsilylmethanol and methanol, trimethylsilylmethanol, and ethanol were prepared and reacted. The amounts of silicon in the nonvolatile products of the reaction were determined and the mole fraction of the silicon derivative present was calculated (Table I).

TABLE I

Competing alcohol	Trial	% Si in products of reaction				K_{Si}/K_{ROH}
Neopentyl	1	10.13	10.04	10.09	10.04	6.56
	2	10.12	10.10			
	3	10.07				
Methyl	1	9.53	9.56			2.92
	2	9.53	9.54			
	3	9.55				
	4	9.53				
Ethyl	1	9.68				3.57
	2	9.62				

The relative reaction rate constants were calculated according to the formula given by Davis and Farnum,[6] where K_{Si}/K_{ROH} is the ratio of the reaction rate constants of the silicon-containing alcohol and the other alcohol concerned.

Method of Analysis for Organo-silicon Compounds.—All determinations of silicon content in the compounds in this communication were carried out by the following procedure: A "Vycor" brand Kjeldahl flask (30-ml. capacity) was brought to constant weight at about 800° in a furnace. The flask was cooled in a desiccator, stoppered tightly to keep moisture from the interior, and permitted to stand in the balance case for from twenty to thirty minutes so that the exterior surfaces reached equilibrium with atmospheric moisture. The weight of the flask and stopper was determined accurately. A sample yielding between 500 and 1500 mg. of silica on oxidation was added to the flask and weighed carefully. About one and one-half ml. of 30% fuming sulfuric acid was added to the flask to dissolve the sample. Fuming nitric acid was cautiously added dropwise with gentle heating between additions until the oxidized material in the flask turned white. The flask was slowly brought to a high temperature to drive off all volatile material, and the flask and contents brought to constant weight at about 800°. The weighing procedure described above was employed again, the gain in weight of the flask being taken as due to silica formed by oxidation. The silica was quite hygroscopic. Therefore, the flask during weighing was stoppered to exclude moisture. All organo-silicon compounds may be analyzed in this manner except those that are volatile or not readily soluble in fuming sulfuric acid.

Discussion

The unusual reactivity of trimethylsilylmethanol in forming the phenylurethan indicates a pronounced activating influence by the silicon atom upon the O–H bond. Primary alcohols branched in the β position are generally less reactive than their normal homologs. The results of several different methods of determining the relative reactivities of alcohols agree quite well in that they usually place the alcohols in the same relative order. Table II shows some of the results of various workers, and the results of this study.

From the data in Table II it can be seen that the effect of branching in the β position is most apparent in neopentyl alcohol. The same effects of branching either are not present in the silicon analog of neopentyl alcohol or they are completely masked by a pronounced activating influence of the silicon atom upon the O–H bond. The large covalent radius 1.17 Å. for the silicon atom compared to 0.77 Å. for carbon causes less packing and thus less interaction between the methyl groups on

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[6] Davis and Farnum, THIS JOURNAL, **56**, 883 (1934).

[7] Rice, Jenkins and Hardin, *J. Am. Pharm. Assoc.*, **27**, 303 (1938).

[8] Whitmore and Rothrock, THIS JOURNAL, **54**, 3431 (1932).

[9] Richard, *Ann. Chemie*, [6] **21**, 337 (1910).

TABLE II

RELATIVE REACTION RATES OF ALIPHATIC ALCOHOLS

Alcohol	K^9	K (this work)	K^{10}	K^{11}	% reacted[12]
$(CH_3)_3SiCH_2OH$	.....	2.92	...	..	..
CH_3OH	1.000	1.00	1.00	1.00	55.6
C_2H_5H	0.961	0.82	0.46	0.81	46.9
n-C_3H_7OH	.782	..	.36	.79	46.9
n-C_4H_9OH	.972	..	.40	.80	46.8
n-$C_5H_{11}OH$	.908	..	.43	.98	..
i-C_4H_9OH	.693	..	.17	.66	..
$(C_2H_5)(CH_3)CHCH_2OH$	.....	..	.19	..	..
$(CH_3)_3CCH_2OH$	.....	.45	...	..	..
$(CH_3)_2CHOH$	.305	..	.054	.55	26.5
$(CH_3)_2(C_2H_5)CHOH$	.321	..	.04	.53	22.6
$(CH_3)_3COH$	.00318	..	.015	..	1.4
$(CH_3)_2(C_2H_5)COH$	.00728	..	.014	..	.8

the silicon atom than would be the case for similar groups on a carbon atom, as has been pointed out by Whitmore and Sommer.[3] The interaction of the closely packed groups on a carbon atom probably is partly responsible for the inactivity of neopentyl alcohol. The lack of this effect, however, can scarcely explain the enhanced activity of its silicon analog which appears to be more active than any other alcohol. The explanation for the enhanced activity of this compound might be related to the highly electronegative nature of the Me_3SiCH_2-radical as found by Whitmore, Sommer and Bernstein,[3,13] who found that order of certain radicals was as follows: phenyl > Me_3SiCH_2- > Me- > Et- > n-Pr- > (n-Bu-, n-Hex-) > Benzyl > (Me_3CCH_2-, t-Bu-) as determined by the method of Kharasch and Marker.[14] This relationship of reactivity of alcohol to electronegativity of the radical seems to hold true for the normal alcohols but glaring exceptions are noticeable where branching in the alcohol occurs. Thus benzyl, neopentyl and t-butyl radicals are about equal in electronegativity, but the corresponding alcohols are quite different in relative reactivities. The reactivity of an alcohol probably is dependent upon the electronegativity of the radical as well as upon the steric effects of structure and the separation of the two effects is not possible.

Trimethylsilylmethanol dissolves sodium slowly at room temperature with the evolution of hydrogen. A sample (22 g.) containing a small amount of dissolved sodium was found to be unchanged by heating at 175° in a sealed tube for four days. The same sample diluted with a mixture of methanol (4 ml.) and water (0.5 ml.) was heated at 180° for sixteen hours followed by heating at 210° for two hours. No appreciable change was observed.

The alcohol dissolved slowly in boiling 75% potassium hydroxide solution over a period of several hours to form a clear solution from which an infusible combustible gel was precipitated by the addition of acid. Apparently cleavage of silicon–carbon bonds occurred resulting in the production of a polymeric siloxane material upon acidification of the solution.

Trimethylsilylmethanol dissolved clean amalgamated aluminum foil very quickly with the evolution of much heat when a trace of carbon tetrachloride was added to catalyze the reaction.

Summary

The synthesis of trimethylsilylmethanol and a study of its chemical reactivity is reported.

PITTSBURGH, PENNSYLVANIA

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[10] Norris, Ashdown and Cortese, THIS JOURNAL, **47**, 837 (1925); **49**, 2640 (1927); found these rate constants for esterification of alcohols with p-nitrobenzoyl chloride recalculated on basis of the rate for methanol equal to unity.

[11] Fehlandt and Adkins, *ibid.*, **57**, 193 (1935); Hatch and Adkins, *ibid.*, **59**, 1694 (1937), found relative reactivities from methanolysis studies.

[12] Menschutkin, *Ann. chim. phys.*, [5] **30**, 81 (1883), reacted alcohols with acetic acid one hour at 155°.

[13] Whitmore and Bernstein, THIS JOURNAL, **60**, 2626 (1938).

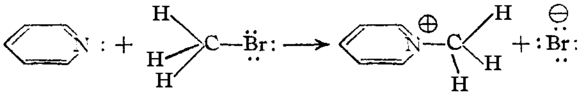
[14] Kharasch and Marker, *ibid.*, **48**, 3140 (1926).

[CONTRIBUTION NO. 1145 FROM THE GATES AND CRELLIN LABORATORIES OF CALIFORNIA INSTITUTE OF TECHNOLOGY AND FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Kinetic Evidence for a Termolecular Mechanism in Displacement Reactions of Triphenylmethyl Halides in Benzene Solution

BY C. GARDNER SWAIN[1]

According to current theory there are only two commonly occurring mechanisms for nucleophilic displacement reactions. One is the bimolecular, kinetically second order (S_N2) substitution or "Walden Inversion."[2] In this mechanism the driving force is exclusively a "push" or *nucleophilic* attack by the entering atom or group, which has an unshared pair of electrons that it is eager to donate in bond formation. The attack is entirely from the back side. An example is the reaction of *primary* halides, such as methyl bromide, with pyridine in benzene solution.



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[1] National Research Fellow 1945–1946; American Chemical Society Fellow 1946–1947. Paper presented at the New York meeting of the American Chemical Society, September 17, 1947.

[2] (a) Walden, *Ber.*, **28**, 1287 (1895); (b) Lewis, "Valence and the Structure of Atoms and Molecules," 1923, p. 113; (c) Hughes, Juliusberger, Masterman, Topley and Weiss, *J. Chem. Soc.*, 1525 (1935); (d) A. G. Evans, "Reactions of Organic Halides in Solution," Manchester University Press (1946); *Trans. Faraday Soc.*, **42**, 719 (1946).