EXPERIMENTAL[13]

Preparation of the diepoxydithymoquinone. A 413 mg. portion of the dithymoquinone, m.p. 198–200°, was dissolved in 10 ml. of pyridine to which 1.0 g. of sodium carbonate was added. To the mixture obtained 5 ml. of 30% hydrogen peroxide in 1 ml. portions was added gradually under stirring. The temperature of the reaction mixture rose to 40° and the liquid slowly became colorless. The solution was allowed to stand at that temperature for several minutes, diluted with 75 ml. of water and the colorless crystals that separated at this point were filtered off and washed with water to give 430 mg. of material m.p. 213–214°. Crystallization from chloroform/acetone mixture yielded colorless long plates weighing 378 mg., m.p. 217.7–218.5° (83%).

Anal. Calcd. for $C_{20}H_{24}O_6$: C, 66.65; H, 6.71; mol. wt., 360. Found: C, 66.42; H, 6.64; mol. weight (camphor), 370.

Ultraviolet absorption spectrum: Inflection point at λ 290 mμ, log ϵ 2.28 (alcohol). Infrared absorption spectrum: ν_{max} 1715 cm.$^{-1}$ (carbonyl, KBr pellet); no OH band (Nujol).

Preparation of diepoxythymoquinone. A 1.148 g. portion of thymoquinone m.p. 44–44.5° was dissolved in 10 ml. of acetone. To the resulting solution 0.5 g. of sodium carbonate, followed by 3 ml. of 30% hydrogen peroxide solution was added and the liquid heated on a steam bath to the complete discoloration point. The mixture obtained was diluted to 125 ml. with water and acidified with 10% hydrochloric acid. Saturation of the solution with sodium sulfate and scratching induced the separation of diepoxide. The mixture was allowed to stand overnight to complete the crystallization. The separated crystalline material was filtered off to give 720 mg. of a colorless solid, m.p. 85–89° (53%). Further purification was achieved by crystallizations from methanol/water and iso-octane that raised the melting point of the material to 89.6–90.4°.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 61.34; H, 6.24.

Ultraviolet absorption spectrum: λ_{max} 307 mμ, log ϵ 1.54; λ_{min} 271 mμ, log ϵ 1.37 (alcohol). Infrared absorption spectrum: ν_{max} 1720–5 cm.$^{-1}$ (carbonyl) (KBr pellet); no OH band (Nujol).

Dithymoquinone was prepared according to Liebermann and Ilinski[14] and was purified by recrystallization from iso-octane chloroform, m.p. 198–200°. Ultraviolet absorption spectrum: λ_{max} 238–239 mμ, log ϵ 4.39; 385 mμ, log ϵ 2.37; λ_{min} 310–312 mμ, log ϵ 1.90 (alcohol). Infrared absorption spectrum: ν_{max} 1665 cm.$^{-1}$ (carbonyl), 1610–1615 cm.$^{-1}$ (conj. double bond) (KBr pellet); no OH band ($CHCl_3$ solution).

Di-2-methylnaphthoquinone was prepared according to Madinaveitia,[10] and crystallized from ethanol/dimethylformamide, m.p. 234–236°. Ultraviolet absorption spectrum: λ_{max} 227 mμ, log ϵ 4.56, infl. point at 254–256 mμ, log ϵ 4.08; λ_{max} 303 mμ, log ϵ 3.37, infl. point at 340–350 mμ, log ϵ 2.34–2.28 (alcohol). Infrared absorption spectrum: ν_{max} 1690 cm.$^{-1}$ (carbonyl), 1595 cm.$^{-1}$ (aromatic) (KBr pellet); no OH band (Nujol).

Epoxy-2-methylnaphthoquinone was prepared according to Fieser *et al.*,[11] m.p. 94–95°.

Ultraviolet absorption spectrum: λ_{max} 227 mμ, log ϵ 4.47; 265–266 mμ, log ϵ 3.76; 303 mμ, log ϵ 3.28; infl. point at 340 mμ, log ϵ 2.41 (alcohol). Infrared absorption spectrum: ν_{max} 1695 cm.$^{-1}$ (carbonyl), 1595 cm.$^{-1}$, (aromatic) (KBr pellet).

Nuclear Magnetic Resonance spectra (Fig. 2) were obtained at 40 mc. frequency using carbon disulfide as the solvent in case of thymoquinone and deuterated chloroform in case of dithymoquinone.

Acknowledgment. The author is indebted to Dr. James N. Shoolery and Mr. Robert C. Jones of Varian Associates for their invaluable cooperation in connection with the recording and interpreting of the NMR spectra.

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[13] All melting points are corrected; microanalysis by Microchemical Laboratory, University of California, Berkeley. Ultraviolet and infrared spectra were run on Beckman DK II and Perkin Elmer Model 21 recording spectrophotometers, respectively, and the NMR spectra on Varian Associates high resolution NMR spectrometer.

[14] C. Liebermann and M. Ilinski, *Ber.* **18**, 3193 (1885).

[CONTRIBUTION OF CENTRAL EXPERIMENT STATION, U. S. DEPARTMENT OF THE INTERIOR, BUREAU OF MINES]

Preparation and Properties of Trimethylsilyl Ethers and Related Compounds

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Preparative methods for trimethylsilyl ethers have been investigated. Hexamethyldisilazane (III) has been found to be a convenient reagent for converting alcohols and primary amines to their trimethylsilyl derivatives. The reaction is apparently acid catalyzed. The trimethylsilyl ethers of less reactive alcohols may be prepared from the reaction of equivalent amounts of trimethylchlorosilane and hexamethyldisilazane with the alcohol. The preparation and properties of 22 new trimethylsilyl derivatives of alcohols, phenols, and amines are reported. Trimethylbutylmercaptosilane has also been prepared.

The potential usefulness of trimethylsilyl ethers in separation procedures was strikingly demonstrated by Martin[1] through the isolation of trimethylolphenol as its trimethylsilyl derivative. More recently, a number of other investigators[2–4] have pointed out the utility of trimethylsilyl derivatives for isolation purposes. These derivatives

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[1] R. W. Martin, *J. Am. Chem. Soc.*, **74**, 3024 (1952).

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

[3] C. A. Burkhard, J. V. Schmitz, and R. E. Burnett, *J. Am. Chem. Soc.*, **75**, 5957 (1953).

[4] C. A. Burkhard, *J. Org. Chem.*, **22**, 592 (1957).

are useful for separation by distillation because of their ease of formation, resistance to oxidation, good heat stability, low viscosity, and the ease of recovery of the parent compound.

In a number of current investigations related to the development of liquid fuels from coal, trimethylsilyl derivatives have been found useful for analytical and identification purposes as well as in purification and separation procedures. For example, it is possible to distill phenolic portions of coal hydrogenation products as trimethylsilyl derivatives at atmospheric pressure without significant decomposition. During the course of these investigations, particularly mass spectrometric work,[5] it was necessary to prepare a number of relatively pure samples of trimethylsilyl ethers. We report here the results of an investigation of the preparation of trimethylsilyl derivatives as well as the properties of these trimethylsilyl ethers (I) and related compounds.

Preparation. The following preparative methods for trimethylsilyl ethers (I) were considered in this study: 1. Preparation of the sodium alkoxide from sodium hydride and an alcohol, followed by reaction with trimethylchlorosilane (II).

$$\mathrm{NaH + ROH \longrightarrow NaOR + H_2} \qquad (1)$$

$$\underset{\mathrm{II}}{\mathrm{(CH_3)_3SiCl}} + \mathrm{NaOR} \longrightarrow \mathrm{NaCl} + \underset{\mathrm{I}}{\mathrm{(CH_3)_3SiOR}} \qquad (2)$$

This modification of a Williamson-type synthesis is similar to the synthesis of triethylsilyl ethers by Roberts and Mazur,[6] who used triethylbromosilane instead of II in reaction (2).[7] While this reaction sequence was used in the preparation of a number of trimethylsilyl ethers, it is limited by the difficulty of obtaining complete initial reaction between the sodium hydride and alcohol. This is probably a mechanical problem. Yields were particularly poor with the higher alcohols, such as decanol.

2. Reaction of an alcohol or phenol with trimethylchlorosilane directly as in (3) or in the presence of an amine as in (4).

$$\mathrm{(CH_3)_3SiCl + ROH \rightleftharpoons (CH_3)_3SiOR + HCl} \qquad (3)$$

$$\mathrm{(CH_3)_3SiCl + ROH + amine \longrightarrow (CH_3)_3SiOR + amine\ hydrochloride\ salt} \qquad (4)$$

For the case where R is aliphatic in (3), the situation is complicated by the fact that an equilibrium is involved,[11] as well as by the possibility of the reaction of the alcohol with hydrochloric acid to give an alkyl halide.[12] The appreciable solubility of hydrochloric acid in alcohol solutions aids the reverse reaction in (3). Use of an aliphatic hydrocarbon solvent and elevated temperatures is desirable to cut down the acid solubility. Importance of the latter factor is illustrated by comparing the attempted preparation of nonyl and decyl trimethylsilyl ethers according to (3). With reaction run at reflux temperatures the use of low-boiling petroleum ether (35°–55°) solvent resulted in recovery of reactants, while product was obtained in good yield from a petroleum ether solvent with a 90°–100° boiling range.

Where the hydroxyl group in (3) is phenolic, interaction between phenol and hydrochloric acid can be ignored and trimethylsilyl ethers can be prepared in good yield.[13]

Reaction according to equation 4 was employed by Sauer[14] in the initial characterization of trimethylsilyl ethers. Under ordinary conditions pyridine is a preferred base[1–4,14,15] for use as the acid acceptor. While we have used this reaction successfully to prepare nonyl trimethylsilyl ether and it is reported to give high yields of product,[2] the use of pyridine and the necessity for filtering and washing the precipitate of pyridine hydrochloride were distinct disadvantages.

3. For routine synthesis, we have found the reaction between hexamethyldisilazane (III) and an alcohol to be most convenient in the preparation of aliphatic trimethylsilyl ethers:[13]

$$\underset{\mathrm{(III)}}{\mathrm{(CH_3)_3SiNHSi(CH_3)_3}} + \mathrm{2ROH \longrightarrow 2ROSi(CH_3)_3 + NH_3} \qquad (5)$$

The reaction of alcohols with III is effectively catalyzed by the availability of a proton, though it does take place in the absence of acid. Acid was gen-

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[5] A. G. Sharkey, Jr., R. A. Friedel, and S. H. Langer, *Anal. Chem.*, **29**, 770 (1957); S. H. Langer, R. A. Friedel, I. Wender, and A. G. Sharkey, *The Use of Trimethylsilyl Derivatives in the Mass Spectrometric Analysis of Fischer-Tropsch Alcohols*, Division of Petroleum Chemistry, Symposium on Synthetic Fuels and Chemicals, 128th Meeting, ACS, Minneapolis, September 1955.

[6] J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

[7] Our use of a commercially available trialkylchlorosilane instead of a trialkylbromosilane in equation 2 is of special significance if the potential reaction between the respective trialkylhalosilanes and unreacted sodium hydride is considered. Sodium hydride apparently will not convert a Si—Cl bond to Si—H.[8,9] However, isolation of excess triethylsilane by Roberts and Mazur[6] in their preparation of triethylsilyl ethers indicates that unreacted sodium hydride does react with triethylbromosilane to give triethylsilane. Triethylsilane reacts almost quantitatively with alcohols as follows:[10]

$$\mathrm{(C_2H_5)_3SiH + ROH \xrightarrow{base} (C_2H_5)_3SiOR + H_2}$$

[8] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 2692 (1947).

[9] C. Eaborn, *J. Chem. Soc.*, 3077 (1950).

[10] F. P. Price, *J. Am. Chem. Soc.*, **69**, 2600 (1947); B. M. Dolgov, N. P. Kharitonov, and M. G. Voronkov, *Zhur. Obschei Khim.*, **24**, 1178 (1954).

[11] W. Gerrard and K. D. Kilburn, *J. Chem. Soc.*, 1536 (1956).

[12] The complex interaction between alcohols and hydrogen halides has recently been reviewed by W. Gerrard, R. W. Madden, and P. Tolcher, *J. Appl. Chem.*, **5**, 28 (1956).

[13] J. L. Speier, *J. Am. Chem. Soc.*, **74**, 1003 (1952).

[14] R. O. Sauer, *J. Am. Chem. Soc.*, **66**, 1707 (1944).

[15] S. W. Kantor, *J. Am. Chem. Soc.*, **75**, 2712 (1953).

erally generated by initial addition of a drop or two of trimethylchorosilane (Equation 3) after which precipitate (presumably ammonium salt) formed immediately.

The previously reported room temperature reaction between 5-chloropentanol and hexamethyldisilazane[13] is probably due to the presence of appreciable amounts of hydrochloric acid from the 5-chloropentanol. With only small amounts of hydrochloric acid present, reflux periods of several hours are necessary for complete reaction between hexamethyldisilazane and aliphatic alcohols.

Hexamethyldisilazane is not available commercially, but is readily prepared from the reaction of trimethylchlorosilane and ammonia.[14,16] It is a preferred reagent for converting suitable alcohols to their trimethylsilyl derivatives. No large amount of precipitate is handled, and the small amount of precipitate formed in the process of catalyzing reaction is removed during the course of the reaction by sublimation into the reflux condenser. The reaction is easily followed by the change (generally a rise) in reflux temperature in the reaction flask or by the evolution of ammonia. The reagent requires few precautions (do not excessively expose to atmospheric moisture) and is not noxious. The alcohol need not be anhydrous, since water reacts with hexamethyldisilazane to give trimethylsilanol and hexamethyldisiloxane,[14,16] both of which can be separated from trimethylsilyl ethers by distillation.

Experiments during the synthesis of 3-heptyl trimethylsilyl ether and the reaction of a commercial primary amyl alcohol mixture with hexamethyldisilazane clearly demonstrated the catalytic effect of hydrogen or ammonium ion on (5) and the retardation of reaction by a low concentration of potassium hydroxide. Similar effects on the reaction of hexamethyldisilazane with water under acidic and bais conditions have been reported.[16]

4. Reaction of alcohol, trimethylchlorosilane, and hexamethyldisilazane where an acid acceptor was necessary:

$$3ROH + (CH_3)_3SiCl + (CH_3)_3SiNHSi(CH_3)_3 \longrightarrow 3ROSi(CH_3)_3 + NH_4Cl \quad (6)$$

This represents a combination of equations (3) and (4), in which hexamethyldisilazane functions as a source of both acid acceptor (ammonia) and trimethylsilyl groups. A minimum amount of precipitate is formed. The reaction was especially useful for preparing trimethylsilyl derivatives of neopentyl and *t*-amyl alcohols. It is also suitable for rapid preparations of trimethylsilyl ethers.

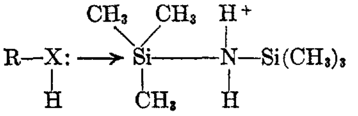
Other reactions of hexamethyldisilazane. Mjorne[17] reported the reaction of hexamethylsilazane with primary amines to give *N*-alkylaminosilanes as follows:

$$(CH_3)_3SiNHSi(CH_3)_3 + RNH_2 \longrightarrow 2(CH_3)_3SiNHR + NH_3 \quad (7)$$

Since reported yields for the *N*-alkyltrimethylsilane were low and because of the effect of hydrogen ion (or ammonium ion) on the reaction of hexamethyldisilazane with alcohols, the effect of a small amount of acid (formed by addition of trimethylchlorosilane) was studied. In the course of the synthesis of *N*-butyl and *N*-amyl trimethylsilyl derivatives we found that the presence of a small amount of acid had a pronounced accelerating effect on reaction of primary amines with hexamethyldisilazane (as evidenced by changes in reflux temperatures). However, a secondary amine did not react with hexamethyldisilazane even in the presence of acid. This difference might be useful for separating or identifying primary aliphatic amines in the presence of secondary and tertiary aliphatic amines.

In the case of butyl mercaptan, no reaction with hexamethyldisilazane takes place in the presence of even a stoichiometric amount of trimethylchlorosilane. However, trimethylbutylmercaptosilane was prepared by reaction of sodium butyl mercaptide with trimethylchlorosilane.

We have found it convenient to visualize the initial reaction of hexamethyldisilazane with an alcohol or amine in the presence of a proton in terms of an intermediate such as



$$\text{R}-\underset{\text{H}}{\text{X}}{:}\longrightarrow \overset{\text{CH}_3\ \ \text{CH}_3}{\underset{\text{CH}_3}{\text{Si}}}-\!\!-\!\!-\overset{\text{H}^+}{\underset{\text{H}}{\text{N}}}-\text{Si}(\text{CH}_3)_3$$

(IV)

where X may be O or NH.[18]

Almost all of our experimental observations can be explained in terms of IV, which may be a "pentacovalent intermediate"[19] or a conventional displacement reaction. Steric requirements would explain the failure of certain alcohols and secondary amines to react with hexamethyldisilazane. The low acidity of amines *per se* and the need for a proton in IV would account for the large accelerating effect of a small amount of acid on reaction of primary amines with hexamethyldisilazane.

Without further study, it is not possible to define the important factors responsible for the failure of butyl mercaptan to react with hexamethyldisilazane. However, in view of the comparatively low energy (compared to other Si bonds) of the Si-S[20] bond, it would seem that the driving force

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[16] R. O. Sauer and R. H. Hasek, *J. Am. Chem. Soc.*, **68**, 241 (1946).

[17] O. Mjorne, *Svensk. Kem. Tidskr.*, **62**, 120 (1950).

[18] This is analogous to the intermediate which may be inferred (principle of microscopic reversibility) for the reaction between alcohol, acid, and hexamethyldisiloxane. W. T. Grubb, *J. Am. Chem. Soc.*, **76**, 3408 (1954).

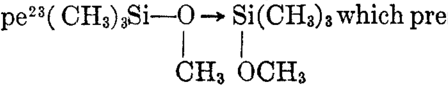
[19] C. G. Swain, R. M. Esteve, and R. H. Jones, *J. Am. Chem. Soc.*, **71**, 965 (1949).

[20] N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Clarendon Press, Oxford, Vol. I, XXXI. M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4125 (1953).

for reaction would also be relatively low.[9] It is of interest that while hydrogen sulfide reacts readily with triethylaminosilane or tripropylaminosilane to give a trialkylthiosilanol, it reacts with hexamethyldisilazane only with great difficulty.[21]

Physical properties. The boiling points, refractive indices, densities, and molar refractivities[22] of compounds prepared in this study are listed in Table I together with related literature data of interest. A comparison of the boiling points of normal aliphatic alcohols and their trimethylsilyl derivatives shows a crossover point in the C_3 and C_4 region above which the trimethylsilyl derivatives have the higher boiling points. Methyl and ethyl alcohols, of course, are cases of relatively strong hydrogen bonding. In general the boiling points of the trimethylsilyl derivatives are about 10°–15° higher than the parent alcohols. The boiling point elevation of 27° in the case of trimethylsilyl derivative of *t*-amyl alcohol is the highest reported for the trimethylsilyl ethers of monohydric alcohols. For amines and mercaptans where hydrogen bonding of the parent compounds plays a smaller role, boiling point elevation due to formation of the trimethylsilyl derivative is of the order of 60°. The lowering of the boiling point of a polyphenol such as resorcinol (b.p. 280°) through formation of its trimethylsilyl ether (b.p. 237°–240°) is another indication that these derivatives may be of special value in purifying compounds of this type. At present phenols are generally isolated as their methyl ether derivatives.

The abnormally high density of methyl trimethylsilyl ether relative to the ethyl ether and higher members of this series may be due to association of type[23] $(CH_3)_3\underset{CH_3}{\underset{|}{Si}}\text{—}\underset{OCH_3}{\underset{|}{O}} \rightarrow Si(CH_3)_3$ which presumably would be sensitive to steric hindrance.



There is reasonably good agreement between observed molar refractivities and those calculated from Warrick's bond refractivities.[22] The normal aliphatic trimethylsilyl ethers agree especially well. In the case of alkoxy groups branched at the 2- and 3-positions, deviations tend to be somewhat greater (calculated values are higher). This effect is apparently similar to that reported by Smith[24] for other alkoxysilanes; in these cases a deviation from the normal increase in bond refractions occurred when methyl groups were substituted for hydrogen atoms in the α- and β-carbons of alkoxy groups.

EXPERIMENTAL

In most preparative procedures, flasks equipped with thermometer wells were used. "Reflux temperature" refers to the temperature of the liquid while reactants were refluxing.

Densities were determined using a graduated 5-ml. Sprengel-Ostwald pycnometer. They were reproducible to 3×10^{-4} upon repeated measurement or independent synthesis. Densities are reported only to the third significant figure, however, for compounds where purity of product did not justify greater accuracy. Physical constants not given in the text are to be found in Table I.

Reactants were protected from moisture by a drying tube containing small amounts of Drierite.

The structures assigned to all trimethylsilyl derivatives described here are consistent with their observed mass spectra.[5] Purity of these products was also checked with the mass spectrometer; peaks characteristic of alcohols[25] were at a minimum intensity. In cases of doubt the trimethylsilyl derivatives were resynthesized.

The trimethylsilyl derivatives described here were prepared on a relatively small scale. Thus the column holdup (4–6 ml.) of the Podbielniak column used for purification appreciably affected the reported yields of pure products.

Materials. Most of the alcohols used were commercially available samples which were purified by distillation through a 2-foot × 8-mm. Podbielniak column. In some cases Eastman high-purity reagents were used directly. Neopentyl alcohol was obtained from the Chemicals Procurement Co. In all cases physical constants agreed with best literature values. Amines were dried by distillation from sodium.

When used directly as a reagent, the Dow Corning technical grade trimethylchlorosilane was distilled through a 12-plate glass helix-packed column. Only heartcut material, b.p. 57.7°, was used (lit. b.p. 57.7°[26]).

Hexamethyldisilazane. We found a hydrocarbon solvent for reaction of trimethylchlorosilane with ammonia gives a better yield and is more convenient than the ether solvent used previously.[14,16]

A 5-liter, 3-necked flask was fitted with stirrer, gas-inlet tube, and condenser, to which was attached a drying tube filled with Drierite. Three liters of petroleum ether (b.p. 60–68°) and 1273.5 g. (11.74 moles) of a technical grade Dow Corning trimethylchlorosilane were added to the flask. Ammonia was bubbled into the mixture for 15 hr. with stirring. When no more heat was being evolved, stirring was discontinued and the mixture was heated to reflux for 1 hr. while ammonia was passed through the mixture. The precipitate was collected on a Büchner funnel and washed with successive 200-, 100-, 100-, and 100-ml. portions of petroleum ether. This portion of filtrate was designated Charge I. The precipitate was further washed with successive 600-, 600-, and 800-ml. portions of petroleum ether, and the filtrate was designated Charge II.

Petroleum ether was stripped from Charge I at a reflux ratio of 10:1 through a 2-foot vacuum-jacketed column containing Helipak packing. Distillation gave a total of 499 g. of hexamethyldisilazane, b.p. 125–125.6°, n_D^{20} 1.4082. An additional 176 g. of product was recovered from Charge II. There was 32 g. of residue. Yield was 71.4% of theoretical.

A. *Reaction of alcohols and hexamethyldisilazane. 1. 1-Trimethylsiloxypropane.* To 12.0 g. (0.2 mole) of propyl alcohol in a flask equipped with condenser and drying tube, 17.6 g. (0.11 mole) of hexamethyldisilazane was added. The reaction temperature was raised to 93° over a period of 5 hr., with accompanying refluxing and evolution of ammonia.

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[21] E. Larsson and R. Mjorne, *Acta Chim. Scand.*, **5**, 964–5 (1951).

[22] E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

[23] W. T. Grubb and R. C. Osthoff, *J. Am. Chem. Soc.*, **75**, 2230 (1953); A. G. MacDiarmid, *Quart. Rev. London*, **10**, 208 (1956).

[24] B. E. F. Smith, *Svensk Kem. Tidskr.*, **61**, 213 (1949).

[25] R. A. Friedel, J. L. Schultz, and A. G. Sharkey, Jr., *Anal. Chem.*, **28**, 926 (1956).

[26] (a) R. O. Sauer, W. J. Scheiber, and E. M. Hadsell, *J. Am. Chem. Soc.*, **70**, 4254 (1948). (b) R. O. Sauer and E. M. Hadsell, *J. Am. Chem. Soc.*, **70**, 4258 (1948).

TABLE I

PROPERTIES OF TRIMETHYLSILYL DERIVATIVES

Trimethylsilyl Derivative	Formula	B.P., °C. (mm.), Heart Cut	n_D^{20}	d_4^{20}	d_4^{25}	MR_D		Analyses						Literature
						Calcd.[a]	Found	Calcd.			Found			
								C	H	Si	C	H	Si	
Trimethylsiloxymethane	$C_4H_{12}OSi$	55.3–55.8 (740)	1.3675	0.7592	0.7537	31.04	30.87							B.p. 57°, n_D^{20} 1.3678,[b] B.p. 55°[c]
Trimethylsiloxyethane	$C_5H_{14}OSi$	74.6 (738)	1.3742	0.7586	0.7534	35.67	35.62							B.p. 75°, n_D^{20} 1.3743, d_4^{20} 0.7573[b]
Trimethylsiloxypropane	$C_6H_{16}OSi$	100.3–100.8 (735)	1.3838	0.7682	0.7633	40.30	40.24	54.5	12.2		54.4 54.5	12.3 12.3		
Trimethylsiloxybutane	$C_7H_{18}OSi$	123.7–125.0 (740)	1.3925	0.7773	0.7727	44.93	44.87	57.5	12.4		57.7 57.8	12.6 12.7		B.p. 124°, n_D^{20} 1.3925, d_4^{20} 0.7774[b]
Trimethylsiloxypentane	$C_8H_{20}OSi$	148.9–149.4 (739)	1.4000	0.7849	0.7805	49.56	49.52	59.9	12.6		60.0 60.0	12.9 12.9		B.p. 145–147°, n_D^{20} 1.4010, d_4^{20} 0.7871[d]
Trimethylsiloxyhexane	$C_9H_{22}OSi$	170.5–170.7 (741)	1.4058	0.7902	0.7862	54.19	54.17	62.0	12.7	16.2	62.2 62.2	13.1 13.1	16.4	
Trimethylsiloxyheptane	$C_{10}H_{24}OSi$	188.9–189.7 (740)	1.4108	0.7951	0.7909	58.82	58.80	63.8	12.8		64.0 63.9	13.0 13.0		
Trimethylsiloxyoctane	$C_{11}H_{26}OSi$	211.2–212.2 (749)	1.4149	0.7993	0.7950	63.45	63.40	65.3	13.0		65.4 65.4	13.0 13.0		
Trimethylsiloxynonane	$C_{12}H_{28}OSi$	228.1–228.9 (744)	1.4189	0.8033	—	68.08	68.03	66.6	13.0		66.8 66.6	13.2 13.2		
Trimethylsiloxydecane	$C_{13}H_{30}OSi$	244–245 (735) 174–174.5 (100)	1.4228	0.8068	0.8029	72.71	72.71	67.8	13.1		68.1 68.1	13.3 13.4		
Trimethylsiloxyundecane	$C_{14}H_{32}OSi$	258–261 (733) 190.6–191.6 (102)	1.4258	0.8096	0.8057	77.34	77.35	68.8	13.3		68.9 69.2	13.3 13.3		
Trimethylsiloxydodecane	$C_{15}H_{34}OSi$	271–273 (742) 198.5–200.6 (100)	1.4289 n_D^{25} 1.4269	0.8125	—	81.97	82.01	69.7	13.3	10.9	70.0 70.0	13.4 13.4	10.6 10.5	
Branched														
1-Trimethylsiloxy-2-methylpropane	$C_7H_{18}OSi$	114.5–114.7 (742)	1.3881	0.7686	—	44.93	44.93	57.5	12.4		57.6 57.7	12.7 12.7		
1-Trimethylsiloxy-2,2-dimethylpropane	$C_8H_{20}OSi$	122.5–122.7 (734)	1.3907	0.7669	0.7623	49.56 49.65[f]	49.64	59.9	12.6	17.5	59.9 60.0	12.9 13.0	17.3	B.p. 122°, n_D^{20} 1.3934, d_4^{20} 0.7632[e]
1-Trimethylsiloxy-2-methylbutane	$C_8H_{20}OSi$	140.0 (744)	1.3980	0.7828	—	49.56	49.43	59.9	12.6		59.9 60.1	12.8 12.9		
1-Trimethylsiloxy-3-methylbutane	$C_8H_{20}OSi$	142 (735)	1.3976	0.7807	—	49.56	49.53	60.0	12.6		59.9 60.2	12.8 12.9		
1-Trimethylsiloxy-2-methylpentane	$C_9H_{22}OSi$	159.3–160.2 (749)	1.4042	0.7884	0.7839	54.19	54.11	62.0	12.7		62.2 62.3	12.9 12.9		
1-Trimethylsiloxy-3-methylpentane	$C_9H_{22}OSi$	163 (733)	1.4061	0.7925	0.7883	54.19	54.05	62.0	12.7		62.2 62.2	13.1 13.1		

TABLE I (*Continued*)

Trimethylsilyl Derivative	Formula	B.P., °C. (mm.), Heart Cut	n_D^{20}	d_4^{20}	d_4^{25}	MR$_D$		Analyses						Literature
								Calcd.			Found			
						Calcd.[a]	Found	C	H	Si	C	H	Si	
1-Trimethylsiloxy-2-ethylbutane	$C_9H_{22}OSi$	157.4–158.4 (741)	1.4062	0.7942	0.7899	54.19	53.95	62.0	12.7		62.4 62.3	12.9 13.0		
1-Trimethylsiloxy-2-ethylhexane	$C_{11}H_{26}OSi$	194.6 (735)	1.4148	0.8008	0.7971	63.39	63.27	65.3	13.0		65.2 65.1	13.0 13.0		
Secondary and tertiary														
2-Trimethylsiloxyhexane	$C_9H_{22}OSi$	154–155 (741)	1.4020	0.7856	0.7811	54.19	54.04	62.0	12.7		62.4 62.3	12.9 13.0		
3-Trimethylsiloxyheptane	$C_{10}H_{24}OSi$	176.1–176.2 (740)	1.4098	0.7955	0.7908	58.82	58.65	63.8	12.8		63.3 63.5	13.0 13.0		
2-Trimethylsiloxy-2-methylbutane	$C_8H_{20}OSi$	129.6–130 (744)	1.3980	0.7834	—	49.56	49.40	59.9	12.6	17.8	60.1 60.0	12.9 12.9	17.5	
Diol derivatives														
1,2-Bis(trimethylsiloxy)-ethane	$C_8H_{22}O_2Si_2$	170.1–170.8 (734)	1.4031	0.8422	0.8376	59.95	59.83	46.5	11.0		46.8 46.5	10.9 10.9		B.p. 165–166°, n_D^{20} 1.4031, d_4^{20} 0.841[g]
1,2-Bis(trimethylsiloxy)-propane	$C_9H_{24}O_2Si_2$	172–172.7 (740)	1.4031	0.8374	0.8328	64.58	64.26	48.8	11.4	25.4	49.0 48.9	11.0 11.1	25.6	B.p. 97° (58 mm.), n_D^{20} 1.4031, d_4^{20} 0.834[g]
Phenolic Derivatives														
Trimethylsiloxybenzene	$C_9H_{14}OSi$	181.9–182.4 (742)	1.4782	0.9256	0.9209	50.80	50.87	—	—		—	—		B.p. 182.5°, n_D^{25} 1.4753, d_4^{25} 0.920[h]
1,3-Bis(trimethylsiloxy)-benzene	$C_{12}H_{22}O_2Si_2$	237–240 (740)	1.4748	0.950	0.946	75.1	75.4	56.6	8.7		57.0 56.9	8.7 8.7		
α-Trimethylsiloxy-naphthalene	$C_{13}H_{16}OSi$	271–272 (742)	1.5590	1.000	—	68.4[i]	69.8	72.2	7.5	13.0	72.4 72.3	7.6 7.5	13.0	
Miscellaneous														
Trimethyl-*N*-butyl-aminosilane	$C_7H_{19}NSi$	134–135 (754)	1.4094 n_D^{25} 1.4071	0.765	—	47.0	47.0	57.8	13.2	N 9.6	58.1 58.0	13.3 13.2	N 9.7	
Trimethyl-*N*-amyl-aminosilane	$C_8H_{21}NSi$	161.4–162.4 (737)	1.4154	0.772	—	51.7	51.7	60.3	13.3	N 8.8	59.9 60.3	13.4 13.3	N 8.7	
Trimethyl-*N*,*N*-diethyl-aminosilane	$C_7H_{19}NSi$	126.8–127.1 (738)	1.4109	—	—	—	—	—	—	—	—	—	—	B.p. 126.1–126.4°, n_D^{20} 1.4112[j]
Trimethylbutyl-mercaptosilane	$C_7H_{18}NSi$	171–172.5 (740)	1.4540	0.842	0.837	52.5	52.3	51.8	11.2	17.3	51.9 51.7	11.4 11.3	17.1	

[a] Ref. 22. [b] Ref. 14. [c] Ref. 15. [d] B. E. F. Smith, Doktorsarhandl, Chalmers Tek. Högskola (1951) [*Chem. Abstr.*, **49,** 909 (1955)]. [e] W. Gerrard and P. Tolcher, *J. Chem. Soc.*, 3640 (1954). [f] Calculated according to Ref. 24. [g] Ref. 2. [h] Ref. 13. [i] Refraction of naphthyl group taken as 42.4, J. Schuyer, L. Blom, and D. W. van Krevelen, *Trans. Faraday Soc.*, **49,** 139 (1953). [j] Ref. 16.

The 26.5 g. of distillable crude product with b.p. 88–103° had n_D^{20} 1.3858–1.3872. Distillation through a Podbielniak column gave 3.9 g. of forerun b.p. 85.8–99.3°, which consisted mostly of propyl alcohol–trimethylsilyl propyl ether azeotrope (b.p. 87.5°). The remaining 15.7 g. (60 percent yield) of distillate had b.p. 100.3–100.8° (735 mm.), n_D^{20} 1.3838. The 4 g. of residue had n_D^{20} 1.4008.

2. 1-Trimethylsiloxyheptane. 1-Heptanol (29.2 g., 0.25 mole) was allowed to react with 24.9 g. (0.15 mole) of hexamethyldisilazane at a temperature of 50° to 168° for 5 hr. After the reaction mixture had stood overnight, the reflux temperature was 175°. Since hexamethyldisilazane boils at 126°, heptanol at 175°, and the final product at 189°, a rise in reflux temperature indicated the disappearance of the hexamethyldisilazane, with consequent formation of reaction product. After 5 more hours of heating, reflux temperature was still 175° and the crude product was bench-distilled. Distillation through a Podbielniak column gave some hexamethyldisilazane and 38.9 g. (82.7 percent yield) of product, b.p. 188.9–189.9° (740 mm.), n_D^{20} 1.4108. The 4.2 g. of residue had n_D^{20} 1.4160.

The trimethylsilyl derivatives of methanol, 1-pentanol, and 1-octanol were prepared by procedures similar to those described above.

B. *Reaction of alcohols and hexamethyldisilazane in the presence of acid (from trimethylchlorosilane). 1. 1-Trimethyl siloxynonane.* To a mixture of 25.9 g. (0.18 mole) of nonyl alcohol and 16.1 g. (0.1 mole) of hexamethyldisilazane two drops of trimethylchlorosilane was added. Precipitate formed immediately and upon gentle heating gas evolution began at 66°. After 2 hours of heating, flask temperature rose to 132°, at which time the precipitate began to sublime out of the flask. Four hours later reflux temperature was 204°. After cooling, bench-distillation gave 1.7 g. of forerun and 36.8 g. (94.6 percent yield) of crude product, b.p. 220–229°, n_D^{20} 1.4180–1.4196. Filtration of cloudy fractions and distillation through a Podbielniak column gave 26.3 g. of pure product, b.p. 228.1–228.9° (734 mm.), n_D^{20} 1.4189–1.4191.

2. 1-Trimethylsiloxy-2-methylbutane. A mixture of 17.6 g. (0.2 mole) 2-methyl-1-butanol, 17.7 g. (0.11 mole) of hexamethyldisilazane, and one drop of trimethylchlorosilane was heated to reflux over a period of 2 hr. During 16 hr. of additional heating, reflux temperature rose from 125° to 134°. Bench-distillation gave 32 g. of product, n_D^{25} 1.3958–1.3961. Distillation through a Podbielniak column gave 24.2 g. (75.3 percent yield) of the pure 2-methyl-1-butyl trimethylsilyl ether, b.p. 138.4–140°, n_D^{20} 1.3980.

The trimethylsilyl derivatives of ethanol, 1-undecanol, 1-dodecanol, isobutyl alcohol, isoamyl alcohol, 3-methyl-1-pentanol, and 2-ethyl-1-hexanol were all prepared by procedures similar to the two above.

3. Attempted preparation of 2-trimethylsiloxy-2-methylbutane. A mixture of 17.6 g. (0.2 mole) *t*-amyl alcohol and 17.7 g. (0.11 mole) of hexamethyldisilazane showed no rise in reflux temperature (103°) after refluxing 16 hr. Addition of a drop of trimethylchlorosilane followed by 6 hr. of heating caused no change in reflux temperature. Bench-distillation resulted in recovery of 17 g. of the original *t*-amyl alcohol, b.p. 100–103° and hexamethyldisilazane. See G-2.

Trimethylsilyl ethers of diols. 4. 1,2-Bis-(trimethylsiloxy)-ethane. A mixture of 9.3 g. (0.15 mole) ethylene glycol, 27.3 g. (0.17 mole) hexamethyldisilazane, and three drops of trimethylchlorosilane was brought to reflux over a period of 1 hr. During this time vigorous gas evolution was noted and the two phases became one. After 3 more hours of heating, reflux temperature rose to 163°. The mixture was bench-distilled and fractionated through a Podbielniak column to give 23.3 g. (75.4 percent) of pure product, b.p. 170.1–171.9° (734 mm.), n_D^{20} 1.4031, and 5.3 g. of residue n_D^{20} 1.4048.

5. 1,2-Bis(trimethylsiloxy)propane. Reagent proportions and results were similar to the above.

C. *Effect of acid and base on reaction of alcohol with hexamethyldisilazane. 1.* A commercial sample of Union Carbide and Carbon oxo *primary* (mostly *normal*) *C_5 alcohols* (35.2 g., 0.4 mole) was mixed with 35.4 g. (0.22 mole) of hexamethyldisilazane. Three 25-ml. aliquots of this mixture were placed in 50-ml. flasks. One drop of trimethylchlorosilane was added to one flask (A), a pellet of potassium hydroxide to another (B), and nothing to the third. All three mixtures were heated in Glass-Col mantles at a variac setting of 35 volts.

Mixture A began to evolve gas in 7 min. at 60° and was at 125° and refluxing in 14 min. Reflux temperature was 134° after another hour of heating and rose to 142° after an additional 10 hr. of heating.

Mixture B began to reflux at 120° after 20 min. of heating. After another hour of heating, reflux temperature was still 120° and no ammonia was evolved, as indicated by litmus paper at the end of the drying tube. Ten more hours of heating caused the reflux temperature to be raised to 124°.

Mixture C was refluxing at 122° after 30 min. of heating and litmus indicated that ammonia was being evolved. An additional hour of heating raised reflux temperature to 124°. After 10 more hours of heating, reflux temperature had risen to 138°.

2. 3-Trimethylsiloxyheptane. In an experiment similar to the above with 3-heptanol and hexamethyldisilazane, the flask containing a drop of trimethylchlorosilane reached maximum reflux temperature, 153°, in 90 min. Another flask containing no trimethylchlorosilane refluxed at 135° after 10 hr. of heating.

D. *Formation of sodium alkoxide, from NaH, followed by reaction with trimethylchlorosilane. 1. 1-Trimethylsiloxybutane* To 8.9 g. (0.37 mole) of sodium hydride at dry ice–acetone temperature in a nitrogen atmosphere, 29.6 g. (0.4 mole of butanol) was added over a period of 30 min. The reaction flask was fitted with a drying tube and condenser. After it was slowly brought to room temperature, the flask was heated for 1 hr. on a steam bath. There was vigorous evolution of gas. While the flask was held at about 60° on the steam bath, unreacted butanol (8.9 g.) was pumped off at 3 mm. A total of 33.2 g. (0.305 mole) of trimethylchlorosilane was then added, dropwise, over a period of 30 min. with cooling. After standing overnight and refluxing for 5 hr. at 118°, the product was distilled to give a total of 38.5 g. with n_D^{20} 1.3902–1.3925. The flask residue still contained unreacted sodium hydride which reacted vigorously when ethyl alcohol was added to the flask. Careful distillation of crude product removed 4.4 g. of butyl alcohol–trimethylsilyl butyl ether mixture.[14] The remaining distillate had b.p. 123.7–125° (737 mm.), n_D^{20} 1.3924–1.3925. Yield of pure product was 62 percent (correcting for recovered alcohol).

2. 1-Trimethylsiloxypentane. A method of preparation similar to that described in 1 above, gave a yield of 49 percent trimethylsilyl pentyl ether. Another synthesis with solvent heptane and stirrer did not improve the yield.

3. 1-Trimethylsiloxydecane. To 7.9 g. (0.33 mole) of sodium hydride and 100 ml. of ethyl ether in a 3-necked reaction flask, 46.4 g. (0.3 mole) of decyl alcohol was added with stirring. The mixture was refluxed for 4 hr. with stirring and heat was turned off. Trimethylchlorosilane (32.6 g., 0.3 mole) was then added, dropwise, and the mixture stirred and heated for 1 hr. After standing overnight, filtering, and bench-distillation, all material with b.p. above 185° was redistilled through a Podbielniak column. Decyl alcohol, 19.9 g., n_D^{20} 1.4341, b.p. 229°, was recovered, together with several other intermediate cuts. A total of 10.9 g. (15.8 percent yield) of decyl trimethylsilyl ether, b.p. 244–245° (735 mm.), was recovered.

The trimethylsilyl derivatives of 1-hexanol and 2-hexanol also were prepared by initial reaction with sodium hydride followed by reaction with trimethylchlorosilane.

E. *Direct reaction of alcohol or phenol with trimethylchlorosilane. 1. 1-Trimethylsiloxynonane.* A mixture of 43.2 g.

nonyl alcohol (0.3 mole), 32.6 g. trimethylchlorosilane (0.3 mole), and 125 ml. of petroleum ether (b.p. 34.5–55°) was refluxed for 6 hr. and bench-distilled. Petroleum ether-trimethylchlorosilane and nonyl alcohol were recovered from the reaction mixture. No trimethylsilyl ether was recovered.

2. 1-Trimethylsiloxydecane. A mixture of 28.4 g. (0.18 mole) of decyl alcohol, 21.7 g. (0.2 mole) trimethylchlorosilane, and 20 ml. of petroleum ether (b.p. 90–98°) was refluxed for 13 hr., during which time considerable hydrochloric acid was evolved and reaction flask temperature rose from 68° to 121°. The mixture was bench-distilled and stripped of lower boiling fractions. The 35.1 g. (84.7 percent yield) of crude product had b.p. 240–244°, n_D^{20} 1.4228–1.4232. Further fractionation at lower pressure gave pure trimethylsilyl decyl ether, b.p. 174.5° (100 mm.), n_D^{20} 1.4228.

Phenolic trimethylsilyl ethers. 3. Trimethylsiloxybenzene.[13] To 37.4 g. of phenol (0.4 mole), 54.5 g. of trimethylchlorosilane (0.5 mole) was added. After 7 hr. of refluxing, 50 ml. of petroleum ether (b.p. 60–68°) was added. The reaction solution was heated at reflux another 4 hr. and bench-distilled. After stripping, a total of 56.6 g. of material, b.p. 166–178°, n_D^{20} 1.4907–1.4850, was recovered. This product was distilled through a 2-foot Podbielniak column to give 2 g. of material, b.p. 112–174°, and 27.0 g. of material with a boiling point of 174° to 181.9°. Much of the latter was an azeotrope with a b.p. of 175.5°, n_D^{20} 1.5060. The rest of the trimethylsilyl phenyl ether product had b.p. 181.9–182.4° (747 mm.), n_D^{20} 1.4782. The yield of pure product was 20.5 g. Mass spectrometric analysis of the phenol-phenyl ether azeotrope indicated an approximate composition by wt. of 39.5 per cent phenol and 60.5 per cent trimethylsilyl phenyl ether.

4. 1,3-Bis-(trimethylsiloxy)benzene. A mixture of 11.0 g. resorcinol (0.1 mole), 32.7 g. (0.3 mole) trimethylchlorosilane, and 25 ml. petroleum ether (b.p. 90–100°) was refluxed for 24 hr. Flask reflux temperature rose from 64° to 92°. After stripping of petroleum ether and trimethylchlorosilane, bench-distillation gave 19.4 g. (76.4 percent yield of product) with b.p. 237–240°, n_D^{20} 1.4760. Careful fractionation of a part of this gave pure product with b.p. 154–155°/100 mm. and n_D^{20} 1.4748.

The trimethylsilyl derivative of 1-naphthol was prepared by a procedure similar to the above.

F. *Reaction of alcohol with trimethylchlorosilane in presence of pyridine. 1. 1-Trimethylsiloxynonane.* To 27.1 g. (0.25 mole) trimethylchlorosilane in 50 ml. of benzene, a mixture of 57.4 g. (0.6 mole) dry pyridine and 31.7 g. (0.22 mole) of nonyl alcohol was added dropwise with stirring. The mixture was refluxed for 1 hr., filtered, and the precipitate washed with two 50-ml. portions of petroleum ether (b.p. 35–55°). The mixture was bench-distilled and all material boiling below 150° was discarded. Remaining product (b.p. 212–229°) was fractionated to give 23.3 g. (46.7 per cent yield) of trimethylsilyl nonyl ether, n_D^{20} 1.4188–1.4192, b.p. 227.5–229.5° (727 mm.).

G. *Reaction of alcohol, trimethylchlorosilane and hexamethyldisilazane in equivalent amounts. 1. 1-Trimethylsiloxy-2-methylpentane.* This compound was prepared by the dropwise addition of 7.3 g. of trimethylchlorosilane (0.067 mole) in 10 ml. of petroleum ether (b.p. 60–68°) to 20.4 g. (0.2 mole) of 2-methyl-1-pentanol and 10.8 g. (0.067 mole) of hexamethyldisilazane. During the 1-hr. addition period the mixture was stirred. After 2 hr. of heating from 40° to 94°, the reaction mixture was filtered and the precipitate was washed with 20-ml. and 5-ml. portions of petroleum ether. The mixture was bench-distilled and the 33.5 g. of product with b.p. 87–156° was distilled through a Podbielniak column to give 20.4 g. (58.6 per cent yield) of pure trimethylsilyl ether with b.p. 158.2–160.2°, n_D^{20} 1.4042. The 3.7 g. of residue had n_D^{20} 1.4083.

2. 2-Trimethylsiloxy-2-methylbutane. Reaction of 17.6 g. (0.2 mole) *t*-amyl alcohol, 10.7 g. (0.067 mole) hexamethyldisilazane, and 7.5 g. (0.07 mole) of trimethylchlorosilane in 10 ml. petroleum ether (60–68°) as in *1* plus an additional 4 hr. of refluxing after filtration was followed by bench-distillation. Distillation through a Podbielniak column gave 15.9 g. (49.7 percent yield) of *t*-amyl trimethylsilyl ether b.p. 129.6–130° (743 mm.), n_D^{20} 1.3980.

3. Trimethylsiloxy-2,2-dimethylpropane. (neopentyl trimethylsilyl ether). Similar to G-2.

H. *Aminotrimethylsilanes. 1. N,N-Diethylaminotrimethylsilane.* Hexamethyldisilazane and dry diethylamine in the presence of small amounts of trimethylchlorosilane did not react after 20 hr. of reflux. Starting materials were recovered by distillation. The preparation of Sauer and Hasek[16] was slightly modified (petroleum ether solvent) to give a 32.6 percent yield.

2. N-Butylaminotrimethylsilane. A mixture of hexamethyldisilazane (16.6 g., 0.104 mole) and dry *n*-butylamine (14.6 g., 0.2 mole) refluxed for 4 hr. at 85–87°. After cooling, 2 drops of trimethylchlorosilane were added and the mixture was heated to reflux temperature of 105° in 30 min. Reflux temperature rose to 113° in the next 4 hr. and was constant for the next 6 hr. Distillation through a 1-foot Widmer column gave 2.4 g. with b.p. 128–132°, n_D^{25} 1.4058, and 12.5 g. (43 percent yield) with b.p. 132–135° (742 mm.).

Anal. Calcd. for $C_7H_{19}SiN$: neut. equiv., 145.3. Found: neut. equiv. 145.2.

3. N-Amylaminotrimethylsilane. A mixture of 25.7 g. (0.16 mole) of hexamethyldisilazane and 26.1 g. (0.3 mole) of *n*-amylamine was divided into two approximately equal portions and placed in 100-ml. flasks. A drop of trimethylchlorosilane was added to one flask (A) and both solutions were refluxed by heating with Glass-Col mantles at comparable voltage settings. After 16 hr. of reflux, reflux temperature in flask A was 152.5° and in the other flask (B) was 111°. Addition of a drop of trimethylchlorosilane to flask B caused gas evolution immediately and reflux temperature rose to 146° in 8 hr. After additional 8 hr. reflux, contents of the two flasks were combined, bench-distilled, and subjected to fractional distillation in a Podbielniak column. A total of 24.5 g. (51.4 percent yield) of material was recovered with b.p. 160.3–162.4°, n_D^{20} 1.4145–1.4155.

Anal. Calcd. for $C_8H_{21}SiN$: neut. equiv., 159.3. Found: Neut. equiv. 159.0.

I. *Trimethylbutylmercaptosilane. 1.* *n*-Butyl mercaptan (18.1 g., 0.2 mole) and 17.7 g. (0.11 mole) of hexamethyldisilazane with a few drops of trimethylchlorosilane refluxed for 33 hr. at 104–106°. Distillation through a 1-foot Widmer column gave 15.7 g. with b.p. 100–102° (n_D^{20} 1.4332–1.4325) and 12.9 g. of material with b.p. 111–120° (n_D^{25} 1.4212–1.4186). Mass spectrometric analysis indicated lower boiling fractions were mainly butyl mercaptan and higher boiling fractions were hexamethyldisilazane. The 4.6 g. of residue had n_D^{20} 1.4502 and may have contained some butylmercaptotrimethylsilane.

2. *n*-Butyl mercaptan (18 g., 0.2 mole), hexamethyldisilazane (11.3 g., 0.07 mole) and trimethylchlorosilane (7.3 g., 0.07 mole) in the presence of 75 ml. of petroleum ether (b.p. 60–68°) did not react. After 13 hr. of heating there was little precipitate and reflux temperature was 72°. Distillation gave back petroleum ether with trimethylchlorosilane as well as various butyl mercaptan-hexamethyldisilazane mixtures (mass spectrometric analysis).

3. To 4.5 g. (0.196 mole) of sodium and 50 ml. of petroleum ether (b.p. 60–68°), a solution of 18.2 g. (0.18 mole) butyl mercaptan in petroleum ether (50 ml.) was added dropwise with stirring. During the next 4 hr. gas was constantly evolved and a white bulky precipitate formed. After standing overnight the reaction mixture was refluxed for 1 hr. and a solution of trimethylchlorosilane (19.5 g., 0.18 mole) in petroleum ether (40 ml.) was added dropwise with stirring and cooling (ice water). A granular precipitate formed. The reaction mixture was then refluxed for 2 hr. and distilled through a 1-foot Widmer column. Petroleum ether and lower boiling fractions were stripped from the mixture. Then 3.8 g. of material with b.p. 167–171°, n_D^{20} 1.4513, and

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.

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BRUCETON, PA.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

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

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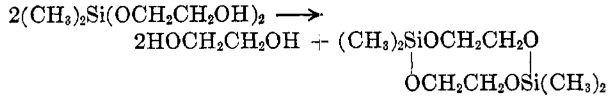
Reactions of di- and triethoxymethylsilanes with diols, triols, and acyloxyols were examined. Bis(hydroxyalkoxy)dimethylsilanes having primary hydroxyl groups could not be isolated from the reaction between diethoxydimethylsilane and diols. A cyclic polymethylenedioxysilane was formed instead and a mole 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.

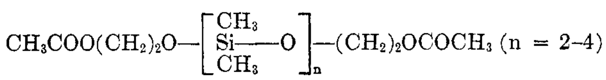
Polymeric reaction products are to be expected if a di- or trifunctional organo-silicon compound is substituted for trimethylchlorosilane or for the trimethylalkoxysilane in these reactions. Structural considerations must also be taken into account, since structure or stereochemistry may favor the formation 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:



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

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,



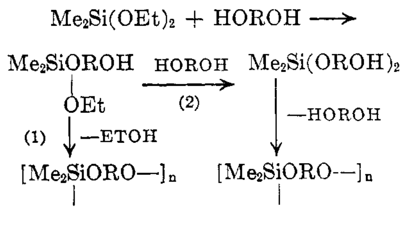
$$CH_3COO(CH_2)_2O{-}\left[\begin{array}{c}CH_3\\ Si{-\!-}O\\ CH_3\end{array}\right]_n{-}(CH_2)_2OCOCH_3 \quad (n = 2\text{–}4)$$

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.

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