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Steric Effects of the *t*-Butyl Group in Organosilicon Compounds[1]

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Steric effects of the *t*-butyl group have made possible the synthesis of a new class of organosilicon compounds, *dialkyldiaminosilanes*. Silanediols containing a *t*-butyl group are extremely resistant toward condensation in comparison with ordinary dialkylsilanediols.

Previously,[2] we reported the synthesis of *t*-butyltrichlorosilane, *t*-butyltrimethylsilane and di-*t*-butyldichlorosilane, as comprising the first examples of *t*-alkylorganosilicon compounds. These substances were prepared through the use of *t*-butyllithium, it having been shown that *t*-alkyl Grignard reagents fail to give *t*-alkylorganosilicon compounds with a variety of starting materials under a wide range of conditions.

In extension of our previous synthesis of di-*t*-butyldichlorosilane, we have now prepared three additional dialkyldichlorosilanes containing a *t*-butyl group, by the general reaction

$$t\text{-BuLi} + \text{RSiCl}_3 \longrightarrow t\text{-BuRSiCl}_2$$

where R is methyl, phenyl and *n*-hexadecyl. In sharp contrast to the reaction of *t*-butyllithium with *t*-butyltrichlorosilane which gave a 59% yield of di-*t*-butyldichlorosilane after four days at 70°,[2,3] the present reactions proceeded smoothly at reflux temperature (37°), required only three or four hours for completion and gave yields of about 70%.

Attempts to effect the synthesis of tri-*t*-butylchlorosilane from *t*-butyllithium and di-*t*-butyldichlorosilane even at an elevated temperature of 160° met with failure.[2,4]

We turn now to a consideration of the products obtained by ammonolysis and hydrolysis of the above four *t*-butyldichlorosilanes, substances whose properties show in striking fashion the profound influence exerted by the *t*-butyl group in inhibiting intermolecular condensation of difunctional silanes.

It has long been known that the silicon–chlorine bond reacts readily with ammonia. The reaction of trialkylchlorosilanes with liquid ammonia gives excellent yields of the corresponding trialkylaminosilane, except in the reaction of trimethylchlorosilane which gives the dimer, $\text{Me}_3\text{SiNHSiMe}_3$, hexamethyldisilazane.[5] Further, ordinary dialkyldichlorosilanes, such as dimethyl- and diethyldichlorosilane react readily with ammonia, but yield no dialkyldiaminosilanes, $\text{R}_2\text{Si(NH}_2)_2$. Instead, cyclic trisilazanes and tetrasilazanes, $(\text{R}_2\text{SiNH})_3$ and $(\text{R}_2\text{SiNH})_4$ are formed exclusively.[6] In the present work ammonolysis of di-*n*-butyldichlorosilane likewise gave no di-*n*-butyldiaminosilane. The product was the cyclic trimer, hexa-*n*-butylcyclotrisilazane. It is evident that in such reactions an unstable diaminosilane is formed which immediately gives intermolecular condensation with elimination of ammonia and formation of Si–NH–Si linkages.

The formation of di-*t*-butyldiaminosilane in excellent yield from the reaction of the dichlorosilane with liquid ammonia is in striking contrast to the above.

$$(t\text{-Bu})_2\text{SiCl}_2 + 4\text{NH}_3 \longrightarrow (t\text{-Bu})_2\text{Si(NH}_2)_2 + 2\text{NH}_4\text{Cl}$$

Di-*t*-butyldiaminosilane is a clear, water-white liquid with an unpleasant ammoniacal odor; *it can be distilled at atmospheric pressure (190°) without decomposition.*

Subsequent to the synthesis of di-*t*-butyldiaminosilane, which provided the first example of a dialkyldiaminosilane,[7] it was found that *t*-butylmethyl-, *t*-butylphenyl- and *t*-butyl-*n*-hexadecyldichlorosilane, could readily be converted to the corresponding dialkyldiaminosilanes. Thus, the presence of even a single *t*-butyl group on silicon permits the formation of a variety of stable dialkyldiaminosilanes.

Dialkylsilanediols, $\text{R}_2\text{Si(OH)}_2$, *e.g.*, diethyl-, di-*n*-propyl- and di-*n*-butylsilanediol have been prepared by carefully controlled hydrolysis of the corresponding dichlorosilanes,[8] while hydrolysis of the difluorosilanes has given diisopropyl-, diisobutyl- and dicyclohexylsilanediol.[9] The three dialkylsilanediols containing primary alkyl groups are obtained as white solids that melt in the vicinity of

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(1) Paper 38 in a series on organosilicon chemistry; for 37 see THIS JOURNAL, "New Intramolecular Rearrangements of α-Chloroalkylsilanes" Sommer, *et al.*, in press. Taken from the Ph.D. thesis of L. J. Tyler, The Pennsylvania State College, 1948.

(2) L. J. Tyler, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **69**, 981 (1947); *ibid.*, **70**, 2876 (1948).

(3) This temperature was obtained by removing a large portion of the pentane by distillation.

(4) In this connection it is of some interest to note that triisopropylchlorosilane, but not tetraisopropylsilane, has been synthesized by reaction of isopropyllithium with silicon tetrachloride; H. Gilman and R. N. Clark, THIS JOURNAL, **69**, 1499 (1947).

(5) R. O. Sauer and R. H. Hasek, *ibid.*, **68**, 241 (1946).

(6) S. D. Brewer and C. P. Haber, *ibid.*, **70**, 3888 (1948).

(7) Prior to this work the synthesis of organosilicate compounds of the type $(\text{RO})_2\text{Si(NH}_2)_2$ was reported; these compounds have no carbon–silicon linkages and hence are not classed as organosilicon compounds; C. S. Miner, Jr., *et al.*, *Ind. Eng. Chem.*, **39**, 1368 (1947).

(8) P. D. George, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **75**, 1585 (1953).

(9) C. Eaborn, *J. Chem. Soc.*, 2840 (1952).

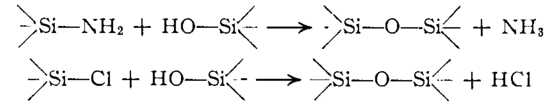
100°, are heat-sensitive toward condensation at this temperature, and are also readily condensed with elimination of water by the action of strong acid or base.[8] Diisopropylsilanediol is reported as not being decomposed when heated at 130° for some hours.[9] Data on the thermal stability of diisobutyl- and dicyclohexylsilanediol are not available. Recently, the synthesis of dimethylsilanediol from hydrolysis of dimethyldiethoxysilane has been reported. This substance is a white solid (m.p. 96–98°) which is very sensitive to condensation catalysts such as traces of acidic or alkaline material.[10]

In the present work hydrolysis of di-*t*-butyldichlorosilane readily gave di-*t*-butylsilanediol, a white crystalline solid (m.p. 152°), *which distilled without decomposition at a temperature of 210°.*

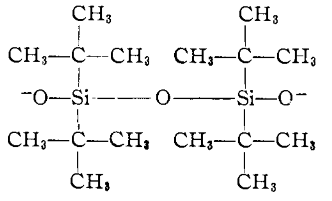
The thermal stability of this substance is equalled by its chemical inertness. Whereas other silanediols are easily polymerized by the action of strong acids, di-*t*-butylsilanediol was unaffected. Heating with concentrated hydrochloric acid and zinc chloride in an attempt to effect formation of the dichlorosilane gave back unchanged diol. A solution of the diol in concentrated sulfuric acid was heated to 110° and then poured on ice. Again, the diol was recovered.

Other dialkylsilanediols[8] are quantitatively "dehydrated" by refluxing a benzene solution of the diol with iodine. This procedure had no effect on di-*t*-butylsilanediol. Moreover, a mixture of this diol and iodine can be sublimed above 200° and the diol can be recovered unchanged.

The above data may be summarized in the statement that di-*t*-butylsilanediol does not undergo the intermolecular dehydration reaction so common to other silanediols. In harmony with this conclusion is the failure of di-*t*-butylsilanediol to react with di-*t*-butyldiaminosilane or di-*t*-butyldichlorosilane. These reactions would ordinarily proceed readily giving intermolecular condensation with formation of Si–O–Si linkages and elimination of ammonia or hydrogen chloride, respectively.

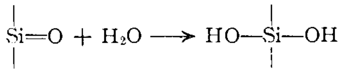


In every case investigated there is apparent the remarkable resistance that di-*t*-butylsilanes exhibit toward formation of the structural unit



From consideration of the above data there seems to be little doubt that the major factor responsible for the difficulty of obtaining structures of the above type, as well as the stability of di-*t*-butyldiaminosilane (where –NH– would replace –O– in the polymer), is steric hindrance. While a Fisher–Hershfelder model of the compound $(t\text{-Bu})_2(\mathrm{OH})\mathrm{Si{-}O{-}Si(OH)}(t\text{-Bu})_2$ may be constructed, thus indicating that *such a structure may be prepared,* the molecular model is quite difficult to construct because of the bulky *t*-butyl groups which are so crowded as to almost completely block free rotation about the bonds in this molecule.

Since di-*t*-butylsilanediol could not be made to undergo intermolecular loss of water, the possibility of intramolecular dehydration was investigated. The product of such a dehydration would be di-*t*-butyloxosilane, a substance having a silicon–oxygen double bond. In fact, the possibility that such a compound might be capable of existence constituted the major reason for our investigation of *t*-butylsilicon compounds. One method of attack on the problem of obtaining (for the first time) compounds having unsaturation stemming from silicon would be to block intermolecular reaction through the attachment to silicon of bulky or highly-branched organic groups. In this connection it seemed clear that a silicon–oxygen double bond, if formed, would be quite reactive due to extensive polarization of that bond, and that the possibility of the reaction



$$\mathrm{Si{=}O + H_2O \longrightarrow HO{-}Si{-}OH}$$

would certainly exist Therefore, dehydrating agents which would combine chemically with the water were tried. However, when di-*t*-butylsilanediol was passed through a tube filled with soda-lime heated to 300°, the only product isolated was unreacted diol. Calcium oxide at 450° also gave diol as the only isolated product. The diol reacted readily with phosphorus pentoxide using an ether solvent, but instead of dehydration of the diol, a complex *t*-butylsilicon phosphate resulted. This on hydrolysis gave back the original diol. Finally, the diol was passed over alumina at 300°. From this experiment there was obtained a 30% recovery of starting material. There was some indication that dehydration had occurred but no dehydrated product could be isolated.

The failure to isolate an oxosilane in the favorable case here investigated shows *either non-formation of the di-t-butyloxosilane or high reactivity and instability of this compound when formed.* In either event, this work constitutes strong additional evidence for the apparently rather general principle that multiple bonds of strength equal to or greater than a corresponding number of single bonds generally occur only with the first row elements. According to Pitzer[11] this situation results from an important inner shell repulsive effect with elements of the second row which largely cancels or overbalances the energy advantage available to first row elements in forming multiple linkages. With first row elements, inner shell repulsive forces are not as important and this permits closer approach and better overlap for all the bonding orbitals.

In addition to di-*t*-butylsilanediol, hydrolysis of the corresponding dichlorosilanes also gave *t*-butylmethyl-, *t*-butylphenyl- and *t*-butyl-*n*-hexadecylsilanediol. These silanediols are also more stable toward thermal polymerization than ordi-

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(10) J. F. Hyde, THIS JOURNAL, **75**, 2166 (1953).

(11) K. S. Pitzer, *ibid.*, **70**, 2140 (1948).

TABLE I

PROPERTIES OF $(t\text{-Bu})RSiCl_2$[a]

R	B.p., °C.	Mm.	Si, % Calcd.	Si, % Found	Cl, % Calcd.	Cl, % Found	Mol. wt. Calcd.	Mol. wt. Found[b]	Yield, %
Me	135[e]	740	16.4	16.3	41.5	41.5	171	169	75
C_6H_5[c]	133	27	12.0	12.0	30.4	30.5	233	228	80
$C_{16}H_{31}$[d]	188	4	7.3	7.4	18.6	18.7	382	390	77

[a] Data for $t\text{-BuMe}_2SiCl$ are: b.p. 125° at 733 mm.; m.p. 91.5°. *Anal.* Calcd. for $C_6H_{15}SiCl$: Si, 18.6; Cl, 23.5; mol. wt., 150.7. Found: Si, 18.3; Cl, 23.4; mol. wt., 151; yield 58%. [b] Cryoscopically in benzene. [c] n^{20}_D 1.5152, d^{20} 1.1062, MR_D 63.6 (calcd. 63.3). [d] n^{20}_D 1.4620, d^{20} 0.931, MR_D 113 (calcd. 113). [e] M.p. 96°.

TABLE II

PROPERTIES OF $(t\text{-Bu})RSi(NH_2)_2$

R	B.p., °C.	Mm.	n^{20}_D	Si, % Calcd.	Si, % Found	N, % Calcd.	N, % Found	Mol. wt. Calcd.	Mol. wt. Found[a]	Yield, %
Me[b]	135	738		21.3	21.3	21.2	21.1	132	137	65
t-Bu	100	50[c]	1.4534	16.1	16.1	16.1	16.0	174	179	50
C_6H_5	149	37	1.5198	14.5	14.6	14.4	14.4	194	190	80
$C_{16}H_{31}$	199	7	1.4604	8.2	8.4	8.2	7.7	343	364	85

[a] Cryoscopically in benzene. [b] M.p. 83°. [c] B.p. 190° at 737 mm.

nary silanediols. Thus, *t*-butylmethylsilanediol may be distilled at 187° and recovered largely unchanged.

It is of some interest to note that the silanediols also are obtained readily by hydrolysis of the corresponding diaminosilanes. In the reaction with relatively small-size reagents such as water the steric effects of *t*-butyl groups on silicon are, as expected, of much lesser importance than in the self-condensation reactions of substances containing these groups.

Hydrolysis of *t*-butyldimethylchlorosilane, prepared by reaction of *t*-butyllithium with dimethyldichlorosilane, gave in excellent yield *t*-butyldimethylsilanol, a clear water-white liquid with a powerful camphoric odor. A solution of this silanol in concentrated sulfuric acid when poured on ice failed to give the siloxane, as did also refluxing with iodine, procedures which give complete condensation of triethylsilanol.[12]

t-Butyldimethylsilanol is unusual in still another of its characteristics. It is the only known trialkylsilanol that readily forms a hemihydrate, m.p. 70°, merely on being poured into distilled water. The hydrate can be sublimed very readily, even at room temperature, and the sublimate is deposited in the form of beautiful needle-like crystals. This property of *t*-butyldimethylsilanol appears even more interesting when it is pointed out that its carbon analog, pentamethylethanol, also forms a hemihydrate quite readily, m.p. 80°. This carbinol is one of very few to exhibit this property.[13,14]

Experimental

Synthesis of New *t*-Butylchlorosilanes.—The procedure used for *t*-butylmethyldichlorosilane will be described as typical of the method employed for all three new dichlorosilanes and for *t*-butyldimethylchlorosilane. To a solution of 1.40 moles of *t*-butyllithium in 180 cc. of pentane there was added 165 g. (1.1 moles) of methyltrichlorosilane during 20 minutes. Reflux continued for one hour after completion of the addition. The reaction mixture was then heated at reflux for an additional hour. The pentane solution was filtered from the lithium chloride. Fractionation gave *t*-butylmethyldichlorosilane. Table I gives pertinent data on the new chlorosilanes.

Synthesis of *t*-Butyldiaminosilanes.—The procedure used for *t*-butylmethyldiaminosilane will be described as representative of the method employed for all of these compounds. A 500-cc. three-necked flask, equipped with a reflux condenser, stirrer and dropping funnel, was immersed in a Dry Ice–acetone-bath. In this was placed 125 cc. of liquid ammonia. Then, there was added, during 30 minutes, a solution of 34 g., 0.2 mole, of *t*-butylmethyldichlorosilane in 225 cc. of pentane. The mixture was stirred vigorously during the addition and for three hours as the excess ammonia was allowed to distil from the mixture.

The ammonium chloride formed was filtered from the reaction mixture, washed thoroughly with pentane and dried. A quantitative yield, 21.0 g., was obtained. The pentane was stripped from the mixture. The residue was a solid at room temperature. An attempt to distil the product at reduced pressure was made. However, difficulty was encountered, because at low pressure the boiling point was below the melting point and extensive sublimation occurred. Fractionation of the sublimed solid at atmospheric pressure gave a 65% yield of *t*-butylmethyldiaminosilane, a white waxy solid which sublimes, even at room temperature, to give leaf-like crystals. It possesses a strong, unpleasant, ammoniacal odor.

The properties of *t*-butyldiaminosilanes are given in Table II.

Treatment of di-*n*-butyldichlorosilane with liquid ammonia according to the procedure described above gave as the only product hexa-*n*-butylcyclotrisilazane, b.p. 193° at 2 mm., n^{20}_D 1.4654, d^{20} 0.8912, molar refraction 146 (calcd. 146), cryoscopic molecular weight in benzene 467 (calcd. 471). *Anal.* Calcd. for $(C_8H_{19}SiN)_3$: Si, 17.8; N, 8.91. Found: Si, 18.0; N, 8.8.

Synthesis of *t*-Butylsilanediols.—The two procedures used for *t*-butylmethylsilanediol will be described as representative of the method employed for all of these compounds.

(a) **Hydrolysis of *t*-Butylmethyldiaminosilane.**—A solution of 4.0 g. (0.03 mole) of *t*-butylmethyldiaminosilane in 10 cc. of methanol was neutralized (methyl red indicator) by the addition of 0.1 *N* HCl. The mixture was extracted three times with 20-cc. portions of ether and the ether was then evaporated from the product. There was obtained 3.5 g. of a white crystalline product, melting 124–130°. This is a 90% yield of crude *t*-butylmethylsilanediol.

Recrystallization from water gave pure *t*-butylmethylsilanediol. In taking melting points it was observed that the melts were clear and no evidence of decomposition was noted.

(b) **Hydrolysis of *t*-Butylmethyldichlorosilane.**—In a 500 cc. three-necked flask, equipped with a modified Hershberg stirrer, were placed 100 cc. of ether, 15 cc. of methanol, 200 g. of ice and 21 g. (0.38 mole) of potassium hydroxide. The reaction flask was immersed in a salt–ice-bath. To the vigorously stirred reaction mixture there was added, during 45 minutes, 34 g. (0.2 mole) of *t*-butylmethyldichlorosilane in 124 cc. of ether. During the addition of the last few cc.

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(12) L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, THIS JOURNAL, **68**, 2282 (1946).

(13) H. A. Butlerow, *Ann.*, **177**, 176 (1875).

(14) This fact as well as others of a related nature will be discussed in a forthcoming manuscript on "Organosilicon Homomorphs."

TABLE III

PROPERTIES OF (t-Bu)RSi(OH)$_2$

R	M.p., °C.	B.p., °C.	B.p., Mm.	Si, % Calcd.	Si, % Found	OH^a, % Calcd.	OH^a, % Found	Yield, % A^c	Yield, % B^d
Me	132	187	740	20.9	20.7	25.3	25.0	90	78
t-Bu	152	210	740	15.9	15.9	19.3	19.0	90	80
C_6H_5^{b}	82	123	3	14.3	14.2	17.3	17.0	74	81
$C_{16}H_{31}$	40–45	194	2	8.14	8.12	9.8	9.1		70

[a] % OH was determined by analysis for active hydrogen in a Zerewitinoff apparatus. [b] This diol forms a hydrate, m.p. 68°. [c] Hydrolysis of the diaminosilane. [d] Hydrolysis of the dichlorosilane.

of this solution the reaction mixture became acidic (phenolphthalein), so an additional 2 g. of potassium hydroxide was added. The mixture was stirred for five minutes and the ether layer was separated. The aqueous layer was extracted three times with 50-cc. portions of ether. All of the ether portions were combined and the ether was evaporated. There was obtained 21 g. of product, a crystalline solid. This represented 0.156 mole, a crude yield of 78% of *t*-butylmethylsilanediol.

The crude product was recrystallized from hot water (m.p. 129–132.5°). Recrystallization from hot xylene gave 14.2 g. of purified product, m.p. 131–132.5° (remelted 131–132.5°). *t*-Butylmethylsilanediol crystallizes from hot water or xylene in the form of white platelets, but if recrystallized from warm water over a two-weeks period, large, clear, cubical crystals are obtained.

This diol does not decompose on melting. A 3.0-g. portion of the diol was distilled without decomposition at 740 mm. Properties of the diols are summarized in Table III.

Synthesis of *t*-Butyldimethylsilanol.—To a mixture of 100 cc. of water, 25 cc. of methanol and 13.5 g., 0.24 mole, of potassium hydroxide cooled to 5° there was added during 20 minutes 38 g., 0.25 mole, of *t*-butyldimethylchlorosilane in 200 cc. of ether. Upon addition of the last few cc. of the chlorosilane solution the reaction mixture became acidic (phenolphthalein). An additional gram of potassium hydroxide was added and the mixture was stirred for ten minutes. The ether layer was separated and the aqueous layer was extracted three times with 200-cc. portions of ether. After removal of the ether, fractionation gave 28.6 g. (0.22 mole) of *t*-butyldimethylsilanol, b.p. 141° (12 mm.), $n^{20}{}_D$ 1.4235, 88% yield. *Anal.* Calcd. for $C_6H_{16}SiO$: Si, 21.21; OH, 12.85. Found: Si, 21.3; OH, 13.0.

The density of the mid-fraction was found to be 0.8397. The molar refraction is 40.15 (calcd. 40.08). This compound is a clear, water-white liquid with a powerful, camphor-like odor. It is unusual in one respect. This unique characteristic is its formation of a hydrate. Hydration occurs very readily, even on exposure to moist air.

Formation of *t*-Butyldimethylsilanol Hydrate.—*t*-Butyldimethylsilanol, 7.2 g., was poured into 50 cc. of distilled water. Immediately, a white solid formed. This was filtered and dried. There was obtained 7.5 g. of white, crystalline solid. A portion of this was sublimed to give long, needle-like crystals, melting 69–70°. A Zerewitinoff analysis for active hydrogen indicated that this is *a hemihydrate*. [*Anal.* Calcd. for $(C_6H_{15}SiOH)_2 \cdot H_2O$: OH, 18.05. Found: OH, 18.2.] This is the first hydrated silanol reported. This hydrate possesses the powerful camphor-like odor of the anhydrous silanol, and it sublimes quite readily even at room temperature. It loses its water of hydration if placed in a desiccator. Also, distillation of the solid hydrate at atmospheric pressure gives a first fraction containing the water of hydration. The second fraction consists of the anhydrous silanol.

Some Properties of Di-*t*-butylsilanediol.—Reaction with: (a) Di-*t*-butyldiaminosilane: An equimolar mixture of diol and diaminosilane was heated at 175° for an hour. No ammonia was evolved. Treatment of the reaction mixture with water gave a good recovery (95%) of pure diol.

(b) Di-*t*-butyldichlorosilane: In a like manner, a mixture of equivalent amounts of diol and dichlorosilane was heated. No HCl was evolved. On cooling, the diol crystallized; this was separated and recrystallized from carbon tetrachloride. An 85% recovery was obtained.

(c) Iodine: Other dialkylsilanediols are quantitatively dehydrated upon refluxing in benzene with a trace of iodine. This treatment had no effect on di-*t*-butylsilanediol. Moreover, a mixture of 2.0 g. of di-*t*-butylsilanediol and 0.4 g. of iodine was sublimed above 200°. The sublimate was recrystallized from carbon tetrachloride and 1.6 g. of diol was recovered, melting 150–153°.

(d) Concd. hydrochloric acid: Dialkylsilanediols are readily condensed by refluxing in a solvent containing a trace of concd. hydrochloric acid. This treatment had no effect on di-*t*-butylsilanediol. In an attempt to prepare di-*t*-butyldichlorosilane, di-*t*-butylsilanediol, 3.52 g. (0.02 mole) was heated for one hour with 0.12 mole of concd. hydrochloric acid containing 0.1 mole of anhydrous zinc chloride. On cooling, crystals of the diol reappeared. These were separated, washed and dried. After recrystallization from carbon tetrachloride there was obtained 2.8 g., melting 150–152°.

(e) Phosphorus pentoxide: In a 50-cc. flask, equipped with a reflux condenser, there was placed 5 g. of phosphorus pentoxide in 35 cc. of anhydrous ether. There was then added 2.0 g. of di-*t*-butylsilanediol. There was a slow reaction evolving enough heat to maintain reflux for 20 minutes. The phosphorus pentoxide became sirupy indicating absorption of water. After an hour the ether was decanted and evaporated. The product was a clear viscous liquid. It had a neutral equivalent of 207. Evidently this was a complex *t*-butylsilicon phosphate. In another identical reaction, the product was hydrolyzed with dilute alkali and there was recovered 1.1 g. of di-*t*-butylsilanediol, m.p. 150.5–152.5°.

(f) Concd. sulfuric acid: Di-*t*-butylsilanediol, 1.60 g., was added to 10 cc. of concd. sulfuric acid. The diol dissolved slowly with a slight heat effect. The solution was heated slowly to 110° and this temperature was maintained for ten minutes. Upon cooling, the mixture was poured onto 35 g. of ice. Immediately a white flocculent precipitate appeared. This was filtered, washed thoroughly with water and dried. Upon recrystallization twice from carbon tetrachloride there was obtained 1.3 g. of white, needle-like crystals, m.p. 151.5–153°, evidently recovered di-*t*-butylsilanediol.

(g) Soda-lime: Di-*t*-butylsilanediol, 2.0 g., was passed through a 10-mm. tube filled with a 50-cm. length of 12 mesh soda-lime heated to 240° in an atmosphere of nitrogen. The only product isolated was 0.25 g. of diol, m.p. 150–153°.

(h) Calcium oxide: Treatment of 2 g. of diol with calcium oxide at 450° gave a recovery of 0.45 g. of diol, m.p. 149–152°.

(i) Activated alumina: Treatment of 3.0 g. of diol with activated alumina in a tube heated to 300°, gave 0.7 g. of recovered diol, m.p. 150.5–153°. Attempts to isolate another product from this reaction were unsuccessful.

Some Properties of *t*-Butyldimethylsilanol.—*t*-Butyldimethylsilanol, 3.0 g., was dissolved in concd. sulfuric acid. The mixture was heated to 100° and then allowed to cool to room temperature. After pouring into water, the sulfuric acid solution gave a white solid. Sublimation of the latter gave 3 g. of *t*-butyldimethylsilanol hemihydrate, m.p. 68–70°.

Triethylsilanol when refluxed with iodine for 30 minutes is completely condensed to the siloxane.[12] Similar treatment of 4 g. of *t*-butyldimethylsilanol gave no siloxane. Fractionation gave back 3.6 g. of unchanged silanol.

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