authentic 1,8-octanediol[28] (m.p. 57.5–58.0°) was 57.5–58.0°. A portion of the diol was treated with 0.2 ml. of phenyl isocyanate and with 2 drops of pyridine as a catalyst. The excess reagents were removed under reduced pressure yielding 0.086 g., melting at 169.0–171.5°. The product was recrystallized from ethyl acetate and ethyl acetate–hexane, yielding 0.025 g. with a melting point and a mixed melting point with the authentic bisphenylurethane derivative of 1,8-octanediol (m.p. 172–173°) of 170–172°.

*Characterization of the ω-hydroxy acid* (VII). A portion of VII (0.40 g.) was dissolved in 20 ml. of water and 0.50 g. of potassium permanganate, and 0.8 ml. of 10% sodium hydroxide was added with stirring. After 30 min. at 20–25° and 2 hr. at 30–35°, the excess permanganate was destroyed by addition of sodium bisulfite, and the reaction mixture was filtered with suction. The filtrate was concentrated, acidified with 2*N* hydrochloric acid, and extracted with ether. The ether extract was evaporated to dryness, and the residue was extracted with hot benzene. After removal of the benzene, the product was recrystallized successively from benzene, chloroform, and chloroform-benzene yielding 0.007 g of VIII, melting at 90–95°; mixed melting point with authentic glutaric acid (m.p. 96.5–97.5°) was 92–96°. The x-ray diffraction pattern of the product was identical to authentic glutaric acid. The methyl esters, prepared with diazomethane,[29] of the combined mother liquor residue consisted of 93% glutaric acid as determined by gas chromatography.

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[28] Suberic acid was reduced to 1,8-octanediol as outlined by R. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947).

[29] F. Arndt, *Org. Syntheses*, Coll. Vol. **II**, 165 (1943)

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE UNIVERSITY]

# Preparation and Reactions of *sym*-Tetraphenyldisilane

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The preparation of *sym*-tetraphenyldisilane (I) is discussed. Various reactions of I have been studied in an attempt to correlate the reactions of *sym*-tetraphenyldisilanediol with those of the carbon analog. A series of novel difunctional disilanes was prepared from I and their reactions studied. A useful quantitative method for the estimation of silicon-silicon and silicon-hydrogen bonds is discussed in detail.

The number of known organosilicon compounds containing one or more silicon-silicon bonds is small compared to the number of compounds containing only one silicon atom or isolated silicon atoms. The majority of these disilanes or polysilanes are fully substituted by alkyl or aryl groups. Some *sym*-difunctional disilanes have been encountered as biproducts in the industrial preparation of chlorosilanes.[1]

An accidental encounter with a *sym*-difunctional disilane is reported in connection with the study of steric effects in organosilicon chemistry.[2] It was found that hexachlorodisilane reacted with four moles of *o*-tolyllithium to give *sym*-tetra-*o*-tolyldisilanediol, subsequent to hydrolysis, whereas hexaphenyldisilane could be obtained by the corresponding reaction with phenyllithium.

Attempts to prepare *sym*-dichlorotetraphenyldisilane by the action of four moles of phenylmagnesium bromide on hexachlorodisilane failed as did the attempted introduction of six phenyl groups by the use of the Grignard reagent.[3]

It was discovered that chlorodiphenylsilane is coupled by the action of magnesium to form *sym*-tetraphenyldisilane.[4] This reaction is comparable

$$2(C_6H_5)_2SiHCl + Mg \longrightarrow (C_6H_5)_2SiHSiH(C_6H_5)_2 + MgCl_2$$

to the coupling reaction of chlorotriphenylsilane with magnesium.[5] This type of coupling may involve the highly reactive silyl Grignard reagent which was likewise considered to be an intermediate in the reaction of cyclohexylmagnesium bromide with chlorotriphenylsilane.[6]

The preparation of *sym*-tetraphenyldisilane is very sensitive to the effectiveness of the initiation. This may be performed by the addition of ethyl iodide in much the same way as difficult preparations of Grignard reagents are initiated. Table I

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[1] M. Kumada and M. Yamaguchi, *J. Chem. Soc., Japan, Ind. Chem. Sect.*, **57**, 175 (1954); *Chem. Abstr.*, **49**, 11542 (1955); M. Kumada and M. Kuriyagawa, Japanese Patent **7223** (1954); *Chem. Abstr.*, **50**, 10125 (1956).

[2] H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **15**, 720 (1950).

[3] H. Gilman and G. D. Lichtenwalter, *J. Org. Chem.*, **24**, 1588 (1959); W. O. Schumb and C. M. Saffer, *J. Am. Chem. Soc.*, **61**, 363 (1939).

[4] H. Gilman and W. Steudel, *Chem. & Ind.*, 1094 (1959).

[5] H. Gilman, D. J. Peterson, and D. Wittenberg, *Chem. & Ind.*, 1479 (1958); M. V. George, D. J. Peterson, and H. Gilman, *J. Am. Chem. Soc.*, **82**, 403 (1960).

[6] T. G. Selin and R. West, *Tetrahedron*, **5**, 97 (1959).

TABLE I

| Preparation of *sym*-Tetraphenyldisilane | | |
|---|---|---|
| G.-atom Mg/mole $(C_6H_5)_2SiHCl$ | Time of Reaction (hr.) | Yield, % |
| 0.55 | 40 | 12 |
| 0.55 | 120 | —[a] |
| 2.00 | 20 | 45–55 |
| 3.00 | 16 | 45 |
| 2.00[b] | 24 | 30 |
| 2.00[c] | 96 | <11 |

[a] The product did not crystallize on prolonged standing. [b] The chlorodiphenylsilane was heated in the presence of magnesium for four hours instead of the normal 30 min. [c] The period of preheating was 5 min. [d] The product was not isolated and the yield represents the percent consumption of chlorodiphenylsilane after the total reaction time.

shows the effect of variation of some experimental factors on the yield of product. The extent of reaction was determined by the removal of aliquots from the reaction mixture and titrating the amount of acid liberated on hydrolysis. The yields given are those of pure crystalline material obtained. The remainder of the material was a viscous oil which did not give crystalline fractions on chromatography.

It is evident from the data presented in Table I that the shorter reaction time favors the formation of the higher yield. A shorter reaction time is a consequence of a more effective initiation and this apparently is dependent on the time of preheating before the solvent, tetrahydrofuran, is added and on the amount of magnesium present. The silyl Grignard reagent, if formed, is consumed immediately as evidenced by the negative Color Test I[7] throughout the reaction.

The *sym*-tetraphenyldisilane gives a positive test for silicon-hydrogen bond with silver nitrate[8] and behaves as a trisubstituted silane against copper (II) chloride in pyridine[9] by giving a green color after prolonged standing only. The compound reacts very rapidly with dilute base to give three moles of hydrogen per mole of compound.

Attempts to hydrolyze *sym*-tetraphenyldisilane directly to *sym*-tetraphenyldisilanediol led to the formation of hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane. Under milder conditions it was possible to isolate the intermediate diphenylsilanediol which is known to undergo dehydration to either hexaphenylcyclotrisiloxane or octaphenylcyclotetrasiloxane under the given conditions.[10] No reaction occurred under acid conditions, and rapid cleavage was caused under slightly basic conditions.

$$(C_6H_5)_2SiHSiH(C_6H_5)_2 \xrightarrow{OH^-} [(C_6H_5)_2Si(OH)_2] \xrightarrow{OH^-} [(C_6H_5)_2SiO]_4$$

$$(C_6H_5)_2SiHSiH(C_6H_5)_2 \longrightarrow (C_6H_5)_2Si(OH)_2 \longrightarrow [(C_6H_5)_2SiO]_3$$

It was thus necessary to proceed by way of the *vic*-dihalo-tetraphenyldisilane which may be hydrolyzed under mild conditions[10] thus preventing cleavage of the silicon-silicon bond.

$$(C_6H_5)_2SiHSiH(C_6H_5)_2 + 2X_2 \xrightarrow{[-2HX]} (C_6H_5)_2SiXSiX(C_6H_5)_2 \xrightarrow{[H_2O]} (C_6H_5)_2SiOHSiOH(C_6H_5)_2$$

The *sym*-dichlorotetraphenyldisilane may be prepared in chloroform or carbon tetrachloride containing small amounts of ether. Chloroform in the absence of ether is undesirable since crystallization could not be induced in preparations performed in the absence of ether. It is conceivable that the ether acts as a hydrogen chloride acceptor and thus facilitates the reaction.

The *sym*-dibromotetraphenyldisilane may, however, be prepared by the addition of bromine in carbon tetrachloride in the absence of ether. The reaction may also be performed by the addition of *N*-bromosuccinimide by the normal type procedure used for this reagent.[11]

Attempts to prepare these compounds directly from dichlorodiphenylsilane or dibromodiphenylsilane by the action of one gram-atom of alkali metal per mole of dihalosilane led to the formation of perphenylated silicohydrocarbons by reactions similar to those first described by Kipping.[12] The use of lithium amalgam,[13] which reacts with dibromodiphenylgermane to give *sym*-dibromotetraphenyldigermane,[14] likewise caused the complete reduction of a fraction of the dihalodiphenylsilane rather than the desired partial reduction of all. A less active metal such as zinc did not react with diphenyldichlorosilane under the conditions employed.

The structure of the *sym*-dichlorotetraphenyldisilane was confirmed by the preparation of the known *sym*-di-*p*-tolytetraphenyldisilane[15] by the action of two moles of *p*-tolyllithium on one mole of dihalodisilane.

The dihalotetraphenyldisilanes could be hydrolyzed under mildly acid conditions to the *sym*-tetraphenyldisilanediol. Under mildly alkaline conditions, ammonium carbonate monohydrate in acetone,[16] condensation to a disiloxanediol occurred, whereas octaphenylcyclotetrasiloxane was formed under strongly alkaline conditions:

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(7) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(8) A. Stock, *Z. Electrochem.*, **32**, 341 (1926).

(9) H. Gilman, H. G. Brooks, and M. B. Hughes, *J. Org. Chem.*, **23**, 1398 (1958).

(10) C. A. Burkhard, *J. Am. Chem. Soc.*, **67**, 2173 (1945).

(11) E. Campaigne and B. F. Tullar, *Org. Syntheses*, **33**, 96 (1953).

(12) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, 830 (1921).

(13) G. Wittig and L. Pohmer, *Ber.*, **89**, 1334 (1956).

(14) H. H. Zeiss, private communication.

(15) H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **75**, 3762 (1953).

(16) T. Takiguchi, *J. Org. Chem.*, **24**, 989 (1959).

$$(C_6H_5)_2SiXSiX(C_6H_5)_2 \xrightarrow{[H_2O]} (C_6H_5)_2SiOHSiOH(C_6H_5)_2 \text{ (acid or neutral cond.)}$$

$$(C_6H_5)_2SiXSiX(C_6H_5)_2 \xrightarrow{[H_2O]} (C_6H_5)_2SiOH(C_6H_5)_2SiOSi(C_6H_5)_2Si(C_6H_5)_2OH \text{ (weakly alkaline cond.)}$$

$$(C_6H_5)_2SiXSiX(C_6H_5)_2 \xrightarrow{[H_2O]} [(C_6H_5)_2Si(OH)_2] \longrightarrow [(C_6H_5)_2SiO]_4 \text{ (strongly alkaline cond.)}$$

Confirmatory evidence for the structure of the compound was obtained by utilizing strongly alkaline conditions on a quantitative scale.

The infrared spectrum of the *sym*-tetraphenyldisilanediol showed the presence of hydrogen bonding both in the solid state and in solution. The spectrum was identical in many respects to that of diphenylsilanediol, although the intramolecular hydrogen bonded O—H stretching frequency was at a higher frequency for the *sym*-tetraphenyldisilanediol than for diphenylsilanediol. This indicates that the hydroxyl groups in the former compound are closer to each other in the *cis*-form than they are in the latter compound.

A chief interest in this compound rested in the possible preparation of a silicon analog of an epoxy compound. It would likewise be interesting to see if the *vic*-silicoglycol underwent a pinacol-pinacolone type rearrangement. A wide variety of conditions was employed to effect the preparation of the epoxy type or the rearrangement, but the conditions which effected dehydration did so by an intermolecular route to a cyclic siloxane and not by an intramolecular route nor by rearrangement. Neither ice-cold concentrated sulfuric acid[17] nor 50% boiling phosphoric acid[18] caused any dehydration. The starting material was recovered ununchanged. Preparation and pyrolysis of the phenylthiourethan did not effect the desired epoxy formation.[19] A procedure utilized in the steroid field for the preparation of 3,9-oxy compounds from the corresponding diols involves heating the diol with pyridine in the presence of *p*-toluenesulfonyl chloride.[20] This method gave a good yield of the cyclic siloxane described later. Attempted dehydration in benzene containing a catalytic amount of *p*-toluenesulfonic acid failed; and unchanged starting material was recovered.[21] More forcing conditions such as heating the compound in a dimethylformamide solution[22] of oxalic acid caused dehydration to the cyclic disiloxane. An unsuccessful attempt to effect the acetal formation with chloral, a typical reaction of *vic*-glycols,[23] likewise failed in the absence or in the presence of *p*-toluenesulfonic acid. The cyclic disiloxane was formed in both cases.

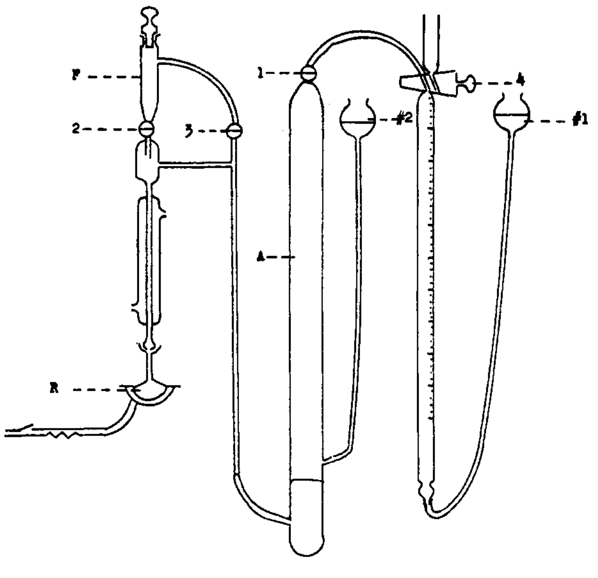
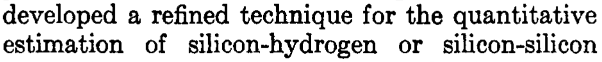


Fig. 1. Apparatus for determination of hydrogen values

From these observations it may be concluded that *sym*-tetraphenyldisilanediol behaves quite differently from benzopinacol which readily undergoes the pinacol-pinacolone rearrangement and dehydration to form epoxytetraphenylethylene.

Intermolecular dehydration is best performed in boiling formic acid. The compound isolated is a siloxane of the structure shown:



$$2(C_6H_5)_2SiOHSiOH(C_6H_5)_2 \xrightarrow{[-2H_2O]} \begin{array}{c} Si(C_6H_5)_2Si(C_6H_5)_2 \\ O \qquad\qquad O \\ Si(C_6H_5)_2Si(C_6H_5)_2 \end{array}$$

This compound was of interest in connection with the identification of various products isolated but not identified by Kipping[12] in an oxidation of octaphenylcyclotetrasilane.

In connection with the identification of the compounds discussed in this investigation there was developed a refined technique for the quantitative estimation of silicon-hydrogen or silicon-silicon groups in an organosilicon compound. The method was first described with little detail by Kipping[24] for the estimation of the silicon-silicon group. The procedure was later modified and extended to the estimation of the silicon-hydrogen group and it

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[17] R. Scholl and G. Born, *Ber.*, **28**, 1364 (1859); H. Meerwein, *Ann.*, **419**, 122, 156 (1910); *Ann.*, **396**, 240 (1913); A. McKenzie and R. Roger, *J. Chem. Soc.*, 844 (1924).

[18] W. M. Dehn and K. E. Jackson, *J. Am. Chem. Soc.*, **55**, 4286 (1933); G. A. Hill and E. W. Flosdorf, *Org. Syntheses*, **5**, 91 (1925).

[19] Erdman, Thesis, Rostock, 1910, p. 65. [V. Grignard, "Traité de Chimie Organique," Masson, Paris, 1941, Ref. 171, p. 79].

[20] H. Heymann and L. F. Fieser, *J. Am. Chem. Soc.*, **73**, 5252 (1951).

[21] E. J. Salmi, *Ber.*, **71B**, 1803 (1938).

[22] D. Vorlander, *Ber.*, **30**, 2266 (1897).

[23] O. Wallach, *Ann.*, **193**, 40 (1878); M. Renoll and M. S. Newman, *Org. Syntheses*, **28**, 73 (1948).

[24] F. S. Kipping, *J. Chem. Soc.*, 848 (1921).

is for this purpose the method has been used most widely for rate studies or otherwise.[25]

An experimental set-up similar to that described in the literature[26] was used. The inability of highly substituted silanes to hydrolyze was reconfirmed for compounds having high steric hindrance. Thus, it was noted that tri-*o*-tolylsilane and tri-*o*-xenylsilane failed to liberate any more than a trace of hydrogen even after 24 hours of heating in refluxing wet piperidine, and the starting material was recovered essentially quantitatively. It appears that the use of the method for the determination of silicon-silicon groups is not limited sterically to the same extent as is the determination of the silicon-hydrogen bond. Thus, *sym*-tetra-*o*-tolyldisilanediol undergoes ready cleavage with the liberation of one mole of hydrogen per mole of compound. Table II represents the determinations carried out on the compounds discussed in this investigation. The term "hydrogen value" refers to the number of milliliters of gas (at S. T. P.) liberated per gram of compound.

TABLE II

"HYDROGEN VALUES" OF VARIOUS COMPOUNDS

| Compound | H-value found, ml./g. | H-value calcd., ml./g. |
|---|---|---|
| $(C_6H_5)_2SiHSiH(C_6H_5)_2$ | 195 | 183 |
| $(C_6H_5)_2SiOHSiOH(C_6H_5)_2$ | 59 | 56 |
| $[(C_6H_5)_2Si(C_6H_5)_2SiO_2]$ | 59.5 | 59 |
| $(C_6H_5)_2SiClSiCl(C_6H_5)_2$ | 52 | 51.5 |

The method may be modified to distinguish between silicon-silicon and silicon-hydrogen groups. A determination of the compound containing both groups is first performed, and another sample of the compound is chlorinated or brominated (under conditions which do not effect silicon-silicon bond cleavage) to convert the silicon-hydrogen bonds to silicon-halogen bonds. The silicon-silicon group is then determined separately for this compound and the difference between the two determinations is due to silicon-hydrogen bonds.

## EXPERIMENTAL[27]

*Reaction of hexachlorodisilane with phenylmagnesium bromide.* The Grignard reagent was prepared by a conventional procedure from 80 g. of bromobenzene and 13.4 g. of magnesium in 300 ml. of ether. A 1-ml. sample was assayed to contain 1.66 mmoles of Grignard reagent per ml. Part of this solution (240 ml., containing 0.400 mole of Grignard reagent) was added dropwise to 26.8 g. of hexachlorodisilane (0.1 mole) in 50 ml. of ether. The solution was stirred well and cooled in ice during the initial part of the reaction. The solution was stirred for 24 hr. after complete addition of the reagent and since Color Test I[7] was still positive, the solution was heated under reflux for another 24 hr. The Color Test was negative and the ether was distilled while petroleum ether (b.p. 60–70°) was added. The total volume of solvents which had been removed was 500 ml. To the remaining suspension of magnesium bromide and chloride was added 100 ml. of benzene and the magnesium halides were removed by filtration under nitrogen pressure. The filtrate was concentrated and the remaining oil distilled under reduced pressure; at 2 mm. pressure there were collected 5 g. of biphenyl, vapor temp. 100–120°, identified by infrared spectra and mixed melting point with an authentic sample, and 6 g. (24%) of dichlorodiphenylsilane at 136–138°/2 mm. At still lower pressures were collected 7 g. (22%) of tetraphenylsilane, b.p. 165–166°/0.07 mm., and a residue which did not crystallize on prolonged standing.

*Preparation of sym-tetraphenyldisilane.* A mixture of 218 g. of chlorodiphenylsilane (1 mole) and 48 g. of magnesium (2 g.-atoms) was heated in a 1 l. flask equipped with a condenser (topped by a nitrogen inlet), a stirrer, and an addition funnel containing 300 ml. of tetrahydrofuran, distilled from sodium wire and lithium aluminum hydride under a nitrogen atmosphere. The heating at 70° was continued for 30 min. and 50–100 ml. of tetrahydrofuran were introduced. If the reaction did not start spontaneously within 5 min. there was added 5 drops of ethyl iodide. The magnesium turned black and heat was generated. The heating mantle was removed and the reaction allowed to proceed for 16–20 hr. at room temperature, while the remaining tetrahydrofuran was added. The extent of reaction may be determined by removing an aliquot of the reaction mixture which has been allowed to settle and adding this to 25 ml. of water and titrating the liberated acid with 0.1*N* sodium hydroxide. The suspension was decanted through a glass wool plug into 500 ml. of 1*N* ice-cooled hydrochloric acid which was stirred rapidly. To the resulting aqueous suspension was added 200 ml. of ether and the aqueous layer was separated and extracted with two 100-ml. portions of ether. The combined organic layers were shaken with 300 ml. of saturated sodium chloride solution and dried over calcium chloride. The solvents were removed and the remaining oil seeded with a small amount of *sym*-tetraphenyldisilane. Crystallization was allowed to proceed for 24 hr. and the solids collected on a Büchner funnel and washed with small amounts of ice-cooled ethanol. The solid was recrystallized from 4:1 petroleum ether (b.p. 60–70°)-benzene to give 87 g. of pure *sym*-tetraphenyldisilane (47%), m.p. 79–80°.

From the mother liquors of the precipitation was obtained another 48 g. of tetraphenyldisilane by distillation, b.p. 175–177°/0.05 mm. (Total yield 145 g. or 74%).

*Anal.* Calcd. for $C_{24}H_{22}Si_2$: C, 78.64; H, 6.05; Si, 15.31. Found: C, 78.42; H, 6.11; Si, 15.32.

*Hydrolysis of sym-tetraphenyldisilane by sodium ethoxide at 0°.* A solution of 0.6 g. of *sym*-tetraphenyldisilane in 30 ml. of ethanol was cooled to 0° and 25 ml. of 0.5*M* sodium ethoxide was added dropwise. A gas was evolved during the 30-min. addition period. To the resulting solution was added 100 ml. of saturated ammonium chloride solution and the aqueous layer was extracted with ether which was dried over Drierite and concentrated. A total of 0.5 g. of a white solid, m.p. 159.5–160°, was collected (70%).

*Anal.* Calcd. for $C_{12}H_{12}SiO_2$: Si, 12.97. Found: Si, 12.97, 12.87. Infrared spectrum: (chloroform solution) 3650, 3300, 3025, 1600, 1420, 1130, 1120 cm$^{-1}$.

By comparison with an authentic sample (infrared spectra and mixture melting point) prepared by conventional

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[25] A. Stock and C. Somieski, *Ber.*, **49**, 111 (1916); F. P. Price, *J. Am. Chem. Soc.*, 69, 2600 (1947); H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, **73**, 3404 (1951); H. Gilman, G. E. Dunn, G. S. Hammond, *J. Am. Chem. Soc.*, **73**, 4499 (1951); R. West, *J. Am. Chem. Soc.*, **76**, 6015 (1954); L. Kaplan, K. E. Wilzbach, *J. Am. Chem. Soc.*, **74**, 6152 (1952) and **77**, 1297 (1955); J. E. Baines and U. C. Eaborn, *J. Chem. Soc.*, 4023 (1955).

[26] G. Fritz and G. Grabe, *Z. anorg. Chem.*, **299**, 302 (1959).

[27] All reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen, and all melting points are uncorrected.

procedures[10] it was concluded that this compound was diphenylsilanediol. A second preparation from *sym*-tetraphenyldisilane was performed under conditions by which it was possible to measure the amount of gas liberated. It was found that 2.97 moles of gas, per mole of starting material, was liberated; theory 3.00.

*Hydrolysis of sym-tetraphenyldisilane by wet piperidine.* To a solution of 1.8 g. of *sym*-tetraphenyldisilane in 20 ml. of piperidine was added 1 ml. of water while external cooling to 0° was provided. There was an immediate evolution of hydrogen, 3.0 moles per mole of compound. The solvents were removed under an air-jet and the resulting oil was chromatographed to yield 1.2 g. of solid, m.p. 186–187°. Infrared spectra[28] and mixed melting point identified this compound as octaphenylcyclotetrasiloxane (62%). Trace amounts of hexaphenylcyclotrisiloxane were identified in one fraction of the eluates.

*Preparation of sym-dichlorotetraphenyldisilane.* To a solution of 10 g. of *sym*-tetraphenyldisilane in 100 ml. of carbon tetrachloride, containing 25 ml. of diethyl ether, was added chlorine gas through a bubbler. The flask was protected from the atmosphere by a calcium chloride drying tube. The addition was continued for 4 hr. and the solvents were removed at reduced pressure (a water aspirator protected by a calcium chloride drying tube) after dry nitrogen had been passed through the bubbler for another 3 hr. to remove the major portion of the hydrogen chloride. The solid crystallized immediately and was recrystallized from benzene–petroleum ether (b.p. 60–70°), 1:1. There was obtained a total of 10.6 g. of recrystallized material, m.p. 114.5–115°. The compound was recrystallized twice from hexane, before analysis, without change in melting point; yield 86%.

*Anal.* Calcd. for $C_{24}H_{20}Si_2Cl_2$: C, 66.20; H, 4.63; Si, 12.89; Cl, 16.28. Found: C, 65.96, 66.10; H, 4.40, 4.28; Si, 12.72, 12.78; Cl, 17.10.

*Preparation of sym-dibromotetraphenyldisilane.* To a solution of 5 g. of *sym*-tetraphenyldisilane (0.0136 mole) in 50 ml. of carbon tetrachloride was added 4.35 g. of bromine (0.0272 mole) in 40 ml. of carbon tetrachloride. The reaction mixture was cooled in an ice bath throughout the addition. The bromine was consumed very readily and it was not until the last drop of bromine solution was added that a slightly yellow color developed. Stirring was continued for another 16 hr. after complete addition and the reaction mixture was allowed to heat to room temperature. On addition of 75 ml. of pentane, the solid *sym*-dibromotetraphenyldisilane precipitated. The solid was filtered off and dried *in vacuo* for 4 hr., m.p. 154.5–155.5° after one recrystallization from a 1:1 mixture of benzene-petroleum ether (b.p. 60–70°). Additional fractions were collected giving a total yield of 87%.

This compound was also prepared by the reaction of 4.8 g. of *N*-bromosuccinimide (0.027 mole) containing 0.1 g. of benzoyl peroxide with 4.0 g. of *sym*-tetraphenyldisilane (0.011 mole) in 40 ml. of refluxing benzene. The solution was heated for 2 hr. after complete addition and then cooled to room temperature. The succinimide was filtered off (2 g. or 75% of theory). The benzene was removed under reduced pressure and 25 ml. of petroleum ether (b.p. 60–70°) was added. Cooling for 16 hr. caused the precipitation of 3.9 g. of *sym*-dibromotetraphenyldisilane, 68%.

*Attempted direct preparation of sym-dichlorotetraphenyldisilane.* To 50.6 g. of dichlorodiphenylsilane in 100 ml. of tetrahydrofuran was added 1.4 g. of lithium metal. A reaction was evidenced by the yellow coloring of the metal. The reaction was allowed to proceed for 48 hr. at which time the lithium had been consumed. The white precipitate which had separated was filtered off and extracted in a Soxhlet apparatus with toluene. From the extracts were obtained 8 g. of octaphenylcyclotetrasilane (22%), m.p. 315–317°.[29] From the ether filtrates were recovered dichlorodiphenylsilane by distillation, b.p. 128–130°/2 mm. 20 g., 39%. The remaining oils did not crystallize on standing and consisted of diphenylsilylene polymers.

*Reaction of dichlorodiphenylsilane with zinc (attempted).* A 50-g. sample of dichlorodiphenylsilane was added to a suspension of 15 g. of finely powdered zinc in 200 ml. of refluxing ether. The reaction mixture was stirred for 48 hr. while the ether was heated to reflux. There was no visual sign of reaction and an aliquot indicated that none of the chlorosilane had reacted. Distillation of the filtrate from the zinc yielded 40 g. of dichlorodiphenylsilane, b.p. 128–130°/2 mm.; 80% recovery.

*Reaction of dichlorodiphenylsilane with lithium amalgam.* Lithium amalgam was prepared from 0.3 g. of lithium (0.0435 g.-atom )in an open Schlenk tube in a slow current of hydrogen. Mercury, 100 g., was heated to 145° and the lithium was added slowly through one of the inlets in the tube. The temperature was raised to 210° after complete addition and the suspension was swirled occasionally during a 10-min. period. The tube was cooled and there was introduced 11 g. of dichlorodiphenylsilane (0.040 mole) in 30 ml. of ether. The tube was cooled in a Dry Ice acetone bath and sealed under an atmosphere of nitrogen. The Schlenk tube was mounted in a Parr hydrogenation apparatus and shaken for 70 hr. (130 rpm). The tube was cooled and opened. The contents of the tube were filtered through a fluted filter and the mercury washed with tetrahydrofuran. The mercury contained a large proportion of unchanged lithium amalgam as evidenced by the evolution of hydrogen on hydrolysis. The organic layer was evaporated and since no solid separated on standing, the oil was distilled to give 4.0 g. of dichlorodiphenylsilane (36% recovery) and various oils, 4.5 g., from which was obtained in a 52% yield hexaphenylcyclotrisiloxane, identified by mixed melting point and infrared spectra.

*Reaction of dibromodiphenylsilane with lithium amalgam.* Dibromodiphenylsilane was prepared from diphenylsilane and bromine in 73% yield, b.p. 180°/12 mm. A portion (15 g.) of this was added to lithium amalgam prepared as described in the previous experiment (0.0435 mole/0.0432 g.-atom). The reaction was carried out in an identical manner to yield by work-up under anhydrous conditions 1.5 g. of lithium bromide (47%). The organic layer did not yield any *sym*-dibromotetraphenyldisilane. A mixture of octaphenylcyclotetrasiloxane and hexaphenylcyclotrisiloxane was obtained by chromatography and a small amount of octaphenylcyclotetrasilane, m.p. 315–317°, 2.6 g. (31%). By distillation there was obtained 30% unchanged dibromodiphenylsilane, b.p. 180–185°/12 mm.

*Preparation of sym-di-p-tolyltetraphenyldisilane.* A 1*M* solution of *p*-tolyllithium was prepared from 17.7 g. of *p*-bromotoluene and lithium in a total of 100 ml. of ether. A portion of this solution (21 ml.; 0.99*M* by analysis) was added to a solution of 2.20 g. (0.005 mole) *sym*-dichlorotetraphenyldisilane in 40 ml. of ether. The solution was stirred for 24 hr. at room temperature, and 100 ml. of saturated aqueous ammonium chloride was added. The product which was insoluble in ether was obtained by filtration. Recrystallization from benzene-chloroform 1:1, yielded 1.74 g. of *sym*-di-*p*-tolyltetraphenyldisilane (70%), m.p. 248–249°. The compound was identified by mixed melting point and comparison of infrared spectra with an authentic sample.

*Hydrolysis of sym-dichlorotetraphenyldisilane.* A solution of 3.8 g. of *sym*-dichlorotetraphenyldisilane (0.0088 mole) in 15 ml. of toluene was added to a well-stirred emulsion of 70 ml. of water and 20 ml. of *tert*-amyl alcohol. The mixture was stirred for 1 hr. at room temperature and for 3 hr. at 0°. The product was obtained from the dried organic layer, which had been combined with ether extracts of the

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(28) C. W. Young and P. C. Servais, C. C. Currie, and M. J. Hunter, *J. Am. Chem. Soc.*, **70**, 3758 (1948).

(29) H. Gilman, D. J. Peterson, A. W. Jarvie, H. J. S. Winkler, *J. Am. Chem. Soc.*, **82**, 2076 (1960).

aqueous layer (three 100-ml. portions), by removal of the solvents. Recrystallization from benzene-petroleum ether (b.p. 60–70°) gave an 83% yield of *sym*-tetraphenyldisilanediol, 3.2 g., m.p. 139–140°.

*Anal.* Calcd. for $C_{24}H_{22}Si_2O_2$: C, 72.32; H, 5.57; Si, 14.08. Found: C, 71.86, 71.96; H, 5.34, 5.34; Si, 13.96, 14.06.

Hydrolysis in acetone with ammonium carbonate monohydrate of 2 g. of *sym*-dichlorotetraphenyldisilane at 50° for 1 hr. and in the refluxing solvent for another hour yielded ammonium chloride which was filtered off and identified by qualitative analysis. The filtrate yielded a small fraction of *sym*-dihydroxytetraphenyldisilane, 0.3 g. (16%), m.p. 138–139° and 1.1 g. of 1,5-dihydroxy-1,1,2,2,4,4,5,5-octaphenyltetrasiladisiloxane-3, m.p. 118–119°, H-value 58.5 ml./g. Calcd. for $C_{48}H_{42}Si_4O_3$, 57.5 ml./g.

*Anal.* Calcd. Si, 14.42. Found: 13.93, 14.02.

Hydrolysis of *sym*-dichlorotetraphenyldisilane in 10% piperidine-water on a quantitative scale gave a hydrogen value of 52 ml./g. Calcd. for this compound is 51.5. From the hydrolysis mixture was isolated a compound which was identified as octaphenylcyclotetrasiloxane by melting points and infrared spectra.

*Attempted dehydrations of sym-tetraphenyldisilanediol.* A suspension of 2 g. of *sym*-tetraphenyldisilanediol in 30 ml. of 88% formic acid was heated to boiling for 30 min. The solution was cooled and poured on 100 ml. of an ice water slurry. The white crystalline compound which was collected on filtration was recrystallized from benzene-petroleum ether (b.p. 60–70°), 1.8 g. or 95% yield, m.p. 219–220°.

*Anal.* Calcd. for $C_{48}H_{40}Si_4O_2$: C, 75.75; H, 5.30; Si, 14.75. Found: C, 75.55, 75.75; H, 5.30, 5.36; Si, 14.60, 14.81.

A finely ground sample of *sym*-tetraphenyldisilanediol was added to 20 ml. of concentrated sulfuric acid which had been cooled to 0°. The suspension was stirred for 0.5 hr. and then poured on cracked ice. Extraction of the resulting suspension with ether and drying of the combined extracts gave a colorless solution which on concentration yielded a solid melting at 137–139° and having an infrared spectrum identical with the starting material. The yield of recovered *sym*-tetraphenyldisilanediol was 65%.

Dehydration of 0.3 g. of diol in 50% phosphoric acid heated to reflux in the presence of an equal volume of toluene, after an initial 10-min. period of heating without toluene, resulted in the recovery of 40% of the starting material containing traces of the linear disiloxane melting at 118–119°.

An 0.5-g. sample of *sym*-tetraphenyldisilanediol was heated with 1 ml. of phenyl isothiocyanate for 5 min. producing a clear solution. A white solid precipitated on cooling the solution and adding petroleum ether (b.p. 60–70°). The solid was collected on a filter and washed with 50% ethanol in order to remove phenylisothiocyanate. The product was recrystallized from benzene-petroleum ether (b.p. 60–70°), m.p. 137–138°, 0.35 g., or 70% recovery.

A solution of 0.4 g. of the diol in 6 ml. of dried pyridine containing 0.8 g. of *p*-toluenesulfonyl chloride was left standing at room temperature for 44 hr. The solution was then heated on a steam bath for 30 min. and cooled in an ice bath. Part of the solvent was evaporated and the remaining oil was chromatographed to yield 0.38 g. of solid, m.p. 219–220°, identified as the cyclic siloxane by its infrared spectrum and mixture melting point with an authentic sample.

A solution of 1 g. of the diol in 50 ml. of benzene containing a trace of *p*-toluenesulfonic acid was refluxed briskly for 4 hr. Any water in the refluxing vapors would have been removed by means of the Deen-Stark trap used. Evaporation of the solvent left the unchanged starting material behind (75% recovery).

A mixture of 1.0 g. of oxalic acid and 0.3 g. of the diol was dissolved in 2 ml. of dimethylformamide and heated in the refluxing solvent for 30 min. The reaction mixture was poured on ice to remove the solvent and the acid. The solid which separated was filtered off and washed with ethanol. Recrystallization yielded the pure cyclic siloxane in 68% yield, m.p. 220–221.°

Chloral hydrate was dehydrated by heating in boiling benzene for 3 hr. The water was separated by azeotropic distillation and collected in a Deen-Stark trap. The benzene solution was cooled and a trace of *p*-toluenesulfonic acid was introduced together with 2.0 g. of the diol. The solvent was brought to a brisk boil which was continued for 20 hr. The solution was concentrated to 5 ml. and chromatographed to yield 1 g. of the cyclic siloxane, m.p. 220–221°.

*Determination of hydrogen values.* The hydrogen value of a compound may be calculated from the molecular weight and the number of silicon-silicon bonds (n) and silicon-hydrogen bonds (m) in the molecule: H-value $= \frac{22.400\,(n + m)}{\text{Mol. Wt.}}$. The hydrogen evolved from silicon-hydrogen bonds is usually evolved more rapidly than that from a silicon-silicon bond.

It is advantageous to use the amount of compound which would liberate a total of 10–15 ml. of hydrogen. Usually 0.1–0.2 g. of compound suffices for the determination. The compound is weighed out directly into the dried flask R and three boiling stones are added. The ball joint at R is greased with Lubriseal and clamped closed. Leveling bulb No. 2 is placed in such a postion that the mineral oil surface is at the same level as the side-arm of the reservoir A. Stopcock 2 is closed and stopcock 3 is opened while 10 ml. of wet piperidine (containing 10% of water by volume) is introduced into the addition funnel F. The addition funnel (F) is closed and stopcock 2 is opened to allow the piperidine to flow into the reaction flask. Stopcocks 2 and 3 are closed immediately after the piperidine has drained out of the addition funnel. The heating mantle under R is turned on and the flow of water through the condenser started. The evolved gases will bubble through the mercury at the bottom of A and displace the mineral oil in A into the leveling bulb No. 2. The heat is left on until no more bubbles pass through the mercury (3–15 hr.). The gas is moved from A into the measuring burette by raising leveling bulb No. 2 and lowering No. 1 while stopcocks 1 and 4 are set in such a position as to allow the gas to flow into the burette. If more than 50 ml. of gas is collected this should be measured off in two portions. Measuring the gases is accomplished by raising leveling bulb No. 1 until the mineral oil inside the bulb is at the same level as the oil inside the burette. If it appears necessary to check whether more gas will be evolved on prolonged heating, it is advisable to lower the leveling bulb No. 2 slowly to its lower position since a sudden change in pressure accompanied thereby will cause the piperidine to boil more rapidly and displace more gas in the condenser than normally. The pressure at the time of reading the volume should be noted as should the temperature of the gas. From the amount of gas evolved, the pressure, the weight of the compound, and the temperature, the hydrogen value of the compound can be calculated if the volume of gas liberated from refluxing an equal volume of wet piperidine is known. This amount of gas is called the "empty value". A choice in calculating the hydrogen value may be made: either the empty value may be converted to S.T.P. and subtracted from the value observed, corrected to S.T.P.; or the empty value may be converted from the conditions under which it was observed to the conditions at which the determination of the hydrogen value was made ($V_{\text{empty}}$) and subtracted from this before the remaining volume is corrected to S.T.P. The volume thus found should be corrected to S.T.P. taking into account the temperature, the pressure, and the vapor pressure of the wet piperidine at the temperature of the condenser:

$$\text{H-value found} = \frac{(V_{\text{found}} - V_{\text{empty}})\cdot 273\cdot(P_{\text{mm.}} - 11)}{g_{\text{cpd.}}\cdot \text{Temp.}_{\text{observed}}\,(\text{K}^\circ)\cdot 760}$$

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, NORTHWESTERN UNIVERSITY]

# Organoboron Compounds. XIII. Boronic Acids with Neighboring Unsaturated Groups[1]

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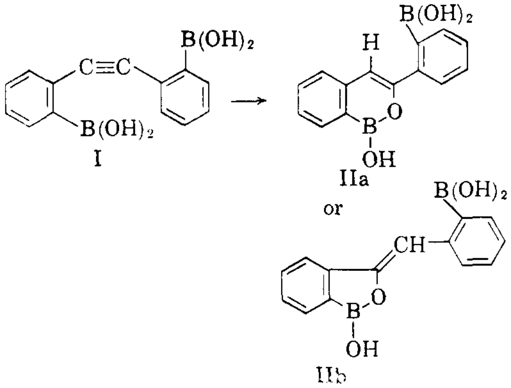
2,2′ Stilbenediboronic acid, 2-vinylbenzeneboronic acid, and 2-tolanboronic acid are described. None of these compounds isomerizes under conditions which convert 2,2′-tolandiboronic acid to a heterocyclic compound (II).

2,2′-Tolandiboronic acid (I) readily isomerizes in an alkaline medium or in solutions containing potassium acid tartrate to give a heterocyclic compound, which has been formulated as either IIa or IIb.[4]

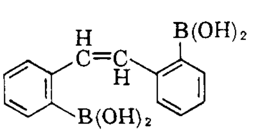

I

IIa

or

IIb

In order to gain further information concerning the reactions of boronic acid groups with neighboring unsaturated linkages, we prepared 2,2′-stilbenediboronic acid (III), 2-vinylbenzeneboronic acid (IV), and 2-tolanboronic acid (V) and subjected them to conditions which would effect the transformation of I to II. Particular attention was directed to 2-tolanboronic acid, for should this compound yield a product analogous to II, it would be possible by oxidative degradation to determine whether the hetero-ring was five- or six-membered.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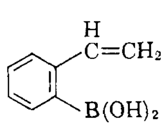
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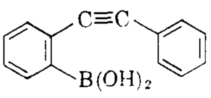
V

Neither the stilbenediboronic acid nor the vinylbenzeneboronic acid yielded isolable rearrangement products under the conditions examined. In each case the major portion of the boronic acid was recovered unchanged, as shown by the infrared spectrum. The vinyl group in 2-vinylbenzeneboronic acid possessed normal reactivity with respect to polymerization. Like 4-vinylbenzeneboronic acid[5] compound IV yielded when warmed with azobisisobutyronitrile a brittle polymer, which was insoluble in ether or benzene but soluble in alkaline solutions.

More surprising, no isomerization was observed with 2-tolanboronic acid.[6] This fact shows that both boronic acid groups in 2,2′-tolandiboronic acid must play a role in the isomerization and suggests that the reaction may involve concerted donation of a proton by one boronic acid group and a hydroxide ion by the other (which is complexed with hydroxide or tartrate ion) to the two carbon atoms joined by the triple bond. Models indicate that a

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(1) For the previous paper in this series see R. L. Letsinger and S. B. Hamilton, *J. Org. Chem.*, **25**, 592 (1960).

(2) National Science Foundation Undergraduate Summer Research Participant.

(3) National Science Foundation Predoctoral Fellow.

(4) R. L. Letsinger and J. R. Nazy, *J. Am. Chem. Soc.*, **81**, 3013 (1959). Product II is unusual in that, though formally a boronate ester, it resists hydrolysis in acidic, neutral and weakly alkaline media and titrates as a monoboronic acid. The recently demonstrated stability of the six-membered heterocyclic B-O-C system in 9,10-boroxarophenanthrene [M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 1344 (1960)] increases the plausibility of structure IIa.

(5) R. L. Letsinger and S. B. Hamilton, *J. Am. Chem. Soc.*, 81, 3009 (1959).

(6) A small amount of 2-bromo-2′-tolanboronic acid was isolated from one of the reactions used in the preparation of 2,2′-tolandiboronic acid (see Ref. 4). The structure, deduced from the mode of formation and analyses of the compound and its dihydrobenzoboradiazole derivative (ref. 4), is strongly supported by the ultraviolet spectrum ($\lambda_{\max}^{C_2H_5OH}$ 287,306; shoulders at 272,297 m$\mu$), which is almost superposable upon the spectrum of 2,2′-tolandiboronic acid Like 2-tolanboronic acid, this compound did not isomerize when warmed in an alkaline, aqueous-alcoholic solution.