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The Reaction of 1,2-Disilyldisiloxane, 1-Silyldisiloxane, and 1,1,1-Trimethyldisiloxane with Boron Trichloride[1a]

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Two new unsymmetrical disiloxanes, 1-silyldisiloxane, $SiH_3SiH_2OSiH_3$, and 1,1,1-trimethyldisiloxane, $(CH_3)_3SiOSiH_3$, have been synthesized and characterized. 1,2-Disilyldisiloxane, $(SiH_3SiH_2)_2O$, underwent reaction with BCl_3 to yield SiH_3SiH_2Cl. Preferential cleavage of certain silicon–oxygen bonds was observed when $(CH_3)_3SiOSiH_3$, $SiH_3SiH_2OSiH_3$, and also a mixture of $(SiH_3SiH_2)_2O$ and $(SiH_3)_2O$ were treated with BCl_3. The results are discussed.

Disiloxane, $(SiH_3)_2O$, has been reported to react readily at −78° with BCl_3 as shown by eq. 1.[2] Although SiH_3OBCl_2 can be isolated it decomposes slowly at −78°

$$(SiH_3)_2O + BCl_3 \longrightarrow SiH_3Cl + SiH_3OBCl_2 \qquad (1)$$

$$3SiH_3OBCl_2 \longrightarrow 3SiH_3Cl + BCl_3 + B_2O_3 \qquad (2)$$

The net reaction between $(SiH_3)_2O$ and BCl_3 may therefore be expressed as

$$3(SiH_3)_2O + 2BCl_3 \longrightarrow 6SiH_3Cl + B_2O_3 \qquad (3)$$

A number of symmetrical disiloxanes[3-5] as well as SiH_3OCH_3[6] have been found to react in an analogous manner with boron halides.

The present investigation was carried out for the purpose of ascertaining whether $(SiH_3SiH_2)_2O$ would react with BCl_3 in a similar manner to $(SiH_3)_2O$ or whether cleavage of silicon–silicon bonds would occur. If only silicon–oxygen bonds underwent reaction then it would be possible to obtain information concerning the relative rates of cleavage of these linkages in $(SiH_3SiH_2)_2O$ and $(SiH_3)_2O$ by BCl_3. The synthesis of the new, simple, unsymmetrical disiloxanes, $SiH_3SiH_2OSiH_3$ and $(CH_3)_3SiOSiH_3$, was carried out so that they might be treated with BCl_3 in order to ascertain whether preferential cleavage of a given silicon–oxygen bond could be observed. Such information should lead to a greater understanding of the general factors governing the reaction of siloxanes with boron halides.

Results

The new disiloxane, 1,1,1-trimethyldisiloxane, $(CH_3)_3SiOSiH_3$, was prepared in good yields by the reaction of $(CH_3)_3SiOH$ with SiH_3I, which occurred rapidly at room temperature or below.

$$(CH_3)_3SiOH + SiH_3I \longrightarrow (CH_3)_3SiOSiH_3 + HI \qquad (4)$$

The compound underwent slow and incomplete disproportionation at temperatures between 0° and room temperature.

$$2(CH_3)_3SiOSiH_3 \longrightarrow [(CH_3)_3Si]_2O + (SiH_3)_2O \qquad (5)$$

The first compound to contain both a disilanyl and a silyl group, $SiH_3SiH_2OSiH_3$, 1-silyldisiloxane (silyl disilanyl ether) was synthesized by the cohydrolysis of SiH_3SiH_2Br and SiH_3I.

$$SiH_3SiH_2Br + SiH_3I + H_2O \longrightarrow SiH_3SiH_2OSiH_3 + HBr + HI \qquad (6)$$

Considerable quantities of the symmetrical ethers, $(SiH_3SiH_2)_2O$ and $(SiH_3)_2O$, were also formed in this reaction. Silyl disilanyl ether was observed to disproportionate at 0°; this occurred more rapidly than with $(CH_3)_3SiOSiH_3$. Disproportionation only took place when liquid phase was present; in the vapor state $SiH_3SiH_2OSiH_3$ appeared to be completely stable. It was most interesting to find that this reaction was reversible and that $SiH_3SiH_2OSiH_3$ could be synthesized from $(SiH_3SiH_2)_2O$ and $(SiH_3)_2O$ at 0°.

$$(SiH_3SiH_2)_2O + (SiH_3)_2O \rightleftarrows 2SiH_3SiH_2OSiH_3 \qquad (7)$$

1,1-Disilyldisiloxane (bisdisilanyl ether), $(SiH_3SiH_2)_2O$, was found to react at −78° with a deficit of BCl_3 according to eq. 8 to give a 92% yield of SiH_3SiH_2Cl. No evidence for any cleavage of the silicon–silicon bonds was observed and no $SiH_3SiH_2OBCl_2$, analogous to the SiH_3OBCl_2 formed from $(SiH_3)_2O$ and BCl_3 (eq. 1), was detected.

$$3(SiH_3SiH_2)_2O + 2BCl_3 \longrightarrow 6SiH_3SiH_2Cl + B_2O_3 \qquad (8)$$

Equimolar quantities of 1,1,1-trimethyldisiloxane and BCl_3 also underwent reaction at −78°. The chief silicon–oxygen bond cleavage reaction which occurred is given by eq. 9.

$$(CH_3)_3SiOSiH_3 + BCl_3 \longrightarrow SiH_3Cl + (CH_3)_3SiOBCl_2 \qquad (9)$$

Silyl chloride and $(CH_3)_3SiOBCl_2$ were produced in approximately equimolar quantities. Some cleavage of the $(CH_3)_3Si$–O bond also took place but only 0.0692 mole of $(CH_3)_3SiCl$ was formed per mole of SiH_3Cl produced. In addition to the silicon–oxygen bond cleavage, a Si–H—B–Cl exchange reaction appeared to occur to give B_2H_6 and a compound tentatively identified as $(CH_3)_3SiOSiH_2Cl$.

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Boron trichloride and excess $SiH_3SiH_2OSiH_3$ were found to react at −78°. The chief reaction which occurred may be summarized by the equation

$$6SiH_3SiH_2OSiH_3 + 2BCl_3 \longrightarrow 6SiH_3SiH_2Cl + 3(SiH_3)_2O + B_2O_3 \quad (10)$$

This reaction could take place *via* the following steps if the SiH_3SiH_2–O bond were presumed to cleave in preference to the SiH_3–O bond

$$SiH_3SiH_2OSiH_3 + BCl_3 \longrightarrow SiH_3SiH_2Cl + SiH_3OBCl_2 \quad (11)$$

$$2SiH_3SiH_2OSiH_3 + SiH_3OBCl_2 \longrightarrow 2SiH_3SiH_2Cl + (SiH_3O)_3B \quad (12)$$

$$2(SiH_3O)_3B \longrightarrow 3(SiH_3)_2O + B_2O_3 \quad (13)$$

It may be noted that the reaction represented by eq. 13 is analogous to that proposed for the decomposition of $[(CH_3)_2(Cl)SiO]_3B$.[7] Disiloxane, $(SiH_3)_2O$, and some SiH_3OBCl_2 and SiH_3Cl were recovered in the reaction products. The presence of the latter compound indicates that some cleavage of the SiH_3–O bond did occur but this was less extensive than the cleavage of the H_3SiSiH_2–O bond as shown by that fact that for every mole of SiH_3SiH_2Cl formed only 0.584 mole of SiH_3Cl was produced. Even if the SiH_3Cl which could be liberated from the SiH_3OBCl_2 (according to eq. 2) which was also produced were added to the SiH_3Cl actually recovered, the SiH_3Cl value would increase to only 0.684 mole.

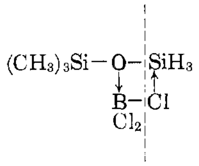
When equimolar quantities of $(SiH_3)_2O$, $(SiH_3SiH_2)_2O$, and BCl_3 were allowed to interact at −78°, preferential reaction of $(SiH_3SiH_2)_2O$ occurred and it was completely consumed according to eq. 8. Fifty-two per cent of the $(SiH_3)_2O$ was recovered unchanged and that which did react apparently did so according to eq. 1 and 2 since some SiH_3OBCl_2 was isolated.

Discussion

It is of particular interest to note that both $(CH_3)_3SiOSiH_3$ and $SiH_3SiH_2OSiH_3$ disproportionate even at temperatures as low as 0°. Disproportionation of unsymmetrical disiloxanes has previously been observed to take place only on heating. Thus $(CH_3)_3SiOSi(C_6H_5)_3$ undergoes disproportionation at 350–370°.[8] However, it has been reported that polysiloxanes of the type $(CH_3SiHO)_x$, containing an Si–H bond, are more susceptible to rearrangement than those containing no Si–H bonds.[9] It would appear likely that when hydrogen atoms rather than bulky organic or inorganic groups are present on the silicon then the silicon atom may be more susceptible to nucleophilic attack by an oxygen atom in a neighboring siloxane molecule. This would favor a greater rate of rearrangement of the system to the more thermodynamically stable state whatever it might be. Conversely, if the reaction of two different symmetrical disiloxanes to form an unsymmetrical disiloxane were thermodynamically favorable, then the above factors would promote a greater reaction rate. This is in qualitative agreement with the low temperature formation of $SiH_3SiH_2OSiH_3$ from the corresponding symmetrical disiloxanes.

The reaction of $(SiH_3SiH_2)_2O$ with BCl_3 (eq. 8) is apparently completely analogous to the over-all reaction of $(SiH_3)_2O$ with BCl_3 (eq. 3). However, in the case of the former compound, no intermediate $SiH_3SiH_2OBCl_2$ species corresponding to the SiH_3OBCl_2 obtained with $(SiH_3)_2O$ was observed. Although the absence of $SiH_3SiH_2OBCl_2$ in the reaction products may be due to slight differences in the manner in which the corresponding reactions of $(SiH_3SiH_2)_2O$ and $(SiH_3)_2O$ with BCl_3 were performed, it appears likely that $SiH_3SiH_2OBCl_2$, if it does exist, is less stable than SiH_3OBCl_2 and that it decomposed during the reaction in an analogous manner to SiH_3OBCl_2 (eq. 2). This conclusion is supported by the observation that some SiH_3OBCl_2 but no $SiH_3SiH_2OBCl_2$ was formed during the reaction of a mixture of $(SiH_3)_2O$ and $(SiH_3SiH_2)_2O$ with BCl_3. This is consistent with the fact that Si_2H_6 and its simple derivatives frequently appear to react more rapidly than analogous compounds which contain no silicon–silicon bond.[10]

It has been suggested that the reaction of a disiloxane with a boron halide might involve a four-center transition complex,[2] as exemplified below for $(CH_3)_3SiOSiH_3$. Cleavage could then occur at the broken line to yield SiH_3Cl and $(CH_3)_3SiOBCl_2$.



$$\begin{array}{l}(CH_3)_3Si-O-SiH_3\\ \qquad\qquad\ \downarrow\quad\ \uparrow\\ \qquad\qquad\ B-Cl\\ \qquad\qquad\ Cl_2\end{array}$$

A similar complex in which the chlorine is attached, instead, to the silicon of the trimethylsilyl group can be formulated. However, it appears that the former complex is the more important for this compound since considerably more SiH_3Cl than $(CH_3)_3SiCl$ was formed during the reaction of $(CH_3)_3SiOSiH_3$ with BCl_3, and no SiH_3OBCl_2 was produced. This is understandable since both the steric requirements of the methyl groups and their inductive effect would tend to reduce nucleophilic attack upon the silicon in the $(CH_3)_3Si$ group. It is assumed that the different rates of cleavage of the H_3Si–O and $(CH_3)_3Si$–O bonds are due to purely kinetic factors and that any changes in the activation energies caused by a difference in the H_3Si–O and $(CH_3)_3Si$–O bond energies is unimportant.

In the reaction of BCl_3 with $SiH_3SiH_2OSiH_3$, considerably more SiH_3SiH_2Cl was produced than SiH_3Cl. The greater ease of cleavage of the SiH_3SiH_2–O bond as compared to the H_3Si–O bond is also evidenced by the fact that $(SiH_3SiH_2)_2O$ was consumed in preference to $(SiH_3)_2O$ when a mixture of the disiloxanes was treated with a deficit of BCl_3. Assuming that the different rates of cleavage are due only to kinetic factors then the

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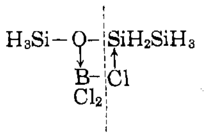
more important complex in the reaction involving $SiH_3SiH_2OSiH_3$ would appear to be



$$H_3Si-\underset{\underset{Cl_2}{\overset{\downarrow}{B}-}}{O}-\underset{\overset{\uparrow}{Cl}}{SiH_2}SiH_3$$

rather than that in which the chlorine is attached to the SiH_3 group bonded directly to the oxygen. This is contrary to what would have been expected from steric considerations since the presence of the large H_3Si group would tend to make the silicon atom to which it was attached less vulnerable to attack. If a H_3SiSiH_2 group is regarded as being derived from a H_3Si group by replacing a hydrogen atom with a H_3Si grouping, then it seems that the H_3Si group in the H_3SiSiH_2 moiety acts as if it were attracting electrons more strongly than the hydrogen it replaced. It is difficult to predict accurately from simple electronegativity data whether the H_3Si group as a whole should have a $+I$ or $-I$ inductive effect, although the relative electronegativities of hydrogen (2.1) and silicon (1.8) might suggest that the H_3Si group would be electron releasing. However, regardless of the expected inductive effect of the H_3Si group, it appears possible that this group, when present in a H_3SiSiH_2 group, might be expected under certain circumstances to effectively withdraw electrons by means of $d\pi$–$d\pi$ bonding between adjacent silicon atoms. The actual transition complex, once formed, is assumed to involve a pentacoordinate silicon atom. The bonding at the silicon may actually approach that of a trigonal bipyramidal sp^3d hybrid.[11] A complex of the type postulated for a "broadside" replacement reaction at silicon[11] is shown in Fig. 1. The H_2SiO group is regarded as lying in the *xy*-plane with the two hydrogen atoms and the oxygen atom being mutually separated from each other by angles of 120°.

If the d_{z^2} silicon orbital is involved in the hybridization, then the d_{xz} orbital would be so situated that it could overlap with a p_x orbital of the chlorine. This would give some measure of $p\pi$–$d\pi$ bonding in the complex in addition to the σ-bond formed by overlap of the chlorine p_z orbital with the silicon $sp^3d_{z^2}$ orbital. Such π-bonding stabilization of the transition complex would be expected to be greater in the case of the SiH_3SiH_2 group since the charge placed upon the α silicon by the π-bond might be transferred in part to the β silicon by means of $d\pi$–$d\pi$ overlap[12] between the adjacent silicon atoms. It has been pointed out[11] that factors which stabilize the complex will also lower the energy of the highest energy transition state and will facilitate reaction. Thus, in analogous reactions involving atoms having lone pairs of electrons, the SiH_3SiH_2 group may be expected to react more rapidly than the H_3Si group. This is consistent with the marked lability of the $SiH_3SiH_2OSiH_3$–$(SiH_3)_2O$–$(SiH_3SiH_2)_2O$ system and the apparent instability of $SiH_3SiH_2OBCl_2$.

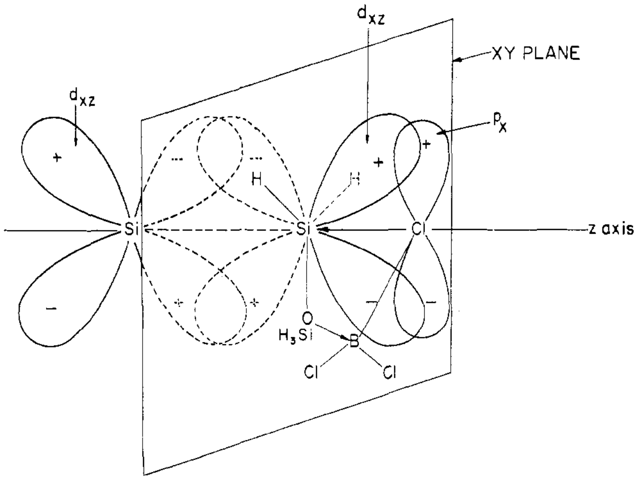


Fig. 1.—$d\pi$–$d\pi$ overlap in a silicon–silicon bond in the transition complex formed from $SiH_3OSiH_2SiH_3$ and BCl_3.

Experimental

Apparatus.—All work was carried out in a Pyrex glass vacuum system. All apparatus and techniques employed were identical with those previously described.[13–16] Mass spectra were obtained by means of a Consolidated Electrodynamics Model 21-130 mass spectrometer. Infrared absorption spectra were recorded with a Perkin-Elmer 137B Infracord spectrophotometer on the gaseous phase at room temperature with the sample confined in a 10-cm. cell fitted with 6-mm. KBr windows cemented with glyptal resin. Proton magnetic resonance spectra were recorded by means of an HR60 Varian Associates spectrometer, Model 4300D, with flux stabilizer, operated at 60 Mc./sec. at room temperature.

Materials.—$(CH_3)_3SiOH$ (b.p. 98–99°, lit.[17] 99° (734 mm.)) was prepared from $[(CH_3)_3Si]_2O$, NH_4F, and H_2SO_4.[17] SiH_3I (mol. wt. found 158.4, calcd. 158.03; vapor pressure at 0° found 125.5 mm., lit.[18] 123.9 mm.) was obtained by allowing HI to react with SiH_4.[18] SiH_3SiH_2Br (mol. wt. found 141.1, calcd. 141.14; vapor pressure at 0° found 44.1 mm., lit.[19] 45.0 mm.; confirmed by infrared[19] and mass spectra) was prepared from Si_2H_6 and HBr.[19] $(SiH_3)_2O$ (mol. wt. found 78.0, calcd. 78.23; vapor pressure at $-64.8°$ found 61.0 mm., lit.[20] 59.2 mm.; confirmed by infrared spectrum[21]) was synthesized by hydrolyzing SiH_3I. $(SiH_3SiH_2)_2O$ (mol. wt. found 139.6, calcd. 138.44; vapor pressure at 0° found 11.2 mm., lit.[12] 12.3 mm.; confirmed by infrared[13] and mass spectra) was prepared by hydrolyzing SiH_3SiH_2Br. Commercial BCl_3 (mol. wt. found 118.7, calcd. 117.20; confirmed by infrared spectrum[22]) was used without further purification.

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Synthesis of $(CH_3)_3SiOSiH_3$.—SiH_3I (12.560 mmoles) and $(CH_3)_3SiOH$ (11.871 mmoles) were combined and allowed to stand for approximately 20 min. at room temperature in a 500-ml. bulb. The products were then distilled into approximately 10 ml. of degassed water in order to hydrolyze any unreacted SiH_3I. Distillation through a series of traps held at −78, −96, and −196° yielded pure $(CH_3)_3SiOSiH_3$ (3.645 mmoles, 30.7% yield; mol. wt. found 120.8, calcd. 120.31; vapor pressure at 0°, 101.3 mm.; m.p. $< -134°$) as a condensate in the −96° trap. The $(CH_3)_3SiOSiH_3$ was further purified by slowly distilling it from a trap held at −78°. In some preparations carried out as above, final purification was effected by slowly distilling the crude compound from a trap held at −78° and rejecting the first and last of the five fractions which distilled.

$(CH_3)_3SiOSiH_3$ has a camphor-like odor and will burn when ignited.

Analysis.—A sample of $(CH_3)_3SiOSiH_3$ (0.9318 mmole; mol. wt. found 121.1, calcd. 120.31; vapor pressure at 0° 103.3 mm.) was hydrolyzed in 35% aqueous degassed NaOH (15 ml.) containing ethanol (2 ml.) and piperidine (2 ml.). Hydrogen present as Si–H was determined by measuring the volume of H_2 (STP) liberated (found 62.4 ml., calcd. 62.62 ml.). Carbon and total hydrogen were determined by standard combustion techniques.[23] *Anal.* Calcd. for $C_3H_{12}Si_2O$: C, 29.95; H, 10.05. Found: C, 29.74; H, 9.93.

Thermal Stability.—After 53 hr. at 0° a sample of $(CH_3)_3SiOSiH_3$ (vapor pressure at 0°, 101.7 mm.) underwent little change in vapor pressure (vapor pressure at 0°, 100.3 mm.). However, some decomposition had occurred since when approximately half the sample was removed by distillation the residue had a vapor pressure at 0° of 61.6 mm. and a molecular weight of 127.6 (calcd. for $(CH_3)_3SiOSiH_3$, 120.31). On distilling the entire sample through a trap held at −112° a small amount of $(SiH_3)_2O$ (identified by infrared spectrum[21]) was obtained in the most volatile fraction. After repeated distillations of the remaining material through a trap held at −78° a small amount of condensate which consisted chiefly of $[(CH_3)_3Si]_2O$ (identified by infrared spectrum)[24] was isolated.

Vapor Pressure.—The vapor pressure of a sample of $(CH_3)_3SiOSiH_3$ (vapor pressure at 0°, 102.3 mm) was determined over mercury in an all-glass tensimeter, the inner surfaces of which had previously been pretreated with a sample of the slightly impure compound. Vapor pressures at various temperatures are given in Table I. Vapor pressures in the range −63.7 to 9.1° are given by the equation

$$\log P_{\text{mm}} = -\frac{1628.80}{t + 273.16} + 7.97040$$

TABLE I

VAPOR PRESSURES OF $(CH_3)_3SiOSiH_3$[a]

Temp., °C.	P, mm., obsd.	P, mm., calcd.	Temp., °C.	P, mm., obsd.	P, mm., calcd.
−63.7	1.4	1.6	−3.3	87.2	86.0
−43.1	7.5	7.8	−0.1	103.6	101.3
−35.6	12.6	13.0	+9.1	163.4	158.4
−23.6	27.5	27.8	−0.1[b]	102.9	101.3
−17.5	39.8	39 8	−17.9[b]	42.2	38.9
−11.2	56.0	56.6	−45.1[b]	8.3	6.7
−8.0	67.7	67.3			

[a] Duration of experiment, 12.5 hr. [b] Pressures observed on decreasing the temperature.

Additional values to those given in Table I were used to derive the above relationship. The extrapolated boiling point is 46.9°, the heat of vaporization is 7.45 kcal. mole^{-1}, and Trouton's constant is 23.3 cal. deg.$^{-1}$ mole^{-1}. The irreversibility of the vapor pressure curve on decreasing the temperature shows that some decomposition had occurred during the experiment. This confirms the thermal stability studies.

Synthesis of $SiH_3SiH_2OSiH_3$. (A) By the Cohydrolysis of SiH_3I and SiH_3SiH_2Br.—A mixture of SiH_3I (15.086 mmoles) and SiH_3SiH_2Br (5.030 mmoles) was distilled into a 500-ml. flask containing 15 ml. of degassed water. An immediate reaction commenced upon thawing, and after swirling the contents of the flask for approximately 5 min. at room temperature a small quantity of hydrogen was found to be present. The products were distilled through successive traps held at −46, −96, and −196°. Bisdisilanyl ether collected in the −46° trap while $(SiH_3)_2O$ collected in the −196° trap. The crude $SiH_3SiH_2OSiH_3$ which condensed in the −96° trap was permitted to distil slowly from a trap held at −64° to yield the pure compound (~0.9 mmole; 18% yield; mol. wt. found 108.0, calcd. 108.34; vapor pressure at −24.2° found 31.5 mm., calcd., 30.9 mm.; m.p. $< -134°$).

(B) **By the Equilibration of $(SiH_3SiH_2)_2O$ and $(SiH_3)_2O$.**—$(SiH_3)_2O$ (0.308 mmole) and $(SiH_3SiH_2)_2O$ (0.282 mmole) were combined and held at 0°. The vapor pressure of the mixture at this temperature increased from 63.3 to 65.3 mm. during 5 hr., and after 21 hr. it maintained a constant value of 67.9 mm. The infrared spectrum of the mixture showed the presence of some $SiH_3SiH_2OSiH_3$. An additional 0.553 mmole of $(SiH_3)_2O$ was then added to the mixture, which was held for 16.5 hr. at room temperature in a 10-ml. all-glass tube. The material was then distilled several times through successive traps held at −64, −112, and −196° to give pure $SiH_3SiH_2OSiH_3$ (0.183 mmole, 32.4% yield; mol. wt. found 110.5, calcd. 108.34; vapor pressure at −23.8° found 31.3 mm., calcd. 31.6 mm.; infrared spectrum identical with that of material obtained by method A) as a condensate in the −112° trap. The condensate in the −196° trap was identified as $(SiH_3)_2O$ (0.752 mmole; vapor pressure at −63.4° found 60.8 mm., lit.[20] 64.9 mm.; confirmed by infrared spectrum[21]), and the condensate in the −64° trap was found to be $(SiH_3SiH_2)_2O$ (0.143 mmole; vapor pressure at 0° found 12.6 mm., lit.[13] 12.3 mm.; confirmed by infrared spectrum[12]). The total recovery of volatile material was 94.3%.

Analysis.—$SiH_3SiH_2OSiH_3$ (0.378 mmole; mol. wt. found 107.6, calcd. 108.34; vapor pressure at −22.6° found 36.5 mm., calcd. 34.0 mm.) upon hydrolysis in 35% aqueous degassed NaOH (15 ml.) containing ethanol (2 ml.) and piperidine (2 ml.) yielded 76.1 ml. of H_2 (STP) (calcd. 76.20 ml.). Silicon was determined as SiO_2[25] after evaporation of volatile material by heating in a platinum basin. *Anal.* Calcd.: Si, 77.8. Found: Si, 77.1.

Thermal Stability. (A) Gas Phase.—No change was observed in the infrared spectrum of a sample of gaseous $SiH_3SiH_2OSiH_3$ when it was allowed to stand in an infrared gas cell for 80 min. at room temperature.

(B) **Liquid Phase.**—The vapor pressure of a sample of $SiH_3SiH_2OSiH_3$ (1.137 mmoles) increased by approximately 50% when it was held at approximately −24° for 2 hr. On holding it at 0° for 22 hr. it increased by approximately another 20%. The material was then distilled several times through successive traps held at −64, −96, and −196°. Pure $(SiH_3SiH_2)_2O$ (0.282 mmole; mol. wt. found 139.6, calcd. 138.44; vapor pressure at 0° found 12.7 mm., lit.[13] 12.3 mm.; confirmed by infrared spectrum[13]) condensed in the −64° trap, while pure $(SiH_3)_2O$ (0.308 mmole, mol. wt. found 77.2, calcd. 78.23; vapor pressure at −63.6° found, 60.7 mm., lit.[20] 64.1 mm.; confirmed by infrared spectrum[21]) collected in the −196° trap. Unchanged $SiH_3SiH_2OSiH_3$ (0.494 mmole; mol. wt. found 109.2, calcd. 108.34; vapor pressure at −23.8° found 31.6 mm., calcd. 31.6 mm.; confirmed by infrared spectrum) condensed in the −96° trap.

It is most important to note that the stability of $SiH_3SiH_2OSiH_3$ is apparently affected greatly by the presence of minute quantities of unknown impurities with which it might become

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[23] Analysis was performed by Micro-Analysis Inc., Wilmington, Del. Sample was transported in Dry Ice.

[24] H. Kriegsmann, *Z. Elektrochem.*, **61**, 1088 (1957).

[25] A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis, Theory and Practice," 2nd Ed., Longmans, Green and Co., London, 1951, p. 503.

contaminated during certain manipulations in the vacuum system. Thus a sample of the freshly distilled compound will maintain a constant vapor pressure at approximately −24° for up to an hour, but after determining its molecular weight or measuring its infrared spectrum the vapor pressure of the same sample will begin to increase rapidly (within 5 min.) at this temperature.

Vapor Pressure.—The vapor pressure of $SiH_3SiH_2OSiH_3$ (vapor pressure at −23.6° found 33.0 mm. (constant), calcd. 32.0 mm.) was determined by using an apparatus consisting of a side arm attached to a mercury manometer. The apparatus was pretreated with a sample of $SiH_3SiH_2OSiH_3$. Vapor pressures at various temperatures are given in Table II. Vapor pressures in the range −59.9 to 12.0° are given by the equation

TABLE II

VAPOR PRESSURES OF $SiH_3OSiH_2SiH_3$[a]

Temp., °C.	*P*, mm., obsd.	*P*, mm., calcd.	Temp., °C.	*P*, mm., obsd.	*P*, mm., calcd.
−59.9	2.3	2.4	−8.9	74.0	74.2
−46.4	7.0	7.0	−5.7[c]	88.5	88.0
−45.8[c]	7.3	7.3	0.0[c]	119.1	118.1
−36.7	13.9	13.9	+9.7	187.5	189.6
−33.5	17.2	17.1	+12.0[c]	208.2	211.2
−24.1[c]	30.5	31.0	0.0[b,c]	125.8	118.1
−19.9	40.3	39.9	−33.9[b]	17.0	16.7
−15.6	51.2	51.2	−45.3[b,c]	8.7	7.6
			−196[b,c]	0.0	...

[a] Duration of experiment approximately 7 hr. [b] Pressure observed on decreasing the temperature. [c] Results of separate study on a different sample.

$$\log P_{\mathrm{mm}} = -\frac{1638.50}{t + 273.16} + 8.07060$$

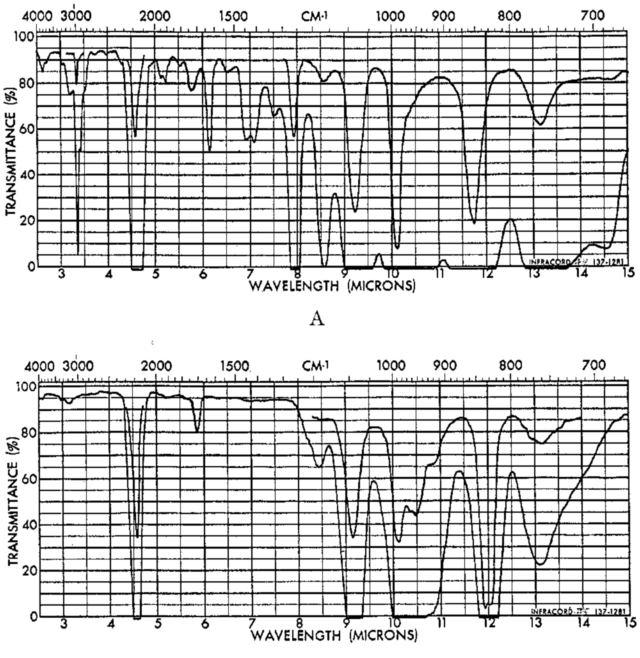
Additional values to those given in Table II were used to derive the above relationship. The extrapolated boiling point is 42.6°, the heat of vaporization is 7.50 kcal. mole^{-1}, and Trouton's constant is 23.8 cal. deg.$^{-1}$ mole^{-1}. The irreversibility of the vapor pressure curve on decreasing the temperature shows that some decomposition had occurred during the experiment. This confirms the thermal stability studies.

Mass Spectra. (A) $(CH_3)_3SiOSiH_3$.—This was determined at an ionizing voltage of 76.0 volts and at an ionizing current of 20 μa. Since peaks of only minute intensity above mass number of 120 were observed, the possibility of the compound being an equimolar mixture of $[(CH_3)_3Si]_2O$ and $(SiH_3)_2O$ was eliminated. A reasonably strong parent ion peak of mass number 120 was observed. Possible assignments for the major fragments (in decreasing order of abundance) are: $(CH_3)_2SiOSiH_3^+$, CH_3SiO^+, $HSiO^+$, $(CH_3)_2SiHOSiH_3^+$ (rearranged fragment), $(CH_3)_2SiOSiH^+$, and CH_3Si^+.

(B) $SiH_3SiH_2OSiH_3$.—This was determined at an ionizing voltage of 74.0 volts and at an ionizing current of 20 μa. Since peaks of only minor intensity above mass number of 108 were observed, the possibility of the compound being an equimolar mixture of $(SiH_3SiH_2)_2O$ and $(SiH_3)_2O$ was eliminated. A reasonably strong parent ion peak of mass number 108 was observed. Possible assignments for the major fragments (in decreasing order of abundance) are: $H_3Si_2O^+$, $H_5Si_2O^+$, $H_4Si_2O^+$, HSi_2O^+, SiH^+, Si_2O^+.

In addition to the expected fragments a number of rearranged fragments were observed in the mass spectra of both $(CH_3)_3SiOSiH_3$ and $SiH_3SiH_2OSiH_3$. Small (parent ion + 1) fragments were also found for these compounds. In both these respects the results are similar to those reported for certain organosilicon and/or organic ethers.[26]

Infrared Absorption Spectra.—The spectrum of $(CH_3)_3SiOSiH_3$ was measured at pressures of 57.0 and 2.6 mm. and that of $SiH_3SiH_2OSiH_3$ at pressures of 14.0 and 1.6 mm. The spectra are given in Fig. 2 and the absorption maxima are listed in Table III.



A

B

Fig. 2.—Infrared absorption spectra of: A, $(CH_3)_3SiOSiH_3$; B, $SiH_3SiH_2OSiH_3$.

TABLE III

INFRARED ABSORPTION MAXIMA OF $(CH_3)_3SiOSiH_3$ AND $SiH_3SiH_2OSiH_3$ (CM.$^{-1}$)

$(CH_3)_3$-$SiOSiH_3$	SiH_3-SiH_2OSiH_3	Assignment	Reference
3850 vvw		Unassigned	
2990 w		C–H stretch	*a*, *b*
2940 vvw			
2190 m	2190 s	Si–H stretch	*b*, *c*
1950 vw		Unassigned	
1920 vw			
1735 vw	1710 vw	Combination antisym. and sym. Si–O–Si stretches	21
1630 vw		Unassigned	
1440 dvw		CH_3 deform. (asym.)	*b*
1420 dvw			
1330 vw		Unassigned	
1260 m		CH_3 deform. (sym.)	*a*, *b*
	1192 vw	Unassigned	
1170 w		CH_3 rock	6
1080 s	1095 s	Antisym. SiOSi stretch	21
989 vs	989 s	Bending of the SiH_2 angles in SiH_3 and/or SiH_2 groups	14, *b*, *c*
	968 w		
	956 m		
	839 dvs		
	830 dvs		
850 s		Si–CH_3 stretch in –$Si(CH_3)_3$	*a*
760 m			
	764 m	SiH_3 and/or SiH_2 rocking	14

[a] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons Inc., New York, N. Y., 1958. [b] E. A. V. Ebsworth, M. Onyszchuk, and N. Sheppard, *J. Chem. Soc.*, 1453 (1958). [c] H. R. Linton, and E. R. Nixon, *Spectrochim. Acta*, **12**, 41 (1958).

Proton Nuclear Magnetic Resonance Spectra.—The proton nuclear magnetic resonance spectra were consistent with the pro-

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(26) A. G. Sharkey, Jr., R. A. Friedel, and S. H. Langer, *Anal. Chem.*, **29**, 770 (1957); F. W. McLafferty, *ibid.*, **29**, 1782 (1957).

TABLE IV

PROTON NUCLEAR MAGNETIC RESONANCE ABSORPTION MAXIMA OF $(CH_3)_3SiOSiH_3$ AND $SiH_3SiH_2OSiH_3$[a]

Compound	Proton environment	Signal ratio	Chemical shift,[b] p.p.m.	$J_{HH'}$, c.p.s.	$J_{^{29}Si-H}$, c.p.s.
$(CH_3)_3SiOSiH_3$[c]	CH_3	3.0	1.35[e]	...	...
	SiH_3	1.0	−3.18[e]	...	216.4
$SiH_3SiH_2OSiH_3$[d]	$H_3Si(O)$	3.0	−3.18[e]	...	219.2
	SiH_2	2.1	−3.69[f]	2.5	210.6
	$H_3Si(SiH_2)$	3.0	−1.78[g]	2.5	192.8

[a] Measured in cyclohexane as internal standard. [b] $<\pm 0.01$ p.p.m. [c] 15% solution (by volume). [d] 25% solution (by volume). [e] Single peak. [f] Quartet. [g] Triplet.

posed structures of the compounds. The data are given in Table IV.

Reaction of $(SiH_3SiH_2)_2O$ with BCl_3.—$(SiH_3SiH_2)_2O$ (0.276 mmole) and BCl_3 (0.139 mmole) were held at −78° for 12 hr. No hydrogen was liberated. When all volatile material had been distilled from the reaction vessel a white solid remained which was assumed to be B_2O_3 by analogy with the products of the similar reaction between $(SiH_3)_2O$ and BCl_3.[2] Unreacted $(SiH_3SiH_2)_2O$ (0.024 mmole; identified by infrared spectrum[13]) was recovered from the products by distillation through a trap held at −78° in which it condensed. Material passing through the trap was slightly impure SiH_3SiH_2Cl (0.384 mmole; mol. wt. found 100.6, calcd. 96.68; confirmed by infrared spectrum[15]).

Pure SiH_3SiH_2Cl (0.345 mmole; mol. wt. found 95.8; confirmed by infrared spectrum[15]) was obtained by slowly distilling the impure material from a trap held at −96°. No evidence was obtained for the formation of any other volatile material.

Reaction of $(CH_3)_3SiOSiH_3$ with BCl_3.—$(CH_3)_3SiOSiH_3$ (0.710 mmole) and BCl_3 (0.710 mmole) were held at −78° for 12 hr. No hydrogen or any nonvolatile material was formed. Slightly impure $(CH_3)_3SiOBCl_2$ (0.408 mmole; mol. wt., found 175.4, calcd. 170.94; vapor pressure at 0° found 6.8 mm., lit.[3] 10.5 mm.; confirmed by mass spectrum) remained as a less volatile fraction each time the products were distilled. Repeated distillation yielded the pure compound (0.0848 mmole; mol. wt. 170.4). Distillation of the remaining products in a low-temperature fractionating column similar to that described by Coates[27] gave B_2H_6 (~0.1 mmole; identified by infrared spectrum[28]), SiH_3Cl (0.347 mmole; mol. wt. found 67.1, calcd. 66.57; confirmed by infrared[29] and mass spectra), and impure BCl_3 (0.0136 g.; mol. wt. found 107.0, calcd. 117.2; confirmed by infrared spectrum[22]). The mass spectrum fragmentation pattern and infrared spectrum of the least volatile fraction of the reactants (0.0356 g.; mol. wt. found 160.1) strongly suggested that it consisted of a mixture of $(CH_3)_3SiCl$ (mol. wt. 108.66) and $(CH_3)_3SiOSiH_2Cl$ (mol. wt. 154.76) together with possibly a small amount of $(CH_3)_3SiOSiHCl_2$ (mol. wt. 189.22). Assuming the presence of only the first two species and by using the unique $[(CH_3)_2SiCl^{35}]^+$ fragment of $(CH_3)_3SiCl$ of mass number 93, a value of 0.024 mmole was obtained for the quantity of $(CH_3)_3SiCl$ present in the mixture. Since the vapor pressure of the mixture at 0° was 23.5 mm. and since the vapor pressure of $(CH_3)_3SiOSiH_3$ at this temperature is 101.8 mm., there could be very little, if any, of the unreacted starting material present. It therefore appears that $(CH_3)_3SiOSiH_3$ and BCl_3 may interact according to eq. 9 and 14 simultaneously. Such a reaction

$$6(CH_3)_3SiOSiH_3 + 2BCl_3 \longrightarrow 6(CH_3)_3SiOSiH_2Cl + B_2H_6 \quad (14)$$

would be somewhat analogous to that which occurs between alkyl halides and certain organosilicon hydrides,[30] *viz.*

$$(C_2H_5)_3SiH + RCl \xrightarrow{Al_2Cl_6} (C_2H_5)_3SiCl + RH \quad (15)$$

Reaction of $SiH_3SiH_2OSiH_3$ with BCl_3.—$SiH_3SiH_2OSiH_3$ (0.373 mmole) and BCl_3 (0.189 mmole) were held at −78° for 12 hr. No hydrogen was liberated. A white solid, presumably B_2O_3, remained in the reaction vessel upon removing the volatile products. On distilling the products through a trap held at −112° a more volatile fraction which consisted of SiH_3Cl and $(SiH_3)_2O$ was obtained. These components could not be separated quantitatively from the mixture (0.0154 g.; mol. wt. found 68.2, calcd. for SiH_3Cl 66.57, calcd. for $(SiH_3)_2O$ 78.23; the infrared[21,29] spectrum showed the presence of SiH_3Cl and $(SiH_3)_2O$ only). Calculations based on the molecular weight observed indicated the presence of 0.194 mmole of SiH_3Cl and 0.032 mmole of $(SiH_3)_2O$ in the mixture.

The substance which remained in the −112° trap was distilled slowly from a trap at −96°. The small amount of material remaining in this trap was found to be impure SiH_3OBCl_2 (0.033 mmole; identified by infrared spectrum[2]). The distillate was passed through a trap held at −112° and thence into a trap immersed in liquid nitrogen. The condensate in the −112° trap was identified as SiH_3SiH_2Cl (0.332 mmole; mol. wt. found 99.4, calcd. 96.68; infrared spectrum identical with that of SiH_3SiH_2Cl[15]). The small amount of material which condensed in the liquid nitrogen trap was found to be $(SiH_3)_2O$ (0.029 mmole; identified by infrared spectrum[21]). The above products represent a 93.6% recovery of SiH_3 groups, an 89.0% recovery of SiH_3SiH_2 groups, and a 104% recovery of chlorine. This means that 2.5 mg. of SiH_3SiH_2 groups was not recovered as volatile product. Whether this is due to experimental loss or to the fact that the proposed cleavage reactions do not occur stoichiometrically is not known. However, it is important to note that even though the percentage recovery of SiH_3SiH_2 groups is less than that of the SiH_3 groups the quantity of SiH_3SiH_2Cl obtained from the reaction is still considerably greater than that of the SiH_3Cl, and the conclusions reached previously are therefore in no way invalidated.

Reaction of a Mixture of $(SiH_3SiH_2)_2O$ and $(SiH_3)_2O$ with BCl_3.—$(SiH_3SiH_2)_2O$ (0.298 mmole) and $(SiH_3)_2O$ (0.301 mmole) were mixed in a 10-ml. reaction vessel into which BCl_3 (0.301 mmole) was then distilled. After raising the temperature to −78° liquid phase only was present in the reaction vessel. It was then shaken and was held at this temperature for 12 hr. No hydrogen was liberated. The volatile products were distilled from the brownish solid residue remaining in the reaction vessel. This was presumed to consist essentially of B_2O_3.

A very small amount of B_2H_6 (~0.1 mmole; identified by infrared spectrum[28]) was first removed from the products by means of a low-temperature fractionating column. The remaining material was distilled through a trap held at −112° and the substance which was not condensed at this temperature was found to be a mixture of SiH_3Cl and $(SiH_3)_2O$ (0.0250 g.; mol. wt. found 71.8, calcd. for SiH_3Cl 66.57, calcd. for $(SiH_3)_2O$ 78.23; the infrared spectrum showed the presence of SiH_3Cl[29] and $(SiH_3)_2O$[21] only). Calculations based on the molecular weight observed indicated the presence of 0.192 mmole of SiH_3Cl and 0.156 mmole of $(SiH_3)_2O$ in the mixture.

The material which condensed in the −112° trap was allowed to distil slowly from a trap held at −96° and was identified as SiH_3SiH_2Cl (0.452 mmole; mol. wt. found 97.6, calcd. 96.68; confirmed by infrared spectrum[15]). The substance which remained in the −96° trap was found to be SiH_3OBCl_2 (0.047 mmole; mol. wt. found 130.5, calcd. 128.85; confirmed by infrared spectrum[2]). The above products represent a 91.5% recovery of SiH_3 groups, a 75.8% recovery of SiH_3SiH_2 groups, and an 81.7% recovery of chlorine. It should be noted that even though the percentage recovery of SiH_3 groups was greater than that obtained for SiH_3SiH_2 groups, considerably more SiH_3SiH_2Cl than SiH_3Cl was produced in the reaction. It is possible that some side reaction may have been at least partly responsible for the lower percentage recovery of SiH_3SiH_2 groups, since this was the only experiment involving BCl_3 in which a colored nonvolatile residue was produced.

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(27) G. E. Coates, *J. Chem. Soc.*, 2003 (1951).

(28) W. C. Price, *J. Chem. Phys.*, **16**, 894 (1948).

(29) C. Newman, J. K. O'Loane, S. R. Polo, and M. K. Wilson, *ibid.*, **25**, 855 (1956).

(30) F. C. Whitmore, E. W. Pietrusza, and L. H. Sommer, *J. Am. Chem. Soc.*, **69**, 2108 (1947).