

the usual manner. The product was distilled through a modified Widmer column and a 3-g. cut boiling in the range 148–149° was collected ( $n_D^{20}$  1.4805). This material corresponded in physical constants to 2,5-dihydroanisole (b.p. 148–149°,  $n_D^{20}$  1.4782) reported by Wilds.<sup>21</sup> A 2,4-dinitrophenylhydrazone of this cut using the Wilds procedure<sup>21</sup> at 0° melted at 132–133° and gave no melting point depression with authentic 3-cyclohexanone 2,4-dinitrophenylhydrazone. An estimated minimum purity of 90% was obtained by determining the yield of this derivative. Since both 2,3- and 2,5-dihydroanisole will give this hydrazone, ultraviolet absorption was used to estimate the percentage of these two isomers. The results (Cary recording spectrophotometer) showed  $\lambda_{\max}^{\text{abs EtOH}}$  268 m $\mu$  (2000) for the 2,3-dihydroanisole, indicating 47% to be this product and 53% therefore the 2,5-isomer.<sup>22</sup>

**Benzyl Cyanide<sup>23</sup> with Lithium in Ethylamine.**—Distillation of this reduction product gave 7 g. (55%) of liquid boiling 49–52° (2 mm.),  $n_D^{20}$  1.4851 to 1.4868. Using authentic samples of  $\beta$ -(1-cyclohexenyl)-ethylamine and  $\beta$ -cyclohexylethylamine it was observed that the percentage composition *vs.* refractive index relationship was practically linear. Employing this relationship it was adjudged that the above mixture comprised about 90%  $\beta$ -(1-cyclohexenyl)-ethylamine and 10%  $\beta$ -cyclohexylethylamine.

**Authentic  $\beta$ -(1-Cyclohexenyl)-ethylamine.**—The procedure of Schneider and Hellerbach<sup>24</sup> was followed. The final product boiled at 50–51° (1 mm.),  $n_D^{18}$  1.4882. The hydrochloride melted at 162–165° (reported 160–163°).<sup>24</sup> Various derivatives of this authentic sample were prepared, such as the picrate (174–175°), *p*-nitrobenzamide (124–125°), and phenylthiourea (121–122°). The identical derivatives were

(21) A. L. Wilds and N. A. Nelson, *THIS JOURNAL*, **75**, 5360 (1953).

(22) A. J. Birch [*J. Chem. Soc.*, 1551 (1950)] has reported  $\lambda_{\max}^{\text{abs EtOH}}$  268 m $\mu$  (4270) for 2,3-dihydroanisole.

(23) R. Adams and A. F. Thal, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 107.

(24) O. Schneider and J. Hellerbach, *Helv. Chim. Acta*, **33**, 1437 (1950).

obtained from the reduction product and these did not depress the melting points of the authentic specimens. *Anal.* Calcd. for  $C_{14}H_{18}N_4O_7$  (picrate): C, 47.45; H, 5.08. Found: C, 47.65; H, 5.03. Calcd. for  $C_{15}H_{18}N_2O_3$  (*p*-nitrobenzamide): C, 65.69; H, 6.57. Found: C, 65.70; H, 6.48. Calcd. for  $C_{15}H_{20}N_2S$  (thiourea): C, 69.23; H, 7.61; N, 10.76. Found: C, 69.33; H, 7.59; N, 10.99.

**Authentic  $\beta$ -Cyclohexylethylamine.**—Prepared by the catalytic reduction of  $\beta$ -phenylethylamine.<sup>25</sup> The product was obtained in 66% yield boiling at 180–183°,  $n_D^{20}$  1.4649. The presence of this material in the reduction product was established by infrared spectra.

**Benzonitrile with Lithium in Ethylamine.**—Fractionation of the reduction product gave 5.4 g. (47%) of a liquid boiling at 162–164°,  $n_D^{20}$  1.4632. The melting points of the benzamide (105–106°) and picrate (184–185°) agreed well with the literature values<sup>26</sup> for cyclohexanemethylamine.

**Authentic Cyclohexanemethylamine.**—This product was prepared by the sequence: cyclohexanecarboxylic acid  $\rightarrow$  cyclohexanecarbonyl chloride  $\rightarrow$  cyclohexanecarboxamide  $\rightarrow$  cyclohexanemethylamine. Each step was accomplished employing classical procedures. The final step was carried out with lithium aluminum hydride. The authentic material boiled at 161–162° (747 mm.),  $n_D^{20}$  1.4630. The phenylthiourea melting at 128–129° and the picrate at 185–186° were not depressed when admixed with the lithium-amine reduction product.

**Acknowledgment.**—The authors are grateful to the Eli Lilly Co. and the Ethyl Corporation whose financial assistance in the form of free-grant fellowships made this research possible.

(25) B. L. Zenitz, E. B. Macks and M. L. Moore, *THIS JOURNAL*, **69**, 1117 (1947).

(26) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 178; I. M. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, England, 1943, p. 167.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

## The Partial Hydrolysis of Methyltri-*n*-propoxysilane, Methyltriisopropoxysilane and Methyltri-*n*-butoxysilane

BY M. M. SPRUNG AND F. O. GUENTHER

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The hydrolysis of methyltri-*n*-propoxysilane, methyltriisopropoxysilane or methyltri-*n*-butoxysilane in benzene solution with an acid catalyst proceeds with difficulty and leads mainly to resinous products. In isobutyl methyl ketone, low yields of distillable products were obtained. Octamethyloctasilsesquioxane ( $CH_3SiO_{1.6}$ )<sub>8</sub>, was obtained in about 10% yield during the hydrolysis of methyltri-*n*-butoxysilane. The molecular weight was established from the vapor density above the sublimation temperature. A crystalline polycyclosiloxane containing a single functional group (butoxy) was also isolated from the hydrolysis products of methyltri-*n*-butoxysilane.

### Introduction

The sensitivity to hydrolysis of  $MeSi(OMe)_3$ ,  $MeSi(OEt)_3$  and  $EtSi(OEt)_3$  decreases markedly in that order.<sup>1</sup> Methyltripropoxy-, isopropoxy- and butoxysilanes are difficult to hydrolyze. However, when some of the heavy alkoxy groups are removed, the intermediate hydrolysis products are very susceptible to further attack and rapidly condense to resinous products. Yields of lower molecular weight hydrolysis products are accordingly very poor.

Methyltri-*n*-propoxysilane was recovered unchanged after heating for several hours in benzene

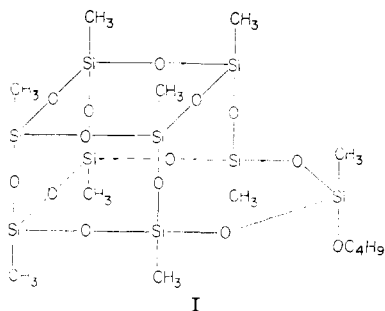
(1) (a) M. M. Sprung and F. O. Guenther, *THIS JOURNAL*, **77**, 3990 (1955); (b) **77**, 3996 (1955); (c) **77**, 4173 (1955). The reader is referred particularly to the first of these papers for a survey of earlier literature.

solution with three molar equivalents of water, 0.09 *N* in hydrochloric acid. With the addition, at the start, of some *n*-propyl alcohol to provide a more favorable reaction medium a low yield of distillable partial hydrolysis products was obtained. The chief components were cyclic tetra- and pentasiloxanes having three to four residual propoxy groups per molecule. A redistilled mid-cut had the composition of a tripropoxybicyclopentasiloxane.<sup>2</sup> The major product was, however, a gelled resin that remained, on the average, one propoxy group for each three siloxane units. The only product obtained from methyltriisopropoxysilane (in benzene with 3 moles of water, 0.09 *N* in HCl) was a gelled

(2) The major component would be 3,9-epoxy-1,3,5,7,9-pentamethyl-1,5,7-tri-*n*-propoxycyclopentasiloxane. No simple isomeric modification of this structure would seem possible.

resin with an average of one isopropoxy group per seven siloxane units. Methyltri-*n*-butoxysilane was recovered unchanged under similar conditions. When higher concentrations of reactants and catalyst were used, a resin having one butoxy group per seven siloxane units resulted. A small amount of high-boiling distillate also was obtained, and a solid with an abnormally high silicon content was found in this. The structure of this solid is discussed below.

Hydrolysis occurred more readily when methyl isobutyl ketone was used as the solvent. Small yields of viscous, oily distillates were obtained. Crystalline solids appeared when methanol solutions of these products were held at refrigerator temperatures. A purified specimen was obtained only in the case of methyltri-*n*-butoxysilane. Analysis established the rather surprising empirical formula,  $C_{13}H_{36}Si_9O_{14}$ . An infrared spectrum showed that hydroxyl and methoxyl were absent, but that butoxyl was present. Formula I is tentatively suggested. The unique feature of this structure is the retention of a single alkylalkoxysiloxane unit ( $R-(R'O)SiO$ ) in an otherwise highly symmetrical, cage-like molecule. The fact that this alkoxy group can no longer react intramolecularly with a second functional group may help account for its persistence in the high-boiling distillate.



**Octamethyloctasilsesquioxane ("Octamethyl T-8") (I).**—This interesting, cage-like molecule, discussed in an earlier paper,<sup>1a</sup> was obtained in somewhat greater quantities during the hydrolysis of methyltri-*n*-butoxysilane. An old sample of the trialkoxysilane, possibly partially hydrolyzed from long standing, was first used. A solid obtained in 10% yield, analyzed approximately correctly for "methyl T-gel,"  $(CH_3SiO_{1.5})_n$ . Over 90% of this solid could, however, be sublimed, yielding an analytically pure specimen of octamethyloctasilsesquioxane. Freshly distilled samples of the methyltri-*n*-butoxysilane gave only traces of the sublimable solid. Numerous experiments were then run under more stringent hydrolytic conditions, with partially hydrolyzed samples of the starting material, and with the corresponding linear disiloxane. Yields of 1–9% of octamethyloctasilsesquioxane were obtained by the following methods: (1) A small amount resulted from the hydrolysis in benzene if the acid concentration was increased tenfold and the reaction time extended considerably. (2) Methyltri-*n*-butoxysilane was stirred with cold water for two months, then hydrolyzed in benzene, giving about a 5% yield of octamethyloctasilsesquioxane. (3) The methyltributoxysilane was hydrolyzed in isobutyl methyl ketone, using ten times the usual concentration of acid. After filtering the solid formed, the process was repeated twice, as described in the Experimental section. This gave a yield of 8–9%. (4) Dimethyltetra-*n*-butoxydisiloxane was hydrolyzed in benzene (to which a little *n*-butyl alcohol was added) under conditions similar to those described above. About 4% was converted to octamethyloctasilsesquioxane.

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### Experimental

**Materials.**—Methyl isobutyl ketone (from Carbide and Carbon Chemicals Co.) was distilled and a cut boiling at 114.5–115.5°,  $n_D^{20}$  1.3955–1.3958, was used. The benzene was Baker and Adamson reagent grade.

The alkoxy silanes were prepared by addition of the appropriate alcohol (carefully dried) to methyltrichlorosilane in the presence of a slight excess of dimethylaniline.<sup>3</sup> The liquid decanted from the cooled reaction mixture was washed with water to remove excess alcohol and small amounts of dimethylaniline hydrochloride. Methyltri-*n*-propoxysilane and methyltri-*n*-butoxysilane were dried over anhydrous sodium sulfate and distilled directly through an 80-plate column. It was necessary, first, to remove excess free amine from the methyltriisopropoxysilane, by slow addition of anhydrous hydrogen chloride, until no more amine hydrochloride was formed. After filtering, the crude product was washed with water and dried over sodium sulfate. Trace amounts of free amine detected in the distilled methyltri-*n*-propoxysilane were removed by washing with dilute hydrochloric acid. Boiling points, refractive indices and yields are given in Table I.

TABLE I  
METHYLTRIALKOXYSILANES

Product	Yield, %	B. p., °C.	Mm.	$n_D^{20}$
$CH_3Si(OC_3H_7)_3$ (iso)	62	102	100	1.3869
$CH_3Si(OC_3H_7)_3$ ( <i>n</i> )	86	130–133	93	1.4000
$CH_3Si(OC_4H_9)_3$ ( <i>n</i> )	77	146–149	43	1.4110

**Hydrolysis in Benzene. Methyltri-*n*-propoxysilane.**—One-half mole (110.2 g.) of methyltri-*n*-propoxysilane and 500 ml. of reagent-grade benzene were stirred at 70°, and 27.0 ml. of water, containing 5.0 ml. of 0.5 *N* hydrochloric acid, was added. After five hours, 27.2 ml. of water was recovered by distillation through a modified Dean-Stark trap, and the alkoxy silane was recovered unchanged. The experiment was repeated, with the addition of 20 g. (0.33 mole) of *n*-propyl alcohol to the benzene. After five hours at the boiling point (69–70°), 16.6 ml. of water was removed through the Dean-Stark trap, and then the solvents were distilled. On vacuum distillation, 8.5 g. of a heavy liquid was obtained, b. p. 85–133° at 0.4 mm. The residue (30.6 g.) gelled.

**Anal.** Found (in residue): C, 28.9; H, 6.6; Si, 32.6. Calcd. for  $(3(CH_3)_2Si_2O_3 \cdot (C_3H_7)_2O)_n$ : C, 28.6; H, 6.4; Si, 33.3. Found (in oil): C, 37.7; H, 8.2; Si, 26.4; mol. wt., 433; –OH, 0.4 (by the Grignard method). The presence of silanol was confirmed by infrared absorption. A mixture of cyclic tetramers and pentamers with 3–4 alkoxy and 0–1 hydroxyl would fit these analyses. The oil was then rapidly redistilled at 0.3 mm., taking a mid-cut with a nominal boiling point range of 74–91°,  $n_D^{20}$  1.4090. This fraction conforms analytically to 3,9-epoxy-1,3,5,7,9-penta-methyl-1,5,7-tri-*n*-propoxycyclopentasiloxane.

**Anal.** Calcd. for  $C_{14}H_{36}Si_6O_9$ : C, 34.4; H, 7.4; Si, 28.7; mol. wt., 489. Found: C, 33.8; H, 7.5; Si, 28.7; mol. wt. (in benzene), 438.

**Methyltriisopropoxysilane.**—A half-mole of methyltriisopropoxysilane was hydrolyzed in 500 ml. of benzene with 27.0 ml. of water, 0.09 *N* in hydrochloric acid, during 9.5 hours at the boiling point. About half of the starting material was recovered. The product was a resinous solid, corresponding empirically to  $(7(CH_3)_2Si_2O_3 \cdot (C_3H_7)_2O)_n$ .

**Anal.** Found: C, 23.5; H, 5.6; Si, 37.6;  $-OC_3H_7$ , 11.7, 9.2. Calcd.: C, 23.1; H, 5.4; Si, 37.7;  $-OC_3H_7$ , 11.3.

(3) W. Simpson, British Patent 635,725, April 12, 1950.

**Methyltri-*n*-butoxysilane.**—One mole of methyltri-*n*-butoxysilane was treated with three moles of water, 0.22 *N* in hydrochloric acid, in 350 ml. of benzene for 17.5 hours at the boiling point (73–75°). Almost exactly 1.5 moles of water was separated, using a modified Dean–Stark trap, and about the calculated volume of *n*-butyl alcohol was distilled, along with most of the benzene. The oily residue (127 g.) held a colorless solid that weighed 7.5 g. after it was filtered, washed with benzene and dried. *Anal.* Found: C, 18.7; H, 4.9; Si, 42.1;  $-\text{OC}_4\text{H}_9$ , 0.3, 0.1. This product (6.7 g.) was placed in a sublimation chamber at 0.4 mm. and heated at 200°. Almost the entire sample sublimed as a colorless, micro-crystalline solid. It did not melt below 400° and was insoluble in all common organic solvents, in accord with the behavior previously observed for this particular methylsilsesquioxane.<sup>1</sup> The molecular weight, previously unestablished, was determined by subliming a sample into a chamber held at 415° and measuring the vapor density at this temperature. Preliminary experiments showed that the compound was sufficiently stable at this temperature. Changes that occurred due to both polymerization and thermal decomposition were measured and found to remain well within the experimental error during the time required for the vapor density determinations. This constitutes the first unequivocal proof of the existence of octamethyloctasilsesquioxane.<sup>4</sup>

*Anal.* Calcd. for  $\text{C}_8\text{H}_{24}\text{Si}_8\text{O}_{12}$ : C, 17.9; H, 4.5; Si, 41.85; mol. wt., 536.9. Found: C, 18.0; H, 4.7; Si, 41.6; mol. wt., 529–590.

Vacuum distillation of the original oily residue yielded 4.0 g. of a heavy liquid, b.p. about 180–200° at 4 mm. One gram of a colorless solid (m.p. 120–130°) remained after digesting with a cold mixture of benzene and methanol, filtering, and washing with the same solvent mixture.

*Anal.* Found: Si, 38.7;  $-\text{OC}_4\text{H}_9$ , 11.7; mol. wt. (in benzene), 691. This is apparently an impure specimen of the monobutoxy compound to be described more fully below. Calcd.: Si, 37.8;  $-\text{OC}_4\text{H}_9$ , 10.9; mol. wt., 669.

The gelled residue weighed 50.5 g. and corresponded empirically to  $(7(\text{CH}_3)_2\text{Si}_2\text{O}_3(\text{C}_4\text{H}_9)_2\text{O})_n$ .

*Anal.* Found: C, 24.8; H, 5.9; Si, 36.1;  $-\text{OC}_4\text{H}_9$ , 13.2, 15.2. Calcd.: C, 24.7; H, 5.7; Si, 36.7;  $-\text{OC}_4\text{H}_9$ , 13.7.

In an attempt to reproduce the fortuitous conditions that gave the 10% yield of octamethyloctasilsesquioxane, a half-mole of methyltri-*n*-butoxysilane was stirred for two months at room temperature with 5.0 ml. of water. Unreacted water and a small amount of gummy material were removed by filtration, and then 175 ml. of benzene, 25.7 ml. of water and 0.5 ml. of concentrated hydrochloric acid were added and the mixture was heated at the boiling point for 17 hours. Unreacted water (15.3 ml.) was recovered through a Dean–Stark trap and an insoluble solid weighing 1.93 g. was filtered. Sublimation at 200–210° and about 1 mm. pressure gave 1.55 g. (4.6%) of the octasilsesquioxane. After stripping solvents, 6.6 g. of high-boiling oil (b.p. 123–160° at 1 mm.) and 28.2 g. of gelled resin were left.

**Dimethyltetra-*n*-butoxydisiloxane.**—The starting material was the high-boiling end of the distillate from the preparation of methyltri-*n*-butoxysilane. Refractionation in a spinning band column gave 10.7 g., b.p. 99.5–102° at 0.1 mm.,  $n_D^{20}$  1.4132–1.4134,  $d_4^{20}$  0.909–0.912.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{42}\text{Si}_2\text{O}_6$ : C, 54.8; H, 10.7; mol. wt., 394.7; *MRD*, 107.5. Found: C, 54.1; H, 10.9; mol. wt. (in cyclohexane), 396, 357; *MRD*, 108.1.

The disiloxane was recovered unchanged when heated at the boiling point in benzene with three molar equivalents of water, 0.09 *N* in hydrochloric acid. However, when *n*-butyl alcohol was added in an amount equivalent to the dimer used, about a 6% yield of solid resulted after the un-

reacted water and solvents were removed. Sublimation at 200–210° under 1 mm. pressure gave over 80% of this as purified octamethyloctasilsesquioxane.

**Hydrolysis in Methyl Isobutyl Ketone.**—To one-half mole of the methyltrialkoxysilane, dissolved in 500 ml. of methyl isobutyl ketone and heated to the boiling point with stirring, was added 27.0 ml. of water, 0.3 *N* in hydrochloric acid. The reaction was continued for five hours. Unreacted water and solvents were removed at atmospheric pressure, and then volatile hydrolysis products were taken off at 2–5 mm. Yields were very low, varying from 4.0 to 8.8 g., and the boiling ranges were about 140–160° for the *n*- and isopropoxy derivatives and about 160–180° for the butoxy derivative. The crude products were dissolved in about 25 ml. of hot methanol, the solutions filtered and allowed to stand at about 0° for several days. Colorless solids were obtained in each instance, but the melting points were not sharp and the melts were cloudy, indicating the presence of a second, higher-melting, immiscible component.

The experiment was repeated with one-fourth mole of methyltri-*n*-butoxysilane to ascertain the maximum yield of octamethyloctasilsesquioxane formed under these conditions. The reflux period was accordingly extended to 24 hours. After separating excess water, the octamethyloctasilsesquioxane was filtered and sublimed. Water (5.0 ml.) and concentrated hydrochloric acid (0.5 ml.) were added<sup>5</sup> and heating was continued for 24 hours longer. These operations were then repeated. The successive yields of sublimate were 0.99, 0.33 and 0.05 g.; total yield, 8.2%. The decrease in yield shows that the intermediate from which the octamethyloctasilsesquioxane is formed is not itself formed continuously. Repetition of the entire procedure on a half-mole of starting material gave 2.93 g. (8.7%) of sublimed solid. Resublimation was now carried out at 200–210° and less than 1 mm. to obtain a pure sample. Analysis thus far has afforded the only convincing proof of the identity of this substance.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{24}\text{Si}_8\text{O}_{12}$ : C, 17.9; H, 4.5; Si, 41.9. Found: C, 17.7; H, 4.3; Si, 41.4.

The combined high-boiling distillate (14.6 g.) from two one-half-mole runs was then dissolved in 50 ml. of hot methanol, filtered and allowed to stand eight days at –10°. The colorless solid that formed weighed 0.9 g. and melted at 117–119°. The melt was cloudy. After recrystallizing twice from methanol, the melting point was 124–126° and the melt was clear. No significant change in composition could be detected when the crude distillate from two more runs was heated under a reflux condenser in methanol solution for 3.5 hours. The  $-\text{OH}$  and  $-\text{OC}_4\text{H}_9$  contents were 2.0 and 16.2% before such treatment and 2.3 and 18.0% after treatment. The sample was redissolved in methanol and allowed to stand at –10° for three weeks. The solid obtained melted at 124–125°, after recrystallization, and showed no depression when mixed with the earlier sample of the monobutoxypolycyclosiloxane (structure I).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{30}\text{Si}_9\text{O}_{14}$ : C, 23.3; H, 5.4; Si, 37.8;  $\text{OC}_4\text{H}_9$ , 10.9; mol. wt., 669.2. Found: (first sample) C, 23.2, 23.1; H, 6.0, 5.7; Si, 37.1;  $\text{OC}_4\text{H}_9$ , 10.8; mol. wt., 555, 711, 720; (second sample) C, 23.3, 23.4; H, 5.6, 5.5; Si, 37.2.

The action of fresh methanol, containing a catalytic amount of hydrochloric acid, on the recovered oily product from these runs did not produce more of the 125° melting compound.

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(5) The acid concentration is essentially zero after completion of the Dean–Stark trap operation. The acid therefore must be replenished.

(4) (a) D. W. Scott, *THIS JOURNAL*, **68**, 356 (1946), first observed the appearance of a sublimable solid of this empirical composition; (b) A. J. Barry, W. H. Daudt, J. W. Gilkey and J. L. Domicone, Abstracts of Papers, Cincinnati Meeting of the American Chemical Society (1955), discussed the structures of polymethylsilsesquioxanes.