8.6 g. of product with b.p. 171–172.5°, n_D^{20} 1.4540, were obtained. Yield of crude product was 42.5 percent.

Acknowledgment. We wish to thank Lawrence Scarpino, Jr., for his assistance in the preparation and purification of the compounds described here. We also wish to thank Dr. Walter Oppenheimer for silicon analyses.

BRUCETON, PA.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Reactions of Di- and Trifunctional Methylsilanes with Diols, Triols, and Acyloxyols[1]

M. M. SPRUNG

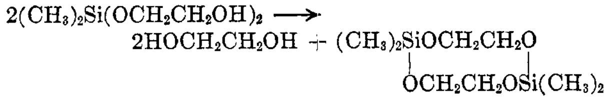
Received July 17, 1957

Reactions of di- and triethoxymethylsilanes with diols, triols, and acyloxyols were examined. Bis(hydroxyalkoxy)dimethylsilanes having primary hydroxyl groups could not be isolated from the reaction between diethoxydimethylsilane and diols. A cyclic polymethylenedioxysilane was formed instead and a mole of the diol was recovered for each two moles employed. A similar disproportionation occurred with acyloxyols. Low yields of bis(hydroxyalkoxy)dimethylsilanes having secondary hydroxy groups were obtained in two instances. Isobutylene glycol reacted to give mainly silicon-free cyclodehydration products. Triols gave polymeric products; a step-wise mechanism for this reaction is suggested. Polymeric products were obtained by treating trifunctional organo-silicon compounds with diols, or by ester interchange between poly(β-hydroxyethoxy)silanes and dialkyl dicarboxylates.

The author and L. S. Nelson[2] have described the preparation of trimethylsilyl derivatives of diols and polyols and discussed their usefulness in certain synthetic problems.

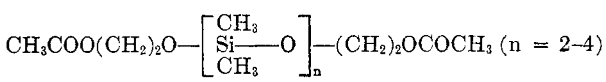
Polymeric reaction products are to be expected if a di- or trifunctional organo-silicon compound is substituted for trimethylchlorosilane or for the trimethylalkoxysilane in these reactions. Structural considerations must also be taken into account, since structure or stereochemistry may favor the formation of monomeric or dimeric ring compounds, over polymer formation. Some generalizations have been established in earlier work.[3–6]

One of the first objectives of the present work was to prepare bis(β-hydroxyethoxy)dimethylsilane from diethoxydimethylsilane and ethylene glycol. Despite the use of an excess of the latter, the products obtained were ethylene glycol and dimeric dimethylethylenedioxysilane, suggesting that if bis(β-hydroxyethoxy)dimethylsilane were indeed formed, disproportionation could have occurred during vacuum distillation, as follows:



$$2(CH_3)_2Si(OCH_2CH_2OH)_2 \longrightarrow 2HOCH_2CH_2OH + \begin{array}{l}(CH_3)_2SiOCH_2CH_2O\\ \quad\;| \qquad\qquad\quad\;\, |\\ \;\;\, OCH_2CH_2OSi(CH_3)_2\end{array}$$

Reaction was then attempted with ethylene glycol monoacetate, since it was felt that the acetoxy groups would stabilize the initial product, and could then be removed by mild saponification procedures. Using either dimethyldichlorosilane or dimethyldiethoxysilane, this result was not achieved. Ethylene glycol diacetate and dimeric dimethylethylenedioxysilane were produced instead, in major proportions. In addition, small amounts of the lower members of a polymer-homologous series,



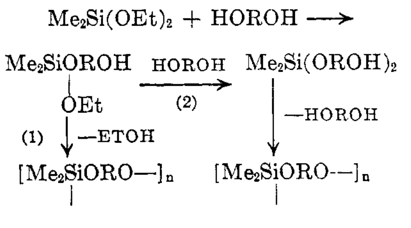
$$CH_3COO(CH_2)_2O\text{—}\left[\begin{array}{c}CH_3\\ Si\text{——}O\\ CH_3\end{array}\right]_n\text{—}(CH_2)_2OCOCH_3\ (n = 2\text{–}4)$$

were obtained. The monomer (n = 1) was not found.

From ethylene glycol monobenzoate and diethoxydimethylsilane a 20% yield of bis(β-benzoxyethoxy)dimethylsilane was obtained; but the major reaction again was disproportionation or its equivalent.

Reactions involving excess trimethylene glycol or hexamethylene glycol gave similar results. Vacuum distillation gave the cyclic dimethylpolymethylenedioxysilane (or left a polymeric product of the same empirical composition) and half of the glycol that would otherwise be combined in the product was recovered.

The formation of the dimethylalkylenedioxysilane can presumably occur in either of two ways:



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[1] Presented before the Polymer Section of the AMERICAN CHEMICAL SOCIETY at the 130th Meeting, Atlantic City, N. J., September 1956.

[2] M. M. Sprung and L. S. Nelson, *J. Org. Chem.*, **20**, 1750 (1955).

[3] F. S. Kipping and J. T. Abrams, *J. Chem. Soc.*, 81 (1944).

[4] R. H. Krieble and C. A. Burkhard, *J. Am. Chem. Soc.*, **69**, 2689 (1947).

[5] H. Staudinger and W. Hahn, *Die Makromolekular Chemie*, **11**, 24 (1953).

[6] W. Hahn, *Die Makromolekular Chemie*, **11**, 51 (1953).

The stability of the hypothetical intermediate, $Me_2Si(OROH)_2$ might depend upon the nature of R and upon whether the hydroxyl groups are primary, secondary, or tertiary. Some light on these relations was obtained by studying propylene glycol, isobutylene glycol, and 3-isopropoxy-1,2-propanediol.

The behavior of propylene glycol was distinctly less simple than that of the primary glycols. Reaction with equimolar quantities of diethoxydimethylsilane did not go to completion. In addition to dimeric dimethylpropylenedioxysilane, a small amount of the bishydroxyalkoxysilane was obtained and some of the glycol was recovered unchanged. Two moles of propylene glycol per mole of diethoxydimethylsilane gave the same products, but considerably more bishydroxyalkoxysilane. This product was not isolated in either case; it was, however, identified as the trimethylsilyl derivative, bis(2-trimethylsiloxy-1-propoxy)dimethylsilane.

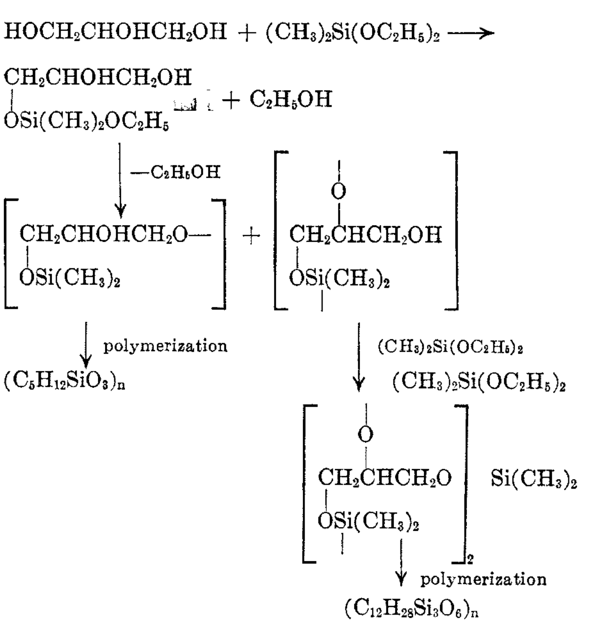
The reaction with isobutylene glycol (catalyzed by strong acid in this case) took an entirely different course. With one mole of diethoxydimethylsilane, several products were formed, among which only poly(dimethylsiloxane) and a small amount of dimethylisobutylenedioxysilane could be identified. With two moles of isobutylene glycol, the silicone and glycol species ended up completely divorced from one another. The final products, in addition to ethyl alcohol, were poly(dimethylsiloxane) and an isobutylene oxide dimer. It was not determined whether the latter was the symmetrical dimer, 2,2,5,5-tetramethyl-1,4-dioxane, or the unsymmetrical rearrangement product, 4,4-dimethyl-2-isopropyl-1,3-dioxolane, or a mixture.

Dimethylisobutylenedioxysilane was prepared from isobutylene glycol and dichlorodimethylsilane. The low boiling point (125°) suggests that it is monomeric when freshly distilled. The molecular weight obtained after a day or two corresponded to that of the dimer, and polymerization continued on further standing.

The reaction of 3-isopropoxy-1,2-propanediol with diethoxydimethylsilane also followed a somewhat complex course. The major product was an azeotrope composed of the cyclic dimer, 2,2,7,7-tetramethyl-4,9-bis(isopropoxymethyl)-1,3,6,8-tetroxa-2,7-disilicane, and the partial reaction product, bis(2-hydroxy-3-isopropoxypropoxy)dimethylsilane. Reaction with trimethylchlorosilane was subsequently employed to effect a separation of the two components. The bishydroxyalkoxy compound was converted to the corresponding bistrimethylsiloxy derivative which could be separated from the cyclic dimer by distillation. Like the simpler polymethylenedioxysilanes, the latter compound polymerized spontaneously on standing.

Although the reaction products of diethoxydimethylsilane with bis-β-hydroxyethyl dicarboxylates were mainly polymeric, there was some disproportionation in each case studied.

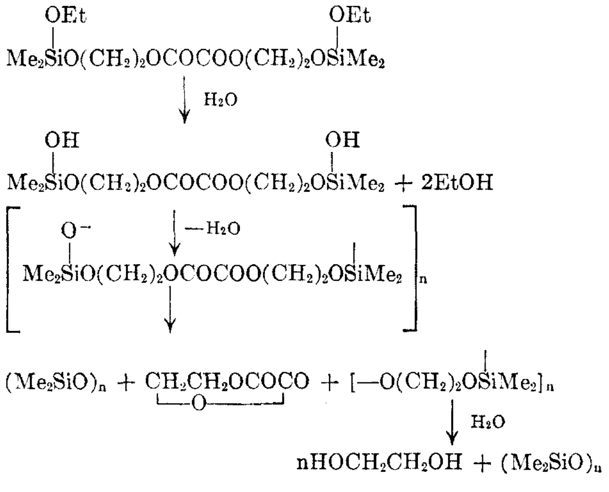
The reaction of diethoxydimethylsilane with triols (glycerol, 1,1,1-trimethylolethane and 1,1,1-trimethylolpropane) gave polymeric products, and eventually gels, as would normally be expected. In one such reaction involving glycerol, the use of a slight excess of the triol furnished a clue as to the reaction mechanism. A volatile liquid product analyzed approximately for a poly(2-hydroxytrimethylenedioxysilane), whereas the major product, an insoluble gel, was apparently a mixture of polymers of this approximate composition and other polymeric species having the educts of the reactants present in the normal stoichiometric proportions (2:3 rather than 2:2). It is tentatively suggested that this reaction may have proceeded as follows:



The volatile product approximated a low polymer of composition, $(C_5H_{12}SiO_3)_n$. The gelled residue was intermediate in composition between $(C_5H_{12}SiO_3)_n$ and $(C_{12}H_{28}Si_3O_6)_n$.

Resin formation was always observed in the reaction of glycols with trifunctional organo-silicon compounds. Some pertinent data are summarized in Table II. Another series of polymers, prepared by ester interchange between poly(β-hydroxyethoxy)silanes and dialkyl esters of dibasic acids, is described in Table III.

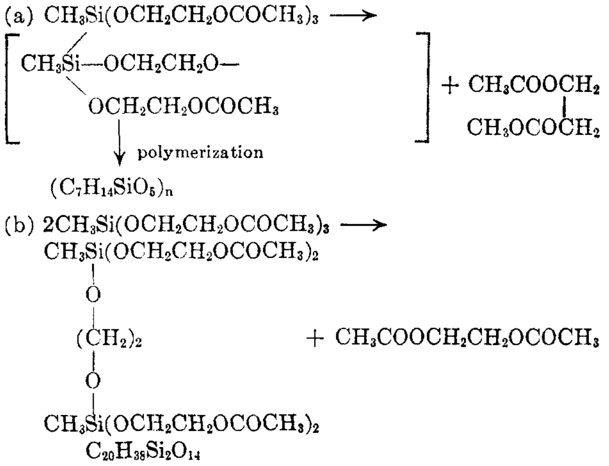
Attempts were made to prepare polymers through controlled hydrolysis of partial reaction products of diethoxydimethylsilane with bis-β-hydroxyethyl dicarboxylates. However, hydrolytic attack at the SiOC bond nullified any propagation of a polymer chain by condensation of silanols to polysiloxanes. For example, in the reactions of diethoxydimethylsilane with bis(β-hydroxyethyl)oxalate, ethylene glycol, poly(dimethylsiloxane) and ethylene oxalate were the final products. A reaction scheme can be formulated as follows:



$$\mathrm{Me_2Si(OEt)O(CH_2)_2OCOCOO(CH_2)_2OSi(OEt)Me_2} \xrightarrow{H_2O} \mathrm{Me_2Si(OH)O(CH_2)_2OCOCOO(CH_2)_2OSi(OH)Me_2} + 2\mathrm{EtOH}$$

$$\xrightarrow{-H_2O} \left[\mathrm{Me_2Si(O^-)O(CH_2)_2OCOCOO(CH_2)_2OSi(-)Me_2}\right]_n \longrightarrow (\mathrm{Me_2SiO})_n + \mathrm{CH_2CH_2OCOCO(-O-)} + [\mathrm{-O(CH_2)_2OSiMe_2}]_n \xrightarrow{H_2O} n\mathrm{HOCH_2CH_2OH} + (\mathrm{Me_2SiO})_n$$

Disproportionation or its equivalent was again noted in the reaction between methyltriethoxysilane and ethylene glycol monoacetate. The product that might otherwise be expected is methyltris(β-acetoxyethoxy)silane. The two liquid distillates actually obtained corresponded analytically to monomeric and dimeric disproportionation products. They could be formed from methyltris(β-acetoxyethoxy)silane by the reactions shown below.



$$\text{(a) } \mathrm{CH_3Si(OCH_2CH_2OCOCH_3)_3} \longrightarrow \left[\mathrm{CH_3Si(-OCH_2CH_2O-)(OCH_2CH_2OCOCH_3)}\right] + \mathrm{CH_3COOCH_2CH_2OCOCH_3} \xrightarrow{\text{polymerization}} (\mathrm{C_7H_{14}SiO_5})_n$$

$$\text{(b) } 2\mathrm{CH_3Si(OCH_2CH_2OCOCH_3)_3} \longrightarrow \mathrm{CH_3Si(OCH_2CH_2OCOCH_3)_2{-}O{-}(CH_2)_2{-}O{-}CH_3Si(OCH_2CH_2OCOCH_3)_2} + \mathrm{CH_3COOCH_2CH_2OCOCH_3}$$

$$\mathrm{C_{20}H_{38}Si_2O_{14}}$$

A continuation of the latter type of intermolecular disproportionation would lead to higher molecular weight products. Resinous products were, in fact, formed, but they were not examined further.

EXPERIMENTAL

Reaction of diethoxydimethylsilane with ethylene glycol. To 124 g. (2 moles) of redistilled ethylene glycol was added 74 g. (0.5 mole) of diethoxydimethylsilane and 0.1 g. of dry Amberlite IR-100H, a cation exchange resin in the acid form (Rohm & Haas Company). Almost exactly one mole of ethanol was distilled through a Vigreux column surmounting the stirred reaction flask, during 240 minutes at 102–169°. The product (150 g.) was filtered to remove the catalyst and distilled under vacuum. Most of it (136 g.) distilled at 90–95° at 14 mm., and consisted of a mixture of a liquid and a solid. The latter, m.p. 53–54°, was identified, after filtration and sublimation, as dimethylethylenedioxysilane.[4] By redistillation of the crude liquid products, it was determined that only ethylene glycol and the 10-membered-ring dimer were present.

1,1,3,3-Tetramethyl-1,3-bis(β-acetoxyethoxy)disiloxane. In an effort to prepare dimethylbis(β-acetoxyethoxy)silane, 2 moles (208 g.) of β-hydroxyethyl acetate (Distillation Products Company, "White Label") was caused to react with one mole (148 g.) of diethoxydimethylsilane in the presence of 0.2 g. of Amberlite IR-100H resin, under a Vigreux column. Approximately the calculated amount of ethanol was collected during 2 hr. at 115–180°. The catalyst was filtered and the product was distilled. A few grams of diethoxydimethylsilane came over first, followed by a complex mixture boiling between 90° and 162° at 23–4 mm. Upon careful redistillation, the major fraction was ethylene glycol diacetate, contaminated with dimethylethylenedioxysilane, which also appeared as a solid in the condenser and receiver. The disiloxane was obtained in low yield (9 g.) as a high boiling by-product (b.p. 106.5–108.5° at 0.2 mm., n_D^{20} 1.4268).

Anal. Calcd. for $C_{12}H_{26}Si_2O_7$: C, 42.6; H, 7.8; Si, 16.6; sapon. equiv. 169.3. Found: C, 43.1; H, 8.2; Si, 17.5; sapon. equiv., 172.5.

1,1,3,3,5,5-Hexamethyl-1,5-bis(β-acetoxyethoxy)trisiloxane and 1,1,3,3,5,5,7,7-octamethyl-1,7-bis(β-acetoxyethoxy)tetrasiloxane. These polymer homologues of the disiloxane were obtained in small amounts during a second attempt to prepare dimethylbis(β-acetoxyethoxy)silane. One mole of dichlorodimethylsilane was added to 2 moles of β-hydroxyethyl acetate in the presence of 2.2 moles (174.2 g.) of pyridine at 12–25°. After heating briefly at the boiling point to conclude the reaction, the mixture was chilled while stirred vigorously, 500 ml. of dry ether was added and the pyridine hydrochloride present was filtered. Ether and excess pyridine were distilled at atmospheric pressure. Vacuum distillation then gave 162 g., boiling range 61° at 28 mm. to 130° at 1 mm. This mixture was redistilled in a 20 plate packed column and the high boiling end in a Piros-Glover spinning band still. Bis(β-acetoxyethoxy)dimethylsilane was not detected, although a small flat (1.2 ml., b.p. 96–100° at 2 mm.) may have concerned this compound. The major product (60 ml.) was ethylene glycol diacetate (b.p. 109.5°, n_D^{20} 1.4160; sapon. equiv.: calcd., 73.05; found, 74.0). The two high boiling fractions were (*a*) 2.8 ml., b.p. 145–8° at 2 mm., n_D^{20} 1.4192 and (*b*) 3.7 ml., b.p. 156–7° at 2 mm., n_D^{20} 1.4179.

Anal. (*a*) Calcd. for $C_{14}H_{32}Si_3O_8$: C, 40.7; H, 7.8; Si, 20.4; sapon. equiv., 206.3. Found: C, 40.2; H, 7.7; Si, 20.2; sapon. equiv., 203.2.

(*b*) Calcd. for $C_{16}H_{38}Si_4O_9$: C, 39.4; H, 7.9; Si, 23.0; sapon. equiv., 243.4. Found: C, 39.0; H, 7.8; Si, 22.3; sapon. equiv., 247.5.

Bis(β-benzoxyethoxy)dimethylsilane. β-Hydroxyethyl benzoate was prepared according to the procedures of Cretcher and Pittenger[7] and Heim and Poe.[8] One mole (166 g.) was heated and stirred with one-half mole (74 g.) of diethoxydimethylsilane and 0.2 g. of Amberlite IR-100H resin for 4 hr. at 102–192°. The distillate obtained (55 ml.) contained some unreacted diethoxydimethylsilane. After removal of the catalyst, distillation at 1 mm. gave 90 g. of recovered β-hydroxyethyl benzoate, b.p. 106–107° at 1 mm.; 74 g. of ethylene glycol dibenzoate, b.p. 184–192° at 1 mm., m.p. 69–70°; and 69.5 g. (20%) of bis(β-benzoxyethoxy)dimethylsilane, b.p. 210–211° at 0.8 mm., n_D^{20} 1.5141. The analytical data were not entirely satisfactory, nor were they improved by a careful redistillation.

Anal. Calcd. for $C_{20}H_{24}SiO_6$: C, 61.7; H, 6.2; Si, 7.2; sapon. equiv., 194.2; mol. wt., 388.5. Found: C, 60.3; H, 6.6; Si, 8.4; sapon. equiv., 201. Found (redistilled sample):

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[7] L. A. Cretcher and W. H. Pittenger, *J. Am. Chem. Soc.*, **47**, 2560 (1925).

[8] H. C. Heim and C. F. Poe, *J. Org. Chem.*, **9**, 299 (1944).

C, 60.4; H, 6.4; Si, 7.7; sapon. equiv., 201.5; mol. wt. (cryoscopically in benzene), 377.

Since the product can be distilled at high temperature without serious breakdown, the disproportionation that is responsible for the low yield must occur principally at some intermediate step in the synthesis.

Reactions with trimethylene- and hexamethylene glycol. One mole of the glycol and one-half mole of diethoxydimethylsilane were heated in the presence of 1.6 g. of the cation exchange resin until the requisite quantity of ethanol had been collected. The excess glycol plus that formed upon disproportionation was recovered by distillation [trimethylene glycol, 43 g., b.p. 107–110° at 10 mm., n_{D}^{20} 1.4382; hexamethylene glycol, 87 g., b.p. 105–114° at 1 mm., m.p. 35.5–36.5°, hydroxyl equiv., 60.5 (calcd., 59.0)]. The trimethylene glycol was preceded by dimethyltrimethylenedioxysilane (45.5 g., b.p. 56–57° at 20 mm., n_{D}^{20} 1.4134–1.4158). The hexamethylene glycol was followed by a small amount of higher boiling liquid (2 g., b.p. ~140° at 1 mm.; hydroxyl equiv., ∞) that appeared to be impure monomeric dimethylhexamethylenedioxysilane.

Anal. Calcd. for $C_8H_{18}O_2Si$: Si, 16.1; mol. wt., 174.3. Found: Si, 15.1; mol. wt., 205.

There was not sufficient sample to establish its authenticity; this monomer has not been reported elsewhere. The distillation residue, a heavy oil, appeared to be polymeric dimethylhexamethylenedioxysilane.

Anal. Calcd. for $(C_8H_{18}O_2Si)_x$: Si, 16.1. Found: Si, 15.7.

Reactions with propylene glycol: (A) *1:1 Reaction with diethoxydimethylsilane.* Equimolar quantities of diethoxydimethylsilane (148 g.) and propylene glycol (76 g.) were caused to react in the presence of 0.3 g. of Amberlite IR-100H resin. The reaction produced 94 g. of volatile liquid, b.p. 78–82°, in 3 hr. In addition to ethyl alcohol, some diethoxydimethylsilane was present. (The azeotrope, about 90% ethanol, boils ~78°). The catalyst was filtered and the product distilled. The major fraction (104.5 g.) boiled at 103–109°/45 mm., the mid-cut at 108°, n_{D}^{20} 1.4347. An infrared spectrogram showed the presence of appreciable amounts of hydroxyl. Apparently this fraction was a mixture of a polymeric dimethylpropylenedioxysilane and propylene glycol, with a third component present in minor amounts as disclosed by the treatment next described.

Anal. Found: C, 45.6; H, 9.6; Si, 18.1; av. mol. wt., 431.

This corresponds to a mixture of 85% $(C_5H_{12}SiO)_n$ and 15% $C_3H_8O_2$. This mixture (100 g.) was now treated with trimethylchlorosilane (45 g.) in excess pyridine (40 g.) and dry ether (100 ml.). After filtering pyridine hydrochloride, ether and excess pyridine were distilled and the residue was fractionated under vacuum. There were three distinct flats. (*a*) b.p. 61.5–63.0° at 37 mm., n_{D}^{20} 1.4114; (*b*) b.p. 69–70.5° at 39 mm., n_{D}^{20} 1.4324; (*c*) 117–126° at 12 mm., n_{D}^{20} 1.4168 (relatively minor). On the basis of analyses and evidence to be presented below, (*a*) is an azeotrope consisting of about 70% dimethylpropylenedioxysilane dimer and about 30% 1,2-bistrimethylsiloxypropane; (*b*) is dimethylpropylenedioxysilane; (*c*) present in very small amounts, is bis(2-trimethylsiloxy-1-propoxy)dimethylsilane (a better sample was obtained later).

Anal. Found (Fract. *a*): C, 46.5; H, 10.4; Si, 22.0. Calcd. for 70% $(C_5H_{12}SiO_2)_n$, 30% $C_9H_{24}Si_2O_2$: C, 46.5; H, 9.7; Si, 22.5.

Found (Fract. *b*): C, 45.4; H, 9.0; Si, 21.1. Calcd. for $(C_5H_{12}SiO_2)_n$: C, 45.4; H, 9.1; Si, 21.3.

(B) *2:1 Reaction with diethoxydimethylsilane.* Two moles (152 g.) of propylene glycol and 1 mole (148 g.) of diethoxydimethylsilane were heated with 0.5 g. of Amberlite resin under conditions similar to those described above. After removing 92 g. (2 moles) of ethanol, the product was distilled, but good separation was not achieved. The cuts were therefore recombined, dissolved in pyridine (174 g.) and ether (200 ml.) and treated with 2.0 moles (217 g.) of trimethylchlorosilane. The resulting product was distilled in a Podbielniak spinning band type column. Three major components were observed again: (1) b.p. 81.5° at 54 mm., n_{D}^{20} 1.4114; (2) b.p. 89–90° at 52 mm., n_{D}^{20} 1.4071; (3) b.p. 103–103.5° at 3 mm., n_{D}^{20} 1.4151. The first of these is the 70:30 azeotrope described above; the second is 1,2-bis-(trimethylsiloxy)-propane;[9] the third is bis(2-trimethylsiloxy-1-propoxy)-dimethylsilane. By using an excess of the glycol, a fairly high yield (about 50 g.) of this substance was obtained.

Anal. Calcd. for 70% $(C_5H_{12}SiO_2)_n$ + 30% $C_9H_{24}Si_2O_2$: C, 46.5; H, 9.7; Si, 22.5. Found (Fract. 1): C, 46.5; H, 9.6; Si, 22.9.

Calcd. for $C_9H_{24}Si_2O_2$: C, 49.1; H, 11.0. Found (Fract. 2): C, 48.6; H, 10.6.

Calcd. for $C_{14}H_{36}Si_3O_4$: C, 47.6; H, 10.3; Si, 23.9; mol. wt., 352.7. Found (Fract. 3): C, 47.9; H, 10.3; Si, 23.8; mol. wt. (in benzene), 335.

(C) *Reaction with dichlorodimethylsilane.* One mole (129 g.) of dichlorodimethylsilane was added dropwise to a solution of 76 g. propylene glycol in 174 g. (2.2 moles) of pyridine, stirred and kept at 25–30° by ice cooling. The pyridine hydrochloride was filtered and washed with 200 ml. of dry ether. The ether and excess pyridine were distilled and then the product was distilled rapidly at reduced pressure. Yield 109.5 g. (83%), b.p. ~75° at 39 mm., n_{D}^{20} 1.4324. The compound polymerizes rapidly on standing at room temperature and a good molecular weight was not obtained, but the boiling point suggests that the freshly distilled product is dimeric.[10]

Anal. Calcd. for $(C_5H_{12}SiO_2)_n$: C, 45.4; H, 9.1; Si, 21.3; mol. wt., 132.2 n. Found: C, 45.6; H, 9.4; Si, 20.6; mol. wt., 965 (cryoscopically in benzene).

Reactions with isobutylene glycol: (A) *1:1 Reaction with diethoxydimethylsilane.* The ion exchange resin was ineffective as a catalyst. Molar quantities of the reactants (148 g. of the dialkoxysilane, 90 g. of the diol) were heated with 0.1 g. of *p*-toluenesulfonic acid under a short packed column. After 3 hr. at 97–162°, 100 g. of distillate was collected, including some dialkoxysilane in addition to ethanol. The less volatile product was distilled under reduced pressure. The major fraction (53–5 g.) boiled at 88–92°/32 mm., n_{D}^{20} 1.4230–1.4236. Physical properties and analyses indicated that a mixture of several components, including dimethylisobutylenedioxysilane, poly(dimethylsiloxane) and dimeric isobutylene oxide was obtained.

Anal. Found: C, 47.8; H, 10.3; Si, 13.8.

There was a sizable distillation residue (29 g.) that was largely poly-(dimethylsiloxane).

Anal. Calcd. for $(C_2H_6SiO)_n$: C, 32.4; H, 8.2. Found: C, 35.6; H, 8.3.

(B) *2:1 Reaction with diethoxydimethylsilane. p*-Toluenesulfonic acid (0.2 g.) served again as the catalyst. The reaction required 3 hrs. at 103–121° (liquid temperature). The ethanol, distilled over in about the expected amount, carried with it about 15 g. of an immiscible liquid that proved to be low polymeric dimethylsiloxane. The product was distilled at 65 mm., taking six cuts up to 120°. Each of these separated into two layers on standing. The lower layers (combined weight, 36 g.) and the distillation residue (30.5 g.) were essentially poly(dimethylsiloxane). The combined upper layers (136 g.) were redistilled in a spinning band column. The major component (91 g., b.p. 76.5° at 98 mm., n_{D}^{20} 1.4087), silicon-free, was apparently dimeric isobutylene oxide. The infrared spectrum was consistent with this structure assignment.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.6; H, 11.2; mol. wt., 144.2. Found: C, 66.2; H, 11.9; mol. wt. (in benzene) 179.

Higher boiling fractions (27 g., b.p. 84–177/48 mm., n_{D}^{20} 1.3971–1.4044) were identified as poly(dimethylsiloxanes). The largest fraction (12.9 g., b.p. 86.5° at 48 mm., n_{D}^{20}

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(9) Ref. 2, p. 1753.

(10) Compare the data in Ref. (4), p. 2691.

TABLE I

POLY-β-DIMETHYLETHYLENEOXYSILOXYETHYLENE DICARBOXYLATES

Bis-β-hydroxyethyl Dicarboxylate	Reaction Temp., °C.	Ethanol Collected, %	Volatile Products, G.	B.P., °C.	Press., Mm.	n_D^{20}	Nonvolatile Products, G.	Physical State
Oxalate	92–167	100	27[a]	60–75	1.0	1.4356	110	Waxy solid[b]
			14.5[a]	93–97	1.0	1.4395		
Phthalate	97–175	95	82[c]	47–200	1.0	—	183	Resinous solid[d]
Terephthalate	100–217	75	—	—	—	—	237	Soft, waxy solid[e]

[a] Both fractions were largely impure dimethylethylenedioxysilane dimer (m.p., after purification, 56–8°). [b] *Anal.* Calcd. for 66% $(C_8H_{14}SiO_6)_n$ (copolymer) plus 34% $(C_4H_4O_4)_n$ (ethylene oxalate): C, 41.1; H, 5.2; Si, 7.9; sapon. equiv., 87. Found: C, 40.4; H, 5.2; Si, 7.9; sapon. equiv., 87. [c] Contained ethanol, ethylene glycol, dimethylethylenedioxysilane and some unreacted diethyl phthalate. [d] Corresponded to a copolymer having an average of 8 units terminated by end groups derived from diethyl phthalate (sapon. equiv.: found, 147, 156; calcd., 150). [e] Melting range, 148–162°.

1.3971) was identified by these properties and by infrared spectrum as octamethylcyclotetrasiloxane.

(C) *Reaction with dichlorodimethylsilane.* The reaction was conducted with 0.78 mole of each reactant in the presence of excess pyridine as described for propylene glycol. The product (82.5 g.) boiled over rather wide limits (118–152° at atmospheric pressure). It was redistilled in a spinning band column, giving 61 g. of dimethylisobutylenedioxysilane, b.p. 125.5–127° at 755 mm., n_D^{20} 1.4283–1.4286.

Anal. Calcd. for $(C_6H_{14}SiO_2)_n$: C, 49.3; H, 9.7; Si, 19.2; mol. wt., 146.3 n. Found: C, 49.6; H, 9.8; Si, 18.7; mol. wt. (in benzene), 294.

2,2,7,7-Tetramethyl-4,9-bis(isopropoxymethyl)-1,3,6,8-tetraoxa-2,7-disilicane and bis(3-isopropoxy-2-trimethylsiloxypropoxy)dimethylsilane. One mole each of diethoxydimethylsilane and 3-isopropoxy-1,2-propanediol were allowed to react together using 0.3 g. of Amberlite resin as catalyst. Reaction began at 95° and nearly the calculated quantity of ethanol distilled over in 135 min. while the temperature was slowly increased to 153°. The crude product (158 g., b.p. 94–117° at 8–1 mm.) showed the presence of unreacted hydroxyl (hydroxyl equiv., 211–355). The presence of bis-(2-hydroxy-3-isopropoxypropoxy)dimethylsilane was therefore suspected. Upon careful redistillation, a fraction weighing 139 g. was obtained with b.p. 96.5–98.5° at 5–6 mm., n_D^{20} 1.4367–1.4380.

Anal. Calcd. for 35% $C_{16}H_{36}Si_2O_{14}$ (cyclic dimer) and 65% $C_{14}H_{32}SiO_6$ (bis-hydroxyalkoxysilane): C, 51.4; H, 9.8; Si, 10.8; OH, 6.8; mol. wt., 343.8. Found: C, 51.0; H, 10.1; Si, 11.2; OH, 8.0; mol. wt., 359.

The constant boiling mixture was dissolved in pyridine (53 g.) and treated in the cold with 43 g. of trimethylchlorosilane. After diluting with ether and filtering the pyridine hydrochloride, the product was again distilled. Two major fractions were obtained: (a) 90 g., b.p. 101–110° at 14 mm., n_D^{20} 1.4296–1.4320; (b) 55.5 g., b.p. 155–157° at 7 mm., n_D^{20} 1.4264–1.4258. Mid-cuts of each fraction were analyzed. Fraction (a) was a polymer of dimethyl-β-iso-propoxymethylethylenedioxysilane, but the observed molecular weight, after standing for a few days, was approximately that of the trimer, rather than the dimer that would be expected from the boiling point.

Anal. Calcd. for $(C_8H_{18}SiO_3)_n$: C, 50.5; H, 9.5; Si, 14.7; mol. wt., 190.3 n. Found: C, 51.0; H, 10.0; Si, 14.3; mol. wt., 525, 515.

Fraction (b) analyzed for bis(2-trimethylsiloxy-3-isopropoxypropoxy)dimethylsilane.

Anal. Calcd. for $C_{20}H_{48}Si_3O_6$: C, 51.2; H, 10.3; Si, 18.0; mol. wt., 468.9. Found: C, 50.8; H, 10.6; Si, 17.6; mol. wt., 502.

Polymeric products from diethoxydimethylsilane and bis-β-hydroxyethyl dicarboxylates. The bis-β-hydroxyethyl dicarboxylates were prepared by ester interchange between the diethyl or dimethyl ester and excess (4 molar equivalents) ethylene glycol in the presence of sodium methylate as catalyst. The excess glycol was removed under reduced pressure (~5 mm.) and the catalyst was absorbed on excess cation exchange resin which was then filtered. The bis-β-hydroxyethyl ester was usually not purified. On long standing, the sirupy products usually crystallized. The purity of bis(β-hydroxyethyl)isophthalate was checked analytically.

Anal. Calcd. for $C_{12}H_{14}O_6$: C, 56.6; H, 5.6. Found: C, 56.2; H, 5.7. The bis-β-hydroxyethyl ester was treated directly with an equimolar amount of diethoxydimethylsilane, using Amberlite resin as the catalyst. The requisite amount of ethanol was distilled over, leaving a sirupy or viscous residue. Low molecular weight components were removed by vacuum distillation. Some data are summarized in Table I.

Diethoxydimethylsilane and triols. The reactants were heated together in the theoretically "balanced" proportions; namely, 1.5 moles of diethoxydimethylsilane to 1 mole of triol (glycerol, trimethylolethane, or trimethylolpropane). (+)-Camphorsulfonic acid was more effective than the cation exchange resin as a catalyst. It was generally possible to drive off nearly the theoretical amount of ethanol before gelation occurred, but the normal end product was a gel. Atypical results were obtained when the reaction was run with glycerol at a somewhat faster rate, so that an appreciable proportion of unreacted diethoxydimethylsilane was carried over with the ethanol. The initial reaction product was a heavy oil, with no trace of gel present. Anhydrous sodium bicarbonate was added to neutralize the (+)-camphorsulfonic acid used as catalyst, and the mixture was filtered through a sintered glass funnel while still warm. Vacuum distillation yielded 44.5 g. of a volatile liquid (b.p. 105–116° at <1 mm., mainly 111–114° at 0.3 mm., n_D^{20} 1.4510). The residue (97 g.) gelled suddenly when the pot temperature reached 138°. The volatile product could not be redistilled unchanged.

Anal. Found (volatile liquid): C, 39.6; H, 8.2; Si, 18.2; mol. wt. (in benzene, after standing 24 hr.), 1505. Calcd. for $(C_5H_{12}SiO_3)_n$: C, 40.5; H, 8.1; Si, 18.9; mol. wt., 148.3 n. Found (gel): Si, 21.4. Calcd. for $(C_{12}H_{28}Si_3O_6)_n$: Si, 23.9.

Reaction of methyltriethoxysilane with diols. The diols used were ethylene glycol and bis-β-hydroxyethyl maleate, succinate, phthalate, and isophthalate (prepared as described previously). Use of diethoxydimethylsilane–methyltriethoxysilane mixtures prolonged the reaction beyond normal gel stage. The catalyst was either (+)-camphorsulfonic acid or the Amberlite cation exchange resin. Results are summarized in Table II.

Attempts to prepare polymers by controlled hydrolysis of partial reaction products. Two moles of diethoxydimethylsilane and one mole of bis-β-hydroxyethyl oxalate were heated with Amberlite resin as the catalyst. When 2 moles

TABLE II

RESINS FROM METHYLTRIETHOXYSILANE AND DIOLS

Diol	Moles Taken	MeSi-(OEt)$_3$, Moles	Me$_2$Si-(OEt)$_2$, Moles	Amberlite IR-100H, g.	Temp., °C.	Time, Min.	Ethanol, %	Product	
								Wt., g.	Physical State
Ethylene glycol	3.0[a]	0.5	—	0.2	108–175	100	100	87	Incipient gel[b]
Bis-β-hydroxyethyl maleate	1.5	1.0	—	0.3[c]	115–156	35	80	246	Gelled
	1.5	0.5	0.75	1.2	115–187	200	90	248	Incipient gel
Bis-β-hydroxyethyl succinate	1.5	0.6	0.6	0.4	119–220	240	100	306	Viscous syrup
Bis-β-hydroxyethyl phthalate	1.5	0.6	0.6	0.4	94–143	145	83	309	Very heavy sirup
Bis-β-hydroxyethyl isophthalate	1.5	0.6	0.6	0.5	101–147	125	87.5	335	Heavy sirup

[a] The excess glycol was distilled under vacuum. [b] Hydroxyl equivalent: found, 71.7; calcd., 75.2 [for methyltris(β-hydroxyethoxy)silane]. The product is obviously polymeric. [c] (+)-Camphorsulfonic acid.

TABLE III

ESTER INTERCHANGE WITH DIALKYL ESTERS

Poly(hydroxyethoxy)silane Nominal Formula	Moles	Ethylene Glycol, Moles	Ester	Moles	NaOMe, g.	Temp., °C.	Time, Min.	Alcohol Distilled, Moles	Reesterification, %	Product
$Si(OCH_2CH_2OH)_4$	0.25	1.0	Dimethyl terephthalate	1.5	4.1	140–219	220	2.2	74	Tough, waxy solid
	0.25	1.0	Diethyl succinate	1.5	4.0	165–216	300	2.15	71.5	Viscous liquid
	0.50	—	Diethyl succinate	1.0	2.0	180–200	15	0.1	3.4	Gelled
$MeSi(OCH_2CH_2OH)_3$	0.33	1.0	Diethyl phthalate	1.5	2.0	157–218	120	1.9	64	Heavy oil
	0.33	1.0	Dimethyl terephthalate	1.5	2.0	143–185	95	2.2	74	Soft, waxy solid
	0.33	1.0	Diethyl oxalate	1.5	1.0	150–170	140	2.7	90	Soft, pasty solid
$MeSi(OCH_2CH_2OH)_3$ $Me_2Si(OCH_2CH_2OH)_2$	0.5 0.5	—	Dimethyl isophthalate	1.25	2.2	119–205	100	2.25	90.5	Heavy, balsam like liquid
$Me_2Si(OCH_2CH_2OH)_2$	1.0	—	Diethyl phthalate	1.0	4.0	130–230	240	2.0	100	Thermoplastic resin

of ethanol was evolved, a mole of water was slowly added through a dropping funnel. About 1.2 moles more of ethanol was collected. The heavy, oily product was filtered from the catalyst and distilled under vacuum. About 30% of the product was distilled between 35° and 3 mm. and 110° at 0.8 mm. After redistillation, two products were identified: octamethylcyclotetrasiloxane (b.p. 35° at 3 mm., n_D^{20} 1.3930) and ethylene glycol (b.p. 59° at 0.1 mm., n_D^{20} 1.4335; C, 38.7%; H, 9.7%). Another 30% of the original reaction mixture then appeared as a solid, b.p. 170–180° at 2 mm. After crystallization from ethyl acetate, it melted at 141–142°, the melting point of monomeric ethylene oxalate.[11] Sapon. equiv.: calcd., 58.04; found, 60.0, 58.1.

Diethoxydimethylsilane and bis-β-hydroxyethyl succinate were treated similarly with 0.05% of their combined weight of (+)-camphorsulfonic acid. When 94% of the calculated amount of ethanol was collected, the catalyst was neutralized with sodium bicarbonate and the liquid was filtered. It was reheated slowly to 200° while a mole of water was added dropwise. Ethanol was again collected, accounting for 60% of the remaining ethoxyl content. The liquid was distilled under vacuum and the following products were recognized: octamethylcyclotetrasiloxane, higher liquid polymers of dimethylsiloxane, dimethylethylenedioxysilane dimer, ethylene glycol. The highest boiling fraction (14.5 g., b.p. 160–175° at 0.3 mm.) probably contained bis-β-hydroxyethyl succinate[12] but this was not definitely established. No monomeric ethylene succinate was detected.

Reaction of methyltriethoxysilane with β-hydroxyethyl acetate. One-half mole (89 g.) of methyltriethoxysilane and 1.5 moles (156 g.) of β-hydroxyethyl acetate, with 0.6 g. of Amberlite resin as catalyst, yielded nearly the theoretical amount of ethanol in 200 minutes at 127–187°. A rough vacuum distillation gave 130 g., b.p. 96–104° at 27 mm. Higher boiling fractions totaled 90.5 g., b.p. 132–177° at 0.5–0.3 mm., sapon. equiv. 163–191.5 [calcd. for methyltris(β-acetoxyethoxy)silane, 117.3]. Upon redistillation, two fairly uniform cuts were obtained: (a) 54.5 g., b.p. 122–130° at 0.7 mm., n_D^{20} 1.442–1.445; and (b) 7.7 g., b.p. 149.5–152.5° at 0.7 mm., n_D^{20} 1.4375–1.4377. Mid cuts had b.p. 128–130° and 150.5–152.5° at 0.7 mm.

Anal. Calcd. for $(C_7H_{14}SiO_5)_n$: C, 40.8; H, 6.8; Si, 13.6; mol. wt., 206.3 n; sapon. equiv., 206.3. Found: (a) C, 41.1; H, 7.0; Si, 13.0; mol. wt., 686–888; sapon. equiv., 192.5.

Calcd. for $C_{20}H_{38}Si_2O_{14}$: C, 43.0; H, 6.9; Si, 10.0; sapon.

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(11) W. H. Carothers, Collected Papers, *High Polymers*, Vol. I, Interscience Publishers (1940), p. 54–5.

(12) Ref. 11, p. 48.

equiv., 139.7. Found: (b) C, 43.3; H, 7.3; Si, 10.1; sapon. equiv., 144.

Ester interchange between "poly(hydroxyethoxy)silanes" and dialkyl esters. "Poly(hydroxyethoxy)silanes" were prepared by treating diethoxydimethylsilane, methyltriethoxysilane or tetraethyl silicate with ethylene glycol. In some cases the excess glycol was distilled under vacuum; in others it was left with the reaction product to serve as a co-reactant. Diethyl oxalate, diethyl phthalate, dimethyl isophthalate, or dimethyl terephthalate were added in amounts equivalent to the total polyols present, and reesterification was carried out under the influence of a catalyst quantity of sodium methylate. Data are shown in Table III.

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SCHENECTADY, N. Y.

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Nuclear Substitution Derivatives of Isonicotinic Acid

H. HERBERT FOX AND J. T. GIBAS

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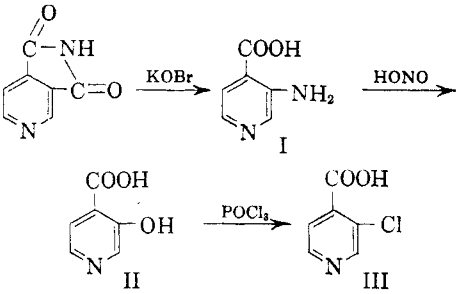
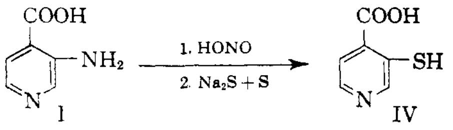
The interaction of isonicotinic acid with thionyl chloride at elevated temperatures in accordance with the Meyer and Graf procedure results in 2-chloroisonicotinic acid. None of the 3-chloroisonicotinic acid reported by Meyer and Graf was isolated.

During the course of investigations into synthetic tuberculostats, 3-hydroxyisonicotinic acid was synthesized[1] in the hope that it would demonstrate anti-tuberculous activity comparable to its benzenoid analog, P.A.S. This hope was not realized but the compound did demonstrate some activity against murine polio (MM strain). To exploit the possibilities presented by this lead, it was decided to prepare a few closely related compounds—notably other hydroxy and mercapto derivatives of isonicotinic acid. The first of these decided on was 3-mercaptoisonicotinic acid. To prepare this compound by what appeared to be the most convenient method, isonicotinic acid was chlorinated with thionyl chloride according to the method of Meyer and Graf[2] to give what they reported to be 3-chloroisonicotinic acid. On treatment of the latter with potassium hydrogen sulfide the desired 3-mercapto compound should be obtained.

This was done and a mercapto compound was isolated which analyzed correctly but which melted with decomposition at 299° (corrected) and gave no color reaction with ferric chloride. According to Sucharda and Troszkiewicz,[3] however, 3-mercaptoisonicotinic acid melts at 255° and gives a blue color with ferric chloride. To resolve this apparent discrepancy, an authentic sample of 3-aminoisonicotinic acid I prepared from chinchomeronimide by means of a Hofmann degradation[4] was diazotized and converted to the corresponding 3-hydroxy compound II which was in turn converted to 3-chloroisonicotinic acid III.



The melting points of the chloro compound obtained by the Meyer and Graf procedure[2] (235–236°) and that of the authentic 3-chloro compound III (228–229°) were too close to be useful for differentiation, but a mixture of the two gave a markedly depressed melting point at 204°. It appeared, therefore, that the chloro compound obtained by the Meyer and Graf procedure as applied in this laboratory could not be 3-chloroisonicotinic acid. This was confirmed by converting an authentic sample of 3-aminoisonicotinic acid to the corresponding 3-mercapto compound IV by the method of Sucharda and Troszkiewicz.[3] The mercapto compound so obtained melted at 265° (Sucharda and Troszkiewicz reported 255°) and gave a blue color with ferric chloride. Moreover, a mixture of the mercapto compound originating *via* the Meyer and Graf procedure and compound IV gave a depressed melting point at 216°.



Under normal circumstances, the evidence presented above would have sufficed to show that

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(1) H. H. Fox, *J. Org. Chem.*, **17**, 542 (1952).

(2) H. Meyer and R. Graf, *Ber.*, **61B**, 2213 (1928).

(3) E. Sucharda and C. Troszkiewicz, *Roczniki Chem.*, 12, 493 (1932).

(4) S. Gabriel and J. Coleman. *Ber.*, **35**, 2832 (1902).