trisilane, and some dichlorosilane. Chlorodisilane[17] was not obtained.

4. **Pyrolysis of Digermane.**—The pyrolysis of digermane was examined in the same flow apparatus as previously described.[1] The product trap was set at −45°. Germane was found in the −196° trap, digermane was found in the −130° trap having passed a −95° trap, and trigermane passed a −36° trap and condensed in a −63° trap. The trigermane was identified by a mass spectrum which contained only peaks from the ions of heavy-atom skeletons, Ge_3^+ (25.5%), Ge_2^+ (64.3%), and Ge^+ (10.2%). The infrared spectrum was identical with that reported by MacKay and Robinson[18] while the strong 812-cm^{-1} absorption from germane[19] and the strong 750-cm^{-1} absorption from digermane[20] were absent.

5. **Thermal Reaction of Ge_2H_6 with $C_2H_5GeD_3$.**—Digermane (0.41 mmol) and ethylgermane-d_3 (1.80 mmol) were pyrolyzed at 280° for 24 hr with the product trap set at −63°. Under the conditions, very small quantities of products were obtained. The product fraction condensed in the −196° trap was identified by infrared and mass spectra to be germane. The strong 706-cm^{-1} band of germane-d_1[21] was absent from the infrared spectrum. The fraction condensed at −95° was the unreacted ethylgermane-d_3. The fraction which passed the −45° trap and condensed in the −63° was a mixture of ethyldigermanes and trigermane. The mass spectrum of this mixture consisted of ions with the following heavy-atom skeletons: Ge_3^+ (7.2), $C_2Ge_2^+$ (22.2), Ge_2^+ (100), C_2Ge^+ (68.9), and Ge^+ (62.2). No diethyldigermanes were observed.

In a control experiment, no products were observed from the 5-hr pyrolysis of ethylgermane-d_3 at 320° with the trap set at −54°, which gave a higher reaction pressure than with the bath set at −63°.

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The Direct Synthesis of Organic Derivatives of Silicon Using Nonhalogenated Organic Compounds

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Some trialkoxysilanes, $(RO)_3SiH$ ($R = CH_3$, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_4H_9$), and tetraalkoxysilanes were prepared directly by the reactions of the appropriate primary alcohol with a silicon–copper contact mixture. Similar attempts with secondary and tertiary alcohols, ethers, and secondary amines gave no silicon-containing products.

Introduction

With the discovery in 1940 of the direct synthesis, the problems of large-scale production of organosilicon halides were solved, in large part. The first paper described the high-temperature reaction of chloromethane with elemental silicon, in the presence of a copper catalyst in a flow system, from which mixtures of methylchlorosilanes were obtained.[2] This process was discovered independently and later by two other chemists.[3] Since that time, much effort has been spent on attempts to elucidate the mechanism of this process and also to extend its application. The scope of the direct synthesis has now been successfully widened to include the reactions of: (a) other aliphatic chloro compounds, *e.g.*, *n*-propyl, isopropyl, etc.;[4–8] (b) aromatic halo compounds, *e.g.*, bromobenzene and chlorobenzene;[9–11] (c) olefinic chloro compounds, *e.g.*, allyl chloride;[12–15] (d) polyfunctional compounds, *e.g.*, dichloroalkanes;[16–21] (e) silicon-containing aliphatic chlorides, *e.g.*, γ-chloropropylmethyldichlorosilane;[22–28] (f) other elements, *e.g.*, germanium, tin, thallium,

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and arsenic;[29–35] (g) other halides;[2] (h) alcohols and phenols, with limited success;[36–44] and (i) ethers, probably with no success.[41,45]

The present work was undertaken in order to study further the reactions of *non*halogenated organic compounds, particularly alcohols, with elemental silicon. It had previously been found that only methanol reacted to any great extent when passed over a silicon–copper contact mixture (prepared by sintering a 9:1 mixture of silicon and copper in hydrogen at ~1000–1100° for *ca.* 2 hr) which had been heated to 250–300°.[36–38] The main product of that reaction was tetramethoxysilane, in *ca.* 40–50% yields, and not dimethyldisilanol or dimethylpolysiloxane, indicating that this reaction takes a different course from that for chloromethane, *viz.*, $4CH_3OH + Si \rightarrow (CH_3O)_4Si + 2H_2$ compared with $2CH_3Cl + Si \rightarrow (CH_3)_2SiCl_2$.

The hydrogen which was evolved complicated the reaction by reducing methanol to methane (which was trapped and identified) and water (which hydrolyzed some tetramethoxysilane to methoxysiloxanes). It was found that the efficiency of the process decreased with time and, after a while, stopped completely.[36]

In an attempt to improve the efficiency of this process, fluidized-bed techniques have been used. It was found that, under certain conditions, all the silicon–copper contact mass was used up, giving mixtures of $(CH_3O)_2SiH_2$, $(CH_3O)_3SiH$, and $(CH_3O)_4Si$ as products.[46] Another approach, which has been suggested, is to use ferrosilicon and calcium silicide as starting materials, in suspension in the esters of silicic and polysilicic acids, but the products of such a synthesis have not been specified.[47]

Results and Discussion

Preliminary investigations in this present work, using methanol and tubes packed with 100 g of a 9:1 silicon–copper contact mixture (prepared by heating the mixture in hydrogen at 1050° for 2 hr) heated to *ca.* 280°, confirmed the above work and indicated that the contact mixture lost its activity rather quickly under those conditions. It was found that for the first 25 ml of methanol passed, *ca.* 75% yields of $(CH_3O)_4Si$ were obtained, while after the passage of 100 ml of methanol, the overall yield had dropped to *ca.* 40–45%. By the time 300 ml of methanol had been passed, no more silicon-containing products were observed. In all these experiments, small amounts of high-boiling liquids and colorless solids also were obtained. Even though no silicon–hydrogen bonded compounds were observed in the distillates boiling below 120°, these high-boiling liquids and solids all showed, in their infrared spectra, absorptions in the silicon–hydrogen stretching vibration region at ~2200 cm^{-1}, plus carbon–hydrogen stretching vibrations typical of methoxy groups.[48] The solids also evolved molecular hydrogen on treatment with mineral acid. These compounds are thought to be cross-linked polysiloxanes with varying numbers of hydrogen atoms and methoxy groups on the silicon atoms.

Owing to the rapid loss of activity in the packed-tube syntheses, probably due to the poisoning of the relatively small active surface available, an experiment was devised in which it was hoped that fresh active surfaces would continually be presented to the methanol. A 9:1 silicon–copper contact mixture was prepared as above, ground into a powder and transferred, under N_2, to a 3-l. reaction vessel containing silicone oil. This suspension was stirred rapidly and heated to *ca.* 280°. Methanol, under a slight pressure of nitrogen, was then added slowly below the surface of the suspension. The condensate was collected and the products separated by distillation. The main products of this reaction were $(CH_3O)_3SiH$ and $(CH_3O)_4Si$, in a combined yield of *ca.* 45% based on complete conversion of the methanol to tetramethoxysilane.

In order to determine whether this adaptation of the direct synthesis would prolong the life of the active catalyst and also to compare the activity of two samples of elemental silicon (one from General Electric Co. and a second from Bremanger Smelteverk, Svelgen, Norway, which had been pretreated with a boiling saturated solution of ferric chloride in concentrated hydrochloric acid so giving a highly etched product of high purity), two series of experiments, similar to the one above, were carried out. In both cases, methanol was added in 100-ml batches and the products of each batch were collected and separated individually. The addition of methanol was continued until all reaction had ceased. Typical results for these experiments are given in Table I.

These experiments show that, while still active, General Electric silicon gave 113.8 g of $(CH_3O)_3SiH$ and 20.9 g of $(CH_3O)_4Si$, equivalent to 163 g of $(CH_3O)_4Si$, from 400 g of methanol, while Bremanger Smelteverk silicon gave only 44.3 g of $(CH_3O)_3SiH$ and 23.9 g of $(CH_3O)_4Si$, equivalent to 79 g of $(CH_3O)_4Si$, from 320 g of methanol. The yields, based on complete conversion of methanol to $(CH_3O)_4Si$, are therefore 34.3 and 20.8%, respectively. These results show that the purer, more highly etched, Bremanger Smelteverk silicon is less active in this process than the General Electric

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TABLE I

RESULTS FOR THE REACTIONS OF METHANOL WITH THE SILICON–COPPER CONTACT MASS

Batch no.	Amt of methanol, g	Amt of condensate, g	Amt of products, g			
			Azeotrope[b] (bp 62–63°)	$(CH_3O)_3SiH$ (bp 82–84°)	$(CH_3O)_4Si$ (bp 120–122°)	Residue[c] (bp >130°)
			Expt 1[a]			
1	80.0	78.9	$57.6\begin{cases} 11.5\ (CH_3O)_3SiH \\ 46.1\ CH_3OH \end{cases}$	6.5	2.3	12.5
2	80.0	91.9	$57.0\begin{cases} 11.4\ (CH_3O)_3SiH \\ 45.6\ CH_3OH \end{cases}$	12.1	2.1	20.7
3	80.0	89.0	$65.0\begin{cases} 13.0\ (CH_3O)_3SiH \\ 52.0\ CH_3OH \end{cases}$	3.6	Nil	20.4
4	80.0	80.8	$59.7\begin{cases} 17.5\ (CH_3O)_3SiH \\ 42.2\ CH_3OH \end{cases}$	12.9	2.8	5.4
5	80.0	82.1	$50.3\begin{cases} 10.1\ (CH_3O)_3SiH \\ 40.2\ CH_3OH \end{cases}$	15.2	13.7	2.9
6	80.0	70.3[d]	Nil	Nil	Nil	6.2
			Expt 2[a]			
1	160.0	180.3	$133.9\begin{cases} 26.8\ (CH_3O)_3SiH \\ 107.1\ CH_3OH \end{cases}$	11.4	18.1	16.9
2	160.0	161.1	Nil[e]	6.1[e]	5.8	16.9
3	80.0	89.4[f]	Nil	Nil	Nil	10.0

[a] Experiment no. 1 is for General Electric silicon; experiment no. 2 is for Bremanger Smelteverk silicon. [b] Shown to consist of 20% $(CH_3O)_3SiH$ and 80% CH_3OH by integration of nmr spectra. [c] Consists of suspension oil with some liquid and solid polysiloxanes. [d] Contains 64.1 g of CH_3OH. [e] Distillate below bp 120°, shown by nmr integration, to contain 6.1 g of $(CH_3O)_3SiH$ and 132.3 g of CH_3OH. [f] Contains 79.4 g of CH_3OH.

TABLE II

RESULTS FOR THE REACTIONS OF HIGHER ALCOHOLS WITH THE SILICON–COPPER CONTACT MASS

Alcohol	Amt of alcohol, g	Temp,[a] °C	Amt of products, g				Overall yield,[d] %
			$(RO)_3SiH$	$(RO)_4Si$	Residue[b]	Recovered alcohol[c]	
Ethyl	240	260–270	27.8	7.0	1.3	188.4	15.5
n-Propyl	240	290–310	9.7	Nil	2.9	217.6	4.8
Isobutyl	80	300	5.6	Nil	0.6	70.6	8.3

[a] Temperature of the suspension medium. [b] Consists of suspension oil, plus very small amounts of alkoxypolysiloxanes. [c] In all cases, small amounts of benzene were also present. [d] Calculated as per cent $(RO)_4Si$, based on complete conversion of all the alcohol to this product.

silicon and indicate that perhaps the small amounts of impurities in elemental silicon are more important for reaction than high surface area.

If the results using General Electric silicon are compared with those obtained previously from a packed-tube experiment which was allowed to proceed to completion,[36] they indicate that this present work succeeds in converting 33% of silicon into organosilicon compounds compared with only 21% for the packed tube.

Because of the success encountered for these syntheses in suspension, similar experiments were then attempted for other alcohols. A previous report states that, in packed-tube experiments, yields approaching 10% of tetraethoxysilane were obtained with ethanol,[36] but no reactions involving alcohols of higher molecular weight have been reported in the literature. In this present work, it was found that the lower primary alcohols, ethanol, 1-propanol, and isobutyl alcohol, reacted with the contact mixture in suspension to give small yields of mainly the trialkoxysilane, but that isopropyl, *n*-butyl, *sec*-butyl, and *t*-butyl alcohols did not react. The positive results are set out in Table II.

For the experiments using isopropyl, *sec*-butyl, and *t*-butyl alcohols, the condensates contained only the alcohol, plus small amounts of benzene and the suspension oil. With 1-butanol, the condensate was thought to contain (besides the unchanged alcohol) butyraldehyde, benzene, and water, plus possibly some butane.

It then seemed important to attempt to extend this work to nonhalogenated organic compounds other than alcohols. Similar experiments were carried out with dimethyl ether, diethyl ether, dimethylamine, and diethylamine, but no silicon-containing products could be detected in any of these experiments.

As the generally accepted order of acidities for alcohols is primary > secondary > tertiary and as only primary alcohols are observed to react in this work, it appears likely that the reactivity of the alcohol is dependent upon its acidity. Using the Taft polar substituent constants, for R in ROH, as measures of acidity,[49] it may be assumed that acidity decreases in the order $CH_3 > C_2H_5 > n\text{-}C_3H_7 > i\text{-}C_4H_9 > n\text{-}C_4H_9 > i\text{-}C_3H_7 > sec\text{-}C_4H_9 > t\text{-}C_4H_9$. It is therefore very interesting to observe that the four most acidic alcohols (on this scale) are the ones that react to give organic derivatives of silicon and also that the yields obtained decrease in approximately the same order as the acidities. Because of this trend, it was considered of interest to study the effect of substitution, in methanol, of electron-withdrawing groups which, it was hoped, would increase the

(49) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

acidity and so increase the yields of products. The phenyl and methoxymethyl groups were chosen as suitable examples, and their reactions with the silicon–copper contact mass were studied.

Under similar reaction conditions to those outlined above, it was found that benzyl alcohol gave no detectable silicon-containing compounds. The products that were observed—benzaldehyde, toluene, benzene, and water—indicated that a reduction process was occurring, possibly similar to that encountered in the reaction of 1-butanol. No other compounds could be isolated from the contact suspension.

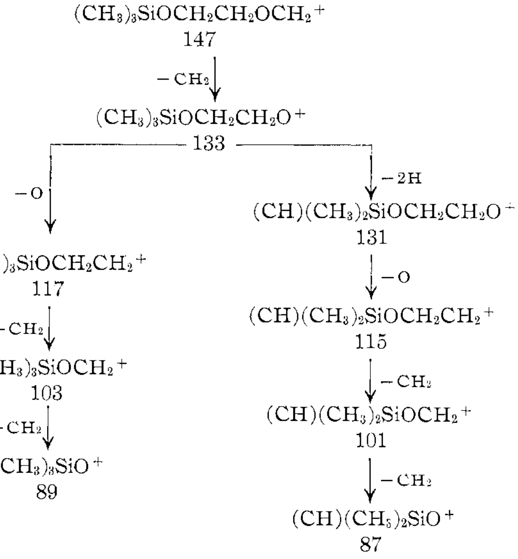
In the reactions involving 2-methoxyethanol, the presence of compounds containing silicon was indicated by both infrared and nuclear magnetic resonance spectroscopy, but much difficulty was encountered during the attempted separation of the small amount of those products from the unreacted alcohol and benzene produced as a by-product. Acetaldehyde was also a product of this reaction. After three distillations on a spinning-band column (of *ca.* 20 theoretical plates), all fractions still contained the alcohol and benzene. The boiling points of the fractions were all in the range 50–100°. The infrared and nmr spectra of all fractions were similar, varying only in the relative intensities of the bands. In the infrared spectra, diagnostic bands at $\sim$3400 cm^{-1} (OH stretching), 1252 cm^{-1} (Si–CH_3 symmetric deformation), and 1200 cm^{-1} (CH_3 rocking), plus bands at 1110 and 840 cm^{-1} (possibly CO and SiO stretching, respectively) but none at $\sim$2200 cm^{-1} (SiH stretching), were observed.[48] In the nmr spectra, resonances at τ 9.88, 9.82, 9.79 (Si–CH_3), 4.3–4.9 (O–CH_2–, etc.), and 5.25 (probably –OH) also helped in indicating the presence of various groupings on silicon. Together, these data indicate a mixture of organosilicon compounds in the condensate, possibly of the types $\geqslant SiCH_3$, $\geqslant SiOCH_3$, $\geqslant SiOCH_2CH_2OCH_3$, $\geqslant SiCH_2CH_2OH$, etc. Mass spectrometry also indicated the presence of organosilicon compounds. A series of fragments was observed that fit the pattern shown in Scheme I.

The fragment of mass 133 could be rewritten as $(CH_3)_2(CH_3O)SiOCH_2CH_2^+$, but the next fragmentation would almost certainly result in the loss of CH_2 (14) or CH_3 (15), whereas only a loss of mass 16 (O) is observed. Also the two hydrogen atoms lost, to give mass 131 from mass 133, need not be from the same methyl group, but it is suggested that they originate from the methyl groups in order to explain the successive losses of mass 14 (CH_2) in the steps mass 115 → mass 101 → mass 87, either from the chain (as shown above) or by loss of the CH_2 groups from the silicon atom or from a combination of both.

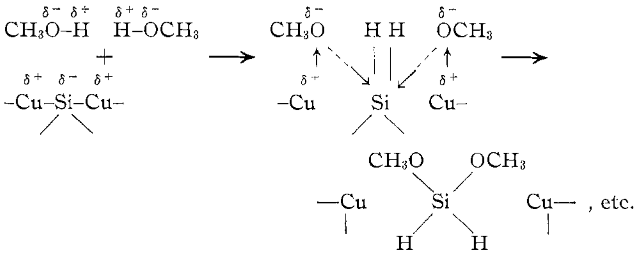
Therefore, the expected reaction pathway, *i.e.*, the reaction of the hydroxyl group to give compounds of the type $(CH_3OCH_2CH_2O)_nSiH_{4-n}$, is not followed in this case, and possibly (instead of the methoxy group increasing the activity of the hydroxyl group) some activation of the ether linkage has occurred. It may be that reactions using alcohols of this type will result in the direct synthesis of the types of products expected from ether reactions, and possibly (using 2-aminoethanol etc.) silicon–nitrogen compounds may be prepared directly also.

Scheme I

Possible Fragmentations of the Product from the Reaction of 2-Methoxyethanol



Mechanism.—If a similar picture to that now generally accepted for the mechanism of the direct reaction of chloromethane[50] is applied to the alcohol reactions, then we have



It has been observed, though, that $(CH_3O)_2Cu$ does not react with elemental silicon at temperatures approaching 400°, when only pyrolysis occurs and methanol and formaldehyde are formed.[51] Therefore, either the polarization on the surface of the contact mixture varies depending upon the reactants, or (more likely) the conditions experienced in these two reactions differ so much as to make such comparisons worthless.

Experimental Section

Preparation of the Contact Mixture.—Elemental silicon (90 g), in the form of small grains (*ca.* 60 mesh), and copper powder (10 g) were mixed together and placed in a silica-glass tube. Hydrogen gas was passed in, and the tube heated to *ca.* 1050° for 2 hr. It was then allowed to cool under hydrogen. The sintered contact mixture was ground up and transferred to a reaction vessel for immediate use.

Reactions of Primary Alcohols with Silicon–Copper Contact Mixtures in Suspension. Methanol.—A dry 3-l. reaction vessel, containing Dow Corning DC710 silicone oil (450 ml) and a 9:1

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(50) W. Noll, "Chemie und Technologie der Silicone," Verlag Chemie GmbH, Weinheim/Bergstrasse, Germany, 1968, p 24, and references therein; see also V. Bažant, *et al.*, "Organosilicon Compounds," Vol. 1, Academic Press, New York, N. Y., 1965.

(51) U. Goetze, private communication.

silicon–copper contact mixture (100 g), was equipped with an electric stirrer, a thermometer probe, an inlet tube that extended below the surface of the reaction suspension, and an exit, leading to a water condenser, a receiver, and a −78° cold trap, protected by a calcium chloride guard tube. The predried apparatus was assembled, and the experiment was carried out, in a stream of nitrogen dried by passage over phosphorus pentoxide.

Methanol (100 ml, 80 g) was then added dropwise, over a 4–5-hr period, to the rapidly stirred reaction suspension heated to *ca.* 280°, and the products were collected and distilled. A 1:4 azeotrope of trimethoxysilane and methanol (50.0 g; bp 62–63°; identified by infrared[52] and nmr spectra), trimethoxysilane (18.2 g; bp 81–83°, lit.[52] bp 84°. *Anal.* Calcd for $C_3H_{10}O_3Si$: C, 29.5; H, 8.3. Found: C, 29.9; H, 8.5; confirmed by infrared spectrum.[52]), tetramethoxysilane (14.4 g; bp 120–122°, lit.[53] bp 121°. *Anal.* Calcd for $C_4H_{12}O_4Si$: C, 31.6; H, 8.0. Found: C, 31.8; H, 8.3; confirmed by infrared spectrum.[48]), and a residue (4.6 g; infrared spectroscopy indicated a mixture of DC710 silicone oil and some polysiloxane) were obtained.

Ethanol.—In a similar experiment, ethanol (300 ml, 237 g) was added to a silicon–copper contact mixture in suspension at 260–270°. On distillation, ethanol (188.4 g; bp 78–80°; identified by infrared spectrum), triethoxysilane (27.8 g; bp 132–134°, lit.[53] bp 131°. *Anal.* Calcd for $C_6H_{16}O_3Si$: C, 43.9; H, 9.8. Found: C, 44.5; H, 9.7), tetraethoxysilane (7.0 g; bp 163–166°, lit.[53] bp 166–168°. *Anal.* Calcd for $C_8H_{20}O_4Si$: C, 46.1; H, 9.7. Found: C, 45.8; H, 9.6; confirmed by infrared spectrum.[48]), and a residue (1.3 g; infrared spectroscopy indicated DC710 silicone oil only) were obtained.

1-Propanol.—In a similar experiment at 290–310°, 1-propanol (300 ml, 240 g) was used. The condensate from the reaction contained unreacted alcohol (217 g; bp 94–98°; identified by infrared spectrum), tri-*n*-propoxysilane (9.7 g; bp 186–188°, lit.[53] bp 190–194°; identified by infrared and nmr spectroscopy; mol wt: found by mass spectrometry, 206; calcd, 206), and a residue (2.9 g; infrared spectroscopy indicated DC710 silicone oil only).

Isobutyl Alcohol.—Isobutyl alcohol (100 ml, 82 g) was used, in a similar experiment, at 300°. On distillation, unreacted alcohol (70.6 g; bp 107–108°; identified by infrared spectrum), triisobutoxysilane (5.6 g; bp 218–222°, lit.[53] bp 224–228°; identified by infrared and nmr spectroscopy; mol wt: found by mass spectrometry, 248; calcd, 248), and a residue (0.6 g; infrared spectroscopy indicated DC710 silicone oil only) were obtained.

1-Butanol.—With 1-butanol (100 ml, 81 g), the condensate foamed considerably upon distillation, and a liquid was trapped at −78°. This liquid boiled at *ca.* 0° and burned when vaporized through a jet. It was thought to be butane. A fraction of boiling range *ca.* 60–100° (33.1 g), which separated into two layers on cooling (infrared and nmr spectroscopy indicated that the upper layer was a mixture of 1-butanol, benzene, and butyraldehyde and the lower layer was water), and some unreacted alcohol (44.3 g; bp 114–118°; identified by infrared spectrum) also were obtained.

Benzyl Alcohol.—Using benzyl alcohol (100 ml, 105 g), the condensate from the reaction at 300° gave, on distillation, the 9:1 azeotrope of benzene and water (51.0 g; bp 66–70°, lit.[54] bp 69°), benzene (23.2 g; bp 78–80°; identified by infrared spectrum), toluene (6.3 g; bp 108–110°; identified by infrared spectrum), benzaldehyde (4.0 g; bp 175–180°; identified by infrared spectrum), unreacted alcohol (7.0 g; bp 198–200°, lit.[54] bp 205°; identified by infrared spectrum), and a residue (12.0 g; infrared spectroscopy indicated DC710 silicone oil only).

2-Methoxyethanol.—Using 2-methoxyethanol (100 ml, 97 g), in a similar experiment at 280°, no pure fractions could be obtained on distillation. Arbitrary cuts in the distillation at 60, 80, and 100° gave fractions containing similar mixtures of products (infrared and nmr spectroscopy indicated mixtures of acetaldehyde, benzene, a silicon–methyl compound, an Si–O–C type of compound, and some unreacted alcohol but no Si–H compounds or DC710 silicone oil). The benzene probably came from the silicone oil, which is apparently a methylphenylpolysiloxane. Unreacted 2-methoxyethanol (86.4 g; identified by infrared spectroscopy) was obtained as a residue.

Other Organic Reactants.—Similar experiments, at temperatures of *ca.* 300°, with isopropyl alcohol, *sec*-butyl alcohol, *t*-butyl alcohol, dimethyl ether, diethyl ether, dimethylamine, and diethylamine gave condensates in which only the reactants and no silicon-containing compounds were observed.

Materials.—The elemental silicon used (except where stated above) was commercial massive silicon, crushed to *ca.* 60-mesh size, obtained from General Electric Co. Silicone Products Department. Copper powder was prepared by the reduction of copper oxide in hydrogen. The alcohols were Fisher Scientific Co. Certified grade, except for benzyl, *sec*-butyl, and 2-methoxyethyl alcohols (which were obtained from Eastman Organic Chemicals) and ethanol (from Commerical Solvents Corp.). In all cases, the alcohols were used as received.

Spectroscopy.—Infrared, nuclear magnetic resonance, and mass spectra were obtained using a Perkin-Elmer 337 grating spectrometer, a Varian Associates A-60 nmr spectrometer, and an AEI MS9 spectrometer, respectively.

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