ture reverse-phase chromatography on paraffin–mineral oil impregnated paper with glacial acetic acid saturated with paraffin–mineral oil according to Fiker and Hajek[5] indicated a C_{26} long-chain fatty alcohol. The recorded[10] melting point for hexacosanol is 78°.

Anal. Calcd. for $C_{26}H_{54}O$: C, 81.60; H, 14.22. Found: C, 81.56; H, 14.01.

The methanol filtrate from the above crystals was evaporated to dryness, and the residue was recrystallized from acetone, chromatographed through acid-washed Magnesol,[11] and recrystallized several times from acetone to yield colorless crystals melting at 76.5–77°. The infrared curve was identical with that of hexacosanol except for the trace bands of magnesium silicate from the Magnesol column which could not be removed. High-temperature reverse-phase paper chromatography by the Fiker and Hajek[5] procedure indicated a C_{20} long-chain fatty alcohol.

Acids from petroleum ether-soluble "neutral" fraction. A sample (2.0 g.) of the acid fraction was chromatographed on alumina, and the column was eluted successively with petroleum ether (b.p. 65–110°), benzene, chloroform, 95% ethanol, and 1% acetic acid in 95% ethanol. The last eluate containing only acidic materials was evaporated under reduced pressure to yield 1.37 g. of product. The material was subjected to reverse-phase chromatography on mineral oil-treated paper in 85% acetic acid at room temperature along with known saturated and unsaturated fatty acids. The papers were examined by means of ultraviolet light before and after iodination and by means of the mercury stain.[3] Confirmatory chromatograms were run in the "peracid" developer.[4] The following acids were found: myristic (85% acetic acid R_f 0.65), palmitic (R_f 0.54), stearic (R_f 0.15), arachidic (R_f 0.09), behenic (R_f 0.04), lignoceric and/or higher (R_f 0.00), arachidonic (R_f 0.39), oleic (R_f 0.50), linoleic (R_f 0.66), and linolenic (R_f 0.74).

Paper chromatography in the butanol saturated with 2% aqueous ammonia, 10:3:3 butanol-pyridine–water, and benzene saturated with formic acid developers and comparison with known compounds[6,7] indicated the presence of vanillic, syringic, ferulic, *p*-coumaric, and *p*-hydroxybenzoic acids.

Saponification of petroleum ether-soluble "neutral" fraction with strong alkali. Fifty grams of the petroleum ether–soluble fraction was boiled under reflux with 500 ml. 2*N* ethanolic potassium hydroxide for 15 hr., and then the ethanol was distilled and replaced with water. The alkaline solution was extracted exhaustively with ether as before, but in this case, chromatography of the ether extract gave no evidence of acidic materials. This unsaponifiable material was obtained as a light tan oil which deposited colorless platelets upon standing. The fraction was diluted with a little petroleum ether (b.p. 30–60)° and filtered. The oil-free crystals were recrystallized several times from ether at −60° to yield colorless platelets melting at 78–90°. Infrared absorption spectra indicated a long-chain fatty alcohol, and high-temperature reverse-phase chromatography by the Fiker and Hajek procedure[5] indicated a C_{27} alcohol.

Anal. Calcd. for $C_{27}H_{56}O$: C, 81.74; H, 14.23. Found: C, 81.75; H, 14.19.

Acknowledgment. The authors wish to thank Dr. W. C. Hamilton, Continental Oil Co., for authentic samples of saturated fatty alcohols and Archer-Daniels-Midland Co. for authentic samples of saturated fatty acids and alcohols.

APPLETON, WIS.

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(10) T. Koyama, and T. Morikita, *Kumamoto Pharm. Bull.*, **1955**, No. 2, 69; *Chem. Abstr.*, **50**, 11228 (1956).

(11) I. A. Pearl and E. E. Dickey, *J. Am. Chem. Soc.*, **73**, 863 (1951).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

The Reaction of Some Silanols and Siloxanes with *n*-Octyl Alcohol

M. M. SPRUNG AND F. O. GUENTHER

Received June 9, 1960

The acid- or base-catalyzed reaction of a number of silanols and siloxanes with *n*-octyl alcohol under nonequilibrium conditions was studied by observing the amount of water formed and the quantitative rate at which it was formed. The reaction is nearly always complicated by simultaneous selfcondensation of the silanol, and by further attack of the reagent upon the siloxane that is formed. By noting the positions at which pronounced "knees" appear in the water-evolution rate curves, and by independently determining the rates of alcoholysis of the siloxanes (when this was feasible), conclusions were reached concerning the extent of selfcondensation of the silanol compared to that of reaction with the alcohol. The nature of the catalyst, the number of alkyl or aryl substituents on silicon, the steric or inductive effects of these substituents, and the ring size (in case of the cyclic polysiloxanes) are all of importance. A number of *n*-octoxysilanes and *n*-octoxysiloxanes were isolated and identified.

INTRODUCTION

Although silanols are known to be involved in most syntheses of organosilicon polymers, the reactions that they undergo have been only scantily considered. The reactions by which silanols are prepared can usually be reversed. For example, some years ago Sommer, Pietrusza, and Whitmore[1] converted triethylsilanol to chlorotriethylsilane, to triethylsiloxyl acetate, to bis(triethylsiloxyl) sulfate, and to sodium triethylsilanolate. Alkali silanolates can be obtained from certain silanols by treatment either with the alkali amide, or with concentrated alkali metal hydroxide.[2] Sauer[3] prepared trimethylsiloxymagnesium iodide from

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(1) L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 2282 (1946).

(2) (a) J. F. Hyde, U. S. Patent **2,567,110**, Sept. 4, 1951; (b) W. S. Tatlock and E. G. Rochow, *J. Am. Chem. Soc.*, **72**, 528 (1950); (c) W. S. Tatlock and E. G. Rochow, *J. Org. Chem.*, **17**, 1955 (1952); (d) J. F. Hyde, O. K. Johannson, W. H. Daudt, R. F. Fleming, H. B. Laudenslager, and M. P. Roche, *J. Am. Chem. Soc.*, **75**, 5615 (1953).

(3) R. O. Sauer, *J. Am. Chem. Soc.*, **66**, 1707 (1944).

trimethylsilanol and methylmagnesium iodide. Recently, Müller, Dathe, and Heinrich[4] observed that certain silanols can be methylated with diazomethane in alcohol solution.

The reaction of a silanol with an alcohol to give an alkoxysilane is quite common in practice, but has received relatively little study, *per se*. A few years ago,[5] Gilman and Miller pointed out that the silanol-alcohol reactions must be taken into consideration in order to account for the observed stoichiometry in the titration of silanols with Karl Fischer reagent. As a mole of silanol is titrated as though it were a mole of water, it seemed that the silanol must react with the large excess of methanol present to give methoxysilane and water. It was noted, further, that the equilibrium was attained slowly when bulky substituents were present in the silanol. The stoichiometry of the Karl Fischer titration would be upset if silanol condensed to a significant extent to give disoloxane, as one mole of silanol then produces only one-half mole of water.

Grubb considered this problem in detail and concluded[6] that under these conditions the reaction of silanols with methanol is rapid compared to selfcondensation. Even under milder conditions the selfcondensation of silanols is not complete when much alcohol is present, but an equilibrium is established in which most of the silanol is present as alkoxysilane. Grubb discussed the equilibria involved:

$$\text{—SiOH} + \text{CH}_3\text{OH} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{—SiOCH}_3 + \text{H}_2\text{O} \qquad (1)$$

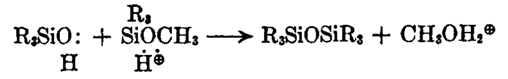
$$\text{—SiOH} + \text{SiOCH}_3 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{—SiOSi—} + \text{CH}_3\text{OH} \qquad (2)$$

$$2\ \text{—SiOH} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \text{—SiOSi—} + \text{H}_2\text{O} \qquad (3)$$

and deduced the constant, $K_4 = K_1K_2 = \frac{k_1}{k_2}\,\frac{k_3}{k_4} = \frac{\text{—(SiOCH}_3)^2(\text{H}_2\text{O})}{(\text{—SiOSi—})}$

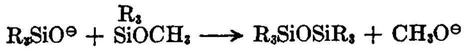
The validity of this expression indicated that the reaction between silanol and methanol was essentially complete. K_4 decreased in going from methanol to ethanol to *n*-propyl alcohol (*i.e.*, relatively more —SiOSi— is present at equilibrium) and the equilibrium was reached more slowly if bulky organic groups were attached to the silicon. A mechanism consistent with the observed facts is "back-side displacement" of the alkoxy group by silanol or by silanolate ion. Steric factors should be of considerable importance in either case.

Acid catalyzed: (4)



$$\underset{\text{H}}{\text{R}_3\text{SiO}}: + \underset{\dot{\text{H}}^{\oplus}}{\overset{\text{R}_3}{\text{SiOCH}_3}} \longrightarrow \text{R}_3\text{SiOSiR}_3 + \text{CH}_3\text{OH}_2^{\oplus}$$

Base catalyzed: (5)



$$\text{R}_3\text{SiO}^{\ominus} + \overset{\text{R}_3}{\text{SiOCH}_3} \longrightarrow \text{R}_3\text{SiOSiR}_3 + \text{CH}_3\text{O}^{\ominus}$$

As nonequilibrium conditions normally prevail when condensations are carried out on functional organosilanes, it seemed of interest to study the silanol-alcohol reaction under nonequilibrium conditions. This was done, however, under conditions so selected that homogeneity was maintained throughout the entire course of the reaction.

At first glance, it appears that reaction (2) might be of minor significance under nonequilibrium conditions, as it lacks the obvious driving force of the other two. The total amount of water released should then assay the relative importance of forward reactions (1) and (3). Actually, however reaction (2) is seldom of entirely minor importance. This disturbing factor makes it difficult to interpret simple water-evolution data. When reaction (3) produces a simple disiloxane, its alcoholysis can be measured independently and an appropriate correction applied. However, when polysiloxanes with complex alcoholysis patterns are involved, evaluation of the data is very much more difficult.

EXPERIMENTAL

To enable azeotropic distillation of water to be used as a quantitative tool, the components of the reaction mixture must be essentially insoluble in water at room temperature. The standard batch formulation chosen for study therefore consisted of 0.1 mole of the silanol, 0.4 mole of *n*-octyl alcohol, 0.0555 g. of catalyst (sodium methylate or *p*-toluenesulfonic acid), and 100 ml. of reagent xylene. Assuming complete reaction with *n*-octyl alcohol this should yield 1.8 ml. of water; exclusive selfcondensation should yield only half, or 0.9 ml. of water. For the alcoholysis of siloxanes, the same quantities of reagents were used, except that sufficient di- or polysiloxane was taken to yield 0.1 mole (1.8 ml.) of water, assuming complete reaction at every siloxane bond. The reactions were run at the boiling point (150°) in a 500 ml. flask equipped with a Dean-Stark trap surmounted by a water-cooled condenser. The system was protected from atmospheric moisture by means of a dry-nitrogen-flushed T-tube or by calcium sulfate drying tubes. Small droplets of water that sometimes clung to the upper walls of the trap were forced into the lower, finely calibrated section by agitation with a snugly fitting coil of Nichrome wire.

RESULTS AND DISCUSSION

Monosilanols. The data in Fig. 1 show that simple monosilanols react readily with *n*-octyl alcohol in the presence of an acid catalyst, that the reactions go nearly to completion, and that selfcondensation of the silanol is of minor consequence. Triethylsilanol reacts considerably faster than trimethylsilanol. This would seem to be attributable to the greater electron releasing effect of the ethyl groups,

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[4] R. Müller, C. Dathe, and L. Heinrich, *J. prakt. Chem.*, 9, 24 (1959).

[5] H. Gilman and L. S. Miller, *J. Am. Chem. Soc.*, **73**, 2367 (1951).

[6] W. T. Grubb, *J. Am. Chem. Soc.*, **76**, 3408 (1954).

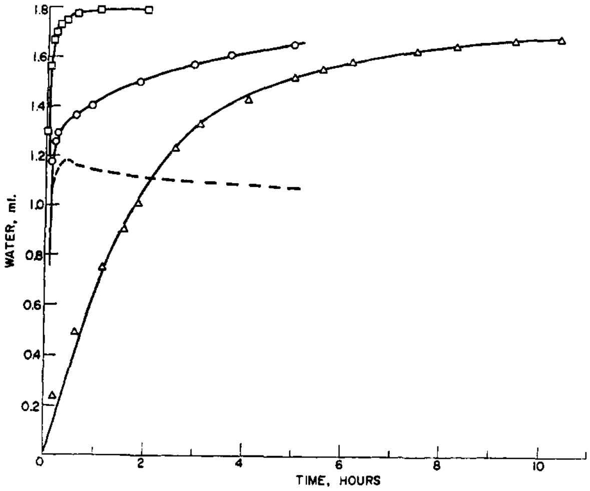

Fig. 1. Monosilanols + *n*-octyl alcohol (acid-catalyzed)

⊙ $(CH_3)_3SiOH$, ◻ $(C_2H_5)_3SiOH$, △ $(C_6H_5)_3SiOH$
- - - -Corrected for alcoholysis of the disiloxane

which allows the protonated alcohol more readily to approach the less positive silicon atom. Triphenylsilanol reacts relatively slowly, a fact attributable both to the opposite inductive effect of the phenyl groups and to steric influences. However, it will be noted that the curve for trimethylsilanol shows a definite "knee." This suggests that the initial, competing reactions of selfcondensation and alkoxysilane formation were essentially complete at this time, and that the subsequent portion of the curve is owing to alcoholysis of the disiloxane. An approximate correction can be made for the hydrolysis of hexamethyldisiloxane, and this corrected curve is shown by the broken line. (The fictitious downward slope is probably owing to the fact that the siloxane content of the mixture varies with time in an uncalculable manner.) However, it appears that in the initial, faster reaction, selfcondensation prevailed over alkoxysilane formation by a factor of about 2:1. For triethylsilanol, however, the data suggest nearly exclusive alkoxysilane formation (confirmation of this viewpoint is furnished by Fig. 6). For triphenylsilanol, alkoxysilane formation is the dominant process and condensation is of minor significance (possible 10% of the total).

Significantly different results were obtained with base as catalyst (Figure 2). The rates are now in the order trimethylsilanol > triphenylsilanol ≫ triethylsilanol. The trimethylsilanol curve has a pronounced "knee." Correction for alcoholysis of the disiloxane (dotted line) indicates that about 33% selfcondensation and 67% alkoxysilane formation had occurred (the reverse of the acid catalyzed result). For triphenylsilanol, an initially rapid reaction (about 70% condensation) is superceded by a slow alcoholysis step. A reasonable correction for alcoholysis could not be made. The very slow rate at which triethylsilanol reacts in a basic medium must mean that steric considerations are more important when the attack is by a siloxy anion than when protonated species are involved.

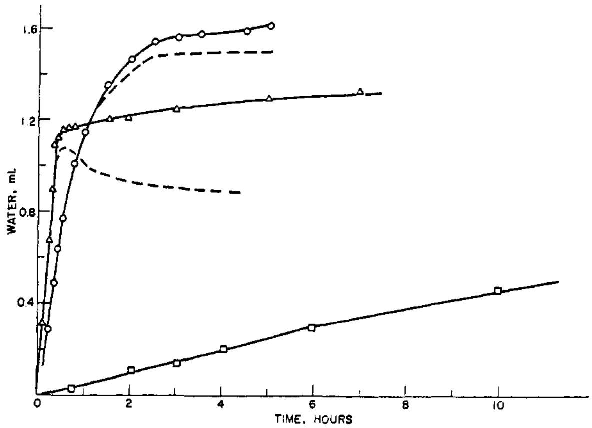

Fig. 2. Monosilanols + *n*-octyl alcohol (base-catalyzed)

⊙ $(CH_3)_3SiOH$, ◻ $(C_2H_5)_3SiOH$, △ $(C_6H_5)_3SiOH$
- - - -Corrected for alcoholysis of the disiloxane

Silanediols and phenylsilanetriol. Three diols (diethylsilanediol, diphenylsilanediol, and tetramethyldisiloxane-1,3-diol) were investigated with the results shown in Figs. 3 and 4. With acid as catalyst, all three diols showed initially rapid rates of reaction. The curves begin to flatten out rapidly, and from the position of the knees it can be inferred that about 20% selfcondensation occurred with the disiloxane diol, about 33% with diethylsilanediol, and considerably more with diphenylsilanediol. The product from the disiloxane diol was distilled, and a rather complex mixture of products was found to be present, including alcoholysis products.

The effect of the basic catalyst was again quite different. Tetramethyldisiloxanediol reacted very rapidly again and alcoholysis of the products (dotted extension of the curve, shown only in part in Fig. 4) ensued extremely rapidly. After about three hours, alcoholysis was virtually complete.

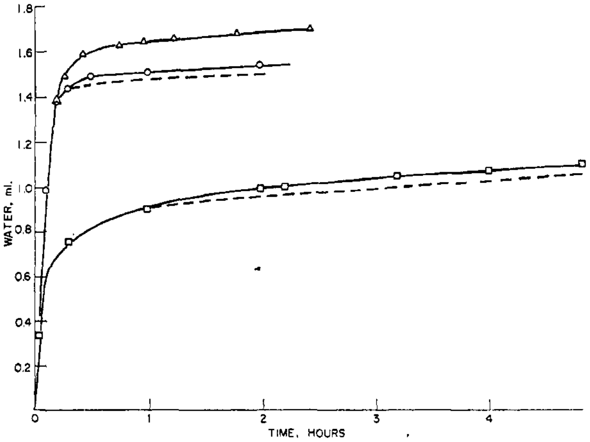

Fig. 3. Silanediols + *n*-octyl alcohol (acid-catalyzed)

⊙ Diethylsilanediol, ◻ diphenylsilanediol, △ tetramethyldisiloxanediol
- - - -Corrected for alcoholysis of the siloxane

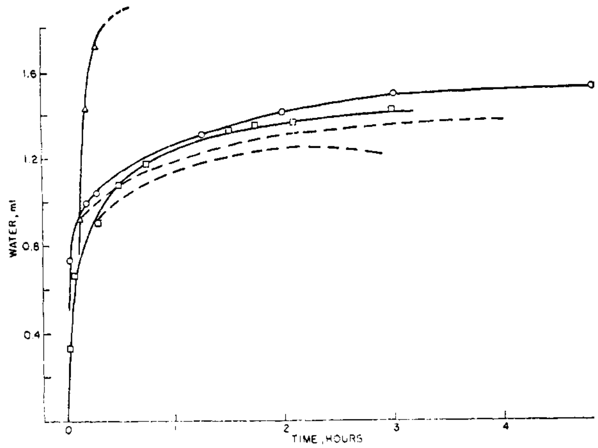

Fig. 4. Silanediols + *n*-octyl alcohol (base-catalyzed)

⊙ Diethylsilanediol, ◻ diphenylsilanediol, △ tetramethyldisiloxanediol
- - - -Corrected for alcoholysis of the siloxane

Only dimethyldi-*n*-octoxysilane was isolated subsequently. The other diols, however, appear to undergo selfcondensation and alkoxysilane formation during the initial stages of the reaction to approximately equal extents. Again, the steric effect of the ethyl group, relative to phenyl, seems to be of more importance in a base-catalyzed than in an acid-catalyzed reaction.

The acid-catalyzed reaction of phenylsilanetriol with *n*-octyl alcohol (Fig. 5) showed a distinct knee, from which it can be concluded that about 60–70% selfcondensation occurred, giving products that are relatively stable towards alcoholysis. The effect of base, on the contrary, was to yield rather rapid and complete formation of the alkoxysilane. Phenyltri-*n*-octoxysilane was isolated from this reaction in good yield (Table I).

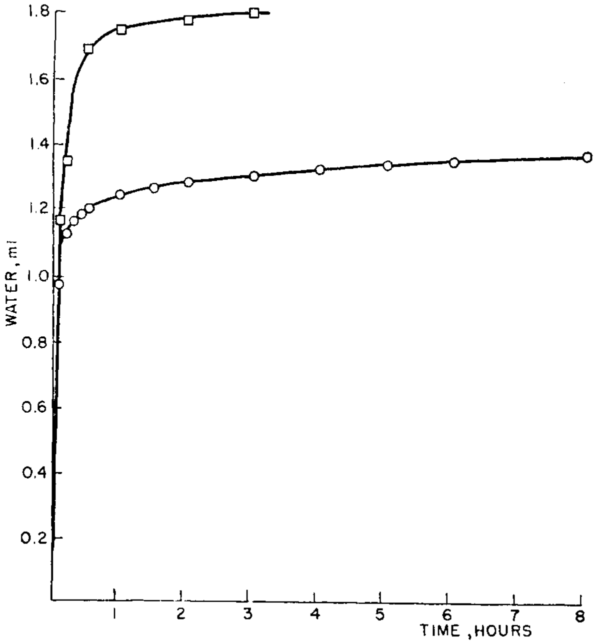

Fig. 5. Phenylsilanetriol + *n*-octyl alcohol

⊙ acid-catalyzed, ◻ base-catalyzed

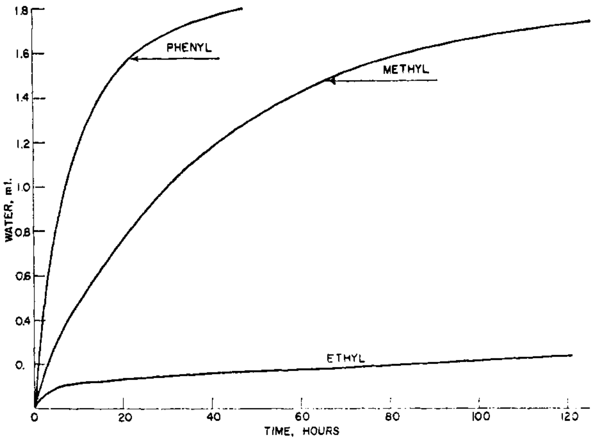

Fig. 6. Hexaorganodisiloxanes + *n*-octyl alcohol (acid-catalyzed)

Siloxanes. Figures 6 and 7 represent the rates of acid and base catalyzed alcoholysis of hexaorganodisiloxanes. When acid catalyzed, the relative reactivities are in the order $(CH_3)_3SiOSi(CH_3)_3 \gg (C_2H_5)_3SiOSiE(C_2H_5)_3 > (C_6H_5)_3SiOSi(C_6H_5)_3$. This again indicates steric blocking by the ethyl group, and both steric hindrance and unfavorable inductive effects for the phenyl group. The effect of the ethyl group, significantly, is the opposite of that observed in the silanol reaction. When the reaction is base-catalyzed, hexamethyldisiloxane and hexaethyldisiloxane occupy the same relative positions with respect to one another; but hexaphenyldisiloxane is alcoholized at a very high rate.

The behavior of cyclic polysiloxanes is shown in Figs. 8 and 9. The alcoholysis rates are again greatly affected by the organic substituents. With acid as catalyst, methyl, ethyl, and phenyl exert the same general influence as was observed for the corresponding disiloxanes. The effect of ring size is also discernible. The steric strain associated with cyclotrisiloxanes is evidenced by the difference in rates of alcoholysis of hexamethylcyclo-

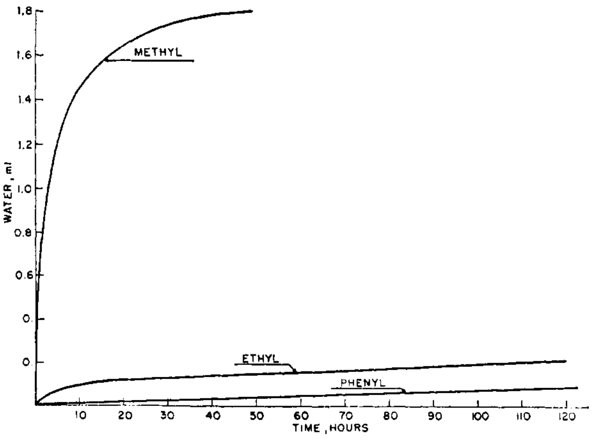

Fig. 7. Hexaorganodisiloxanes + *n*-octyl alcohol (base-catalyzed)

TABLE I

n-OCTOXYSILANES AND *n*-OCTOXYSILOXANES

Product	Formula	Starting Material	Catalyst	Physical Constants				Carbon, %		Hydrogen, %		Silicon, %		MR	
				B.P.	Mm.	d_4^{20}	n_D^{20}	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
n-Octoxytriethylsilane	$C_{14}H_{32}SiO$	Triethylsilanol	Acid	85	1.0	—	1.4337	68.8	69.1	13.2	13.7	11.5	11.3	—	—
n-Octoxytriphenylsilane	$C_{26}H_{32}SiO$	Triphenylsilanol	Acid	192	0.3	1.007	1.5523	—	—	—	—	7.2	7.2	123.2	123.3
Di-*n*-octoxydiphenylsilane	$C_{28}H_{44}SiO_2$	Diphenylsilanediol	Base	199	0.6	0.947	1.4995	76.3	76.1	10.1	10.3	6.4	6.4	136.7	136.8
Dimethyldi-*n*-octoxysilane	$C_{18}H_{40}SiO_2$	"Methyl dimerdiol"[b]	Base	117	0.4	0.845	1.4300	68.3	67.9	12.7	12.8	8.9	9.0	96.9	96.8
Diethyldi-*n*-octoxysilane	$C_{20}H_{44}SiO_2$	Diethylsilanediol	Base	140	0.6	0.852	1.4362	69.7	69.7	12.9	13.2	8.2	8.2	106.2	150.8
Phenyltri-*n*-octoxysilane	$C_{30}H_{56}SiO_3$	Phenylsilanetriol[c]	Base	209	0.4	0.908	1.4642	73.1	73.4	11.4	11.7	5.7	5.8	150.2	149.8
1,5-Di-*n*-octoxyhexamethyltrisiloxane	$C_{22}H_{62}Si_3O_4$	"Methyl-D_3"[d]	Acid	148	0.4	—	1.4228	56.8	56.4	11.3	11.7	18.1	17.9	—	—
1,5-Di-*n*-octoxyhexaethyltrisiloxane	$C_{28}H_{64}Si_3O_4$	"Ethyl-D_3"[e]	Acid	191	0.9	—	1.4393	61.2	61.6	11.8	12.0	15.4	14.8	—	—

[a] A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J. Chem. Soc.*, 531 (1952). [b] Tetramethyldisiloxane-1,3-diol. [c] L. J. Tyler, *J. Am. Chem. Soc.*, **77**, 770 (1955). [d] Hexamethylcyclotrisiloxane. [e] Octomethylcyclotetrasiloxane.

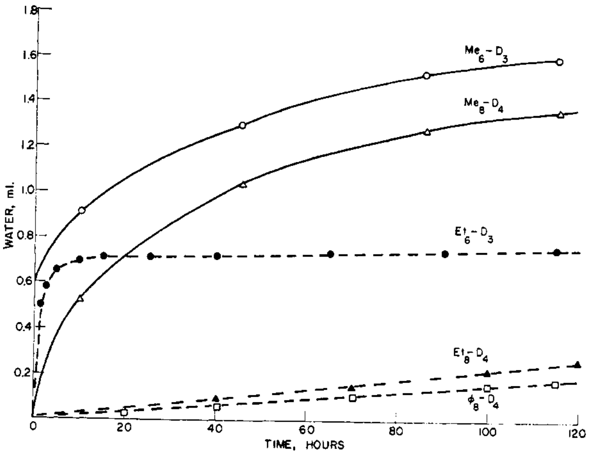

Fig. 8. Cyclic poly(diorganosiloxanes) + *n*-octyl alcohol (acid-catalyzed)

○ ———Hexamethylcyclotrisiloxane
△ ———Octamethylcyclotetrasiloxane
● - - - -Hexaethylcyclotrisiloxane
▲ - - - -Octaethylcyclotetrasiloxane
▣ — — — — -Octaphenylcyclotetrasiloxane

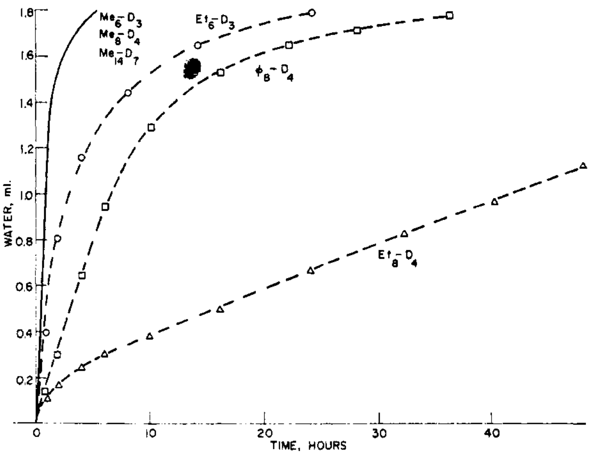

Fig. 9. Cyclic poly(diorganosiloxanes) + *n*-octyl alcohol (base-catalyzed)

———Hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, and tetradecamethylcycloheptasiloxane.
○- - - -Hexaethylcyclotrisiloxane
△ - - - -Octaethylcyclotetrasiloxane
□— — — — -Octaphenylcyclotetrasiloxane

trisiloxane and octomethylcyclotetrasiloxane and of hexaethylcyclotrisiloxane and octaethylcyclotetrasiloxane. The strained trisiloxane rings are opened much more rapidly than the unstrained tetrasiloxane rings. With sodium methylate as catalyst (Fig. 9) the effect of ring strain shows up only in the ethyl compounds. The methyl substituted compounds with 6, 8, and 14 ring members alcoholyze at about the same rate.[7] Possibly the influence of ring strain is obscured here by the more important effect of the low steric requirements

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(7) There was some indication that hexamethylcyclotrisiloxane reacted more rapidly than either octamethylcyclotetrasiloxane or tetradecamethylcycloheptasiloxane.

of the methyl groups themselves. The phenyl substituted polysiloxane again reacted much more readily when the catalyst was basic than when it was acidic.

Good yields of 1,5-di-*n*-octoxyhexamethyltrisiloxane were obtained if the reactions were stopped when about one-third of the total theoretically possible water had been collected. The catalyst was washed out, and the partially alcoholyzed product isolated by vacuum distillation. A continuation of the reaction beyond this point, of course, results in further stepwise alcoholysis, but the subsequent products can not readily be separated from one another.

Isolation of products. The course of the reaction was frequently checked by isolating the products formed. The usual procedure was to strip the xylene and excess *n*-octyl alcohol at about 50 mm. pressure from the water-washed reaction mixture. The residue was distilled at 0.5–1.0 mm. pressure. Midcuts of flats were analyzed. Individual compounds so obtained are listed in Table I. An exception to this procedure was in the base-catalyzed reaction of triphenylsilanol with *n*-octyl alcohol. Here the product, hexaphenyldisiloxane, crystallized from the cooled reaction mixture in a relatively pure state.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, SCIENTIFIC LABORATORY OF THE FORD MOTOR CO.]

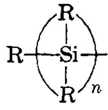
Preparation of Decamethyltetrasilane and Its Lower Homologs

GLENN R. WILSON AND ARTHUR G. SMITH

Received June 2, 1960

The preparations of three new organosilicon compounds—octamethyltrisilane, decamethyltetrasilane, and a hexamethyl dichlorotrisilane—are reported, together with an improved method for preparing hexamethyldisilane.

Despite the phenomenal growth of organosilicon chemistry within the past twenty years, surprisingly few examples of organo-substituted silicon catenations are known. The examples are limited to a series of disilanes (I, $n = 2$) in which the R groups are aryl or alkyl groups (C$_1$–C$_5$)$^{1-4}$; octaphenyltrisilane[5]; the controversial octaphenyltetrasilanes described by Kipping[6] and a possible decaphenyltetrasilane[5]; a cyclic dodecamethylcyclohexasilane[7] and higher molecular weight polydimethylsilanes of indefinite structure.[7–9] Lack of equivalent methods for propagating silicon chains compared with carbon chains coupled with the weaker bond energy (45 kcal./mole)[10] for the silicon-silicon linkage compared with that (80 kcal./mole)[10] for the carbon-carbon linkage probably accounts for the paucity of examples of polysilanes.



I

Our purpose was the preparation of discrete members of a homologous series of polysilanes with the simplest alkyl group (methyl) in order to fill some of the gaps and determine some of their physical properties. At this time we are able to report the successful syntheses of the tri- and tetrasilanes, hexamethyldichlorotrisilane, and an improved laboratory synthesis of hexamethyldisilane (the key starting material for the preparation of the higher homologs).

Since relatively large quantities of hexamethyldisilane were required for subsequent syntheses, an improved and more convenient method for preparing this intermediate over those described in the literature[3,11–13] was required. After investigating several procedures, the coupling of trimethylchlorosilane with sodium-potassium alloy was found to be very satisfactory and preferred over coupling with metallic sodium. The sequence of reactions for preparing the series of polysilanes reported here is summarized in the following equations:

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