

## THE HYDROHALOGENATION OF PERPHENYLCYCLOSILANES

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### SUMMARY

Anhydrous hydrogen halides have been found to react with octaphenylcyclotetrasilane to give the corresponding 1-halo-1,1,2,2,3,3,4,4-octaphenyltetrasilane in good yields. The order of reactivity observed with these reagents under similar conditions is  $\text{HI} > \text{HBr} > \text{HCl}$ . Several halogenated hydrocarbons also bring about cleavage and hydrohalogenation of octaphenylcyclotetrasilane. Some of the halogenated hydrocarbons cause a secondary cleavage of the silicon hydride formed to provide the 1,4-dihalo-1,1,2,2,3,3,4,4-octaphenyltetrasilane derivative. This may provide a route for mixed dihalo derivatives. Decaphenylcyclopentasilane reacts only to a small extent with the same reagents and then to give non-isolable products.

### INTRODUCTION

In general, the silicon-silicon bond in which the silicon atoms are completely substituted with organic groups is relatively stable to cleavage reactions. However, the exceptional reactivity of octaphenylcyclotetrasilane (I) with respect to silicon-silicon scission has been demonstrated\*\*\*. This cyclosilane undergoes ready reaction with halogenated hydrocarbons<sup>2,3</sup>, halogens<sup>2,4,5</sup>, inorganic halides<sup>3,6</sup>, mercuric acetate<sup>7</sup>, and oxidizing agents<sup>1-3,8</sup>.

In contrast to the high reactivity of I, decaphenylcyclopentasilane<sup>9</sup> (II) resists cleavage by nearly all reagents which react rapidly with I<sup>1</sup>. II does react with bromine<sup>10</sup>, chlorine<sup>5</sup>, inorganic halides<sup>11</sup>, 1,1,2,2-tetrachloroethane<sup>5</sup>, and nitrobenzene<sup>8</sup>. Reaction conditions suitable for the cleavage of II often cause secondary cleavage of the resulting linear polysilane at a faster rate than with the cyclosilane.

Extensive study has been made of the desilylation of aryl-substituted silanes with hydrogen halides<sup>11,12,13</sup>. However, no report has been made on the acid cleavage of a silicon-silicon bond of a perphenylpolysilane prior to our findings<sup>1,14</sup>. The present report includes our studies of the cleavage of perphenylcyclosilanes with hydrogen and organic halides.

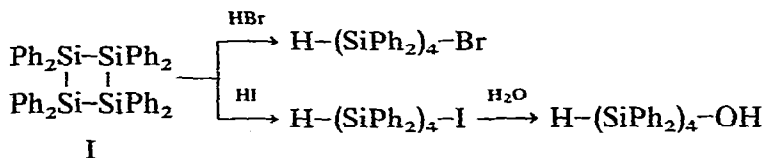
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\*\*\* For a review see ref. 1.

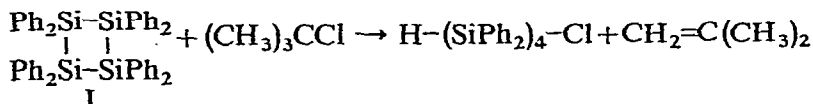
## RESULTS AND DISCUSSION

Hydrogen iodide and hydrogen bromide react with I in refluxing benzene to give, in good yield, 1-iodo-1,1,2,2,3,3,4,4-octaphenyltetrasilane and 1-bromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane, respectively. The iodasilane was not isolated, but was hydrolyzed and characterized as 1-hydroxy-1,1,2,2,3,3,4,4-octaphenyltetrasilane.



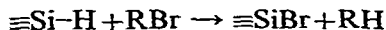
Under similar conditions, octaphenylcyclotetrasilane reacts only slowly with anhydrous hydrogen chloride. After a twelve hour reaction time, 86% of the octaphenylcyclotetrasilane was recovered, whereas with hydrogen iodide and hydrogen bromide, one hour and four hours, respectively, were required to bring about complete disappearance of the cyclotetrasilane. Therefore, the order of reactivity of the hydrogen halides with octaphenylcyclotetrasilane is  $\text{HI} > \text{HBr} > \text{HCl}$ .

Also, I is capable of dehydrohalogenating certain halogenated hydrocarbons. Thus, the cyclotetrasilane reacts with 2,2'-dichlorodiethyl ether, 1,2,3,4,5,6-hexachlorocyclohexane, tert-butyl chloride, tert-butyl bromide and 2-chlorobutane to give the corresponding 1-halo-1,1,2,2,3,3,4,4-octaphenyltetrasilane.



The reaction of I with tert-butyl chloride is very slow at temperatures below  $140^\circ$ , but increasing yields (57–78%) were obtained using xylene, decalin, or *o*-dichlorobenzene as solvent.

A secondary reaction occurs in the case of tert-butyl bromide and 2,2'-dichlorodiethyl ether. Part of the silicon hydride formed is converted to a silicon halide to give the corresponding 1,4-dihalo-1,1,2,2,3,3,4,4-octaphenyltetrasilane. This conversion has already been noted to occur with other silicon hydrides<sup>15,16</sup>. It was observed that the halogenation of a silicon hydride with an alkyl halide does not cause dehydrohalogenation of the alkyl halide. The bromination of triethylsilane with allyl bromide, 2-bromoethyl propionate and *n*-propyl bromide gave yields of 97, 50 and 10% of bromotriethylsilane, respectively<sup>16</sup>. The formation of the corresponding hydrocarbon with no olefin products was observed. It would appear that this reaction does not follow the same mechanistic route observed in the acid halide or tert-butyl halide cleavage of a silicon-silicon bond. If the reaction were the same the results would have been the formation of a silicon halide, an olefin and hydrogen gas.



Octaphenylcyclotetrasilane ring-opening is known to occur with alkyl polyhalo compounds<sup>2,3</sup> and the reaction of I with hexachlorocyclohexane is probably a competitive reaction between halogenation and hydrohalogenation. A mixture of 1,4-dichloro- and 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane was also obtained

with this reagent. The product would depend on the stereochemistry of the hexachloro isomer and whether a *cis* or *trans* elimination occurred. Infrared spectral studies of the hydrocarbon by-products indicated a mixture of chlorohexene isomers. The results from the study of the reaction of I with halogenated hydrocarbons are compiled in Table 1.

TABLE 1

REACTION OF OCTAPHENYLCYCLOTETRASILANE (I) WITH ORGANIC HALIDES

Halide (mole)	Solvent (ml)	I (mole)	Time (h)	Temp. (°C)	Recovered I (%)	Products (%)
(ClCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O (solvent) <sup>a</sup>	(100)	0.02	1.5	Reflux	15	Cl(SiPh <sub>2</sub> ) <sub>4</sub> Cl } (29) H(SiPh <sub>2</sub> ) <sub>4</sub> Cl }
C <sub>6</sub> H <sub>5</sub> Cl <sub>6</sub> (0.04)	Decalin (100)	0.11	5	185	24	H(SiPh <sub>2</sub> ) <sub>4</sub> Cl } (55) Cl(SiPh <sub>2</sub> ) <sub>4</sub> Cl }
n-BuCl (0.30)	Decalin (100)	0.03	72	83	99.1	
n-BuCl (0.92)	Decalin (100)	0.03	23	148		H(SiPh <sub>2</sub> ) <sub>4</sub> Cl (78)
n-BuCl <sup>a</sup> (0.092)	Xylene (200)	0.03	48	133	31	H(SiPh <sub>2</sub> ) <sub>4</sub> Cl (57.3) Isobutylene }
n-BuCl (0.083)	<i>o</i> -Dichlorobenzene (150)	0.055	9	158	27.5	H(SiPh <sub>2</sub> ) <sub>4</sub> Cl (70)
n-BuCl (0.133)	<i>o</i> -Dichlorobenzene (100)	0.01	17	147	85	H(SiPh <sub>2</sub> ) <sub>4</sub> Cl (6.8)
n-BuCl (0.079)	Xylene (100)	0.01	70	129	99	
n-BuCl (0.086)	<i>o</i> -Dichlorobenzene (100)	0.01	67	157	93	
n-BuBr <sup>a</sup> (0.062)	Decalin (100)	0.01	1.5	162		H(SiPh <sub>2</sub> ) <sub>4</sub> Br } (77) Br(SiPh <sub>2</sub> ) <sub>4</sub> Br }

<sup>a</sup> Described in the *Experimental*.

The desilylation of arylsilanes is dependent on inductive, resonance, and steric effects<sup>11,12</sup>. 1,4-Substituted perphenylpolysilane derivatives are highly conjugated<sup>17,18</sup> and also exhibit a great deal of steric hindrance to substitution reactions<sup>19</sup>. These factors and others<sup>20</sup> probably account for the lack of any evidence of silicon-phenyl cleavage occurring under the conditions used. An exception was noted with one pressure reaction of hydrogen chloride and decaphenylcyclopentasilane. Benzene equal to 54% of the available phenyl groups was obtained.

The hydrohalogenation of decaphenylcyclopentasilane (II) was attempted with hydrogen halides and several organic halides. A variety of conditions was tried with regard to solvent, temperature, and duration. In only two instances were there any appreciable reaction and secondary cleavage of the polysilane occurred to give intractable products. No reaction was observed with organic halides. Comparable studies with dodecaphenylcyclohexasilane<sup>20</sup> indicated that the steric effects of the bulky phenyl groups are a major factor in protecting the Si-Si bond from cleavage. The facile reactivities of certain six- and seven-membered ring heterocyclic polysilanes provide evidence for this observation<sup>21</sup>.

The reactivity of I has been attributed<sup>4</sup> to "ring strain and the accompanying

homolytic cleavage to a biradical". However, a discrete silyl radical need not be involved in the ring opening of octaphenylcyclotetrasilane. Ring strain may increase the reactivity of octaphenylcyclotetrasilane due to distortion of the tetrahedral bond angles of silicon. However, this effect need not be so important as it is in carbon chemistry, because the tetrahedral angle of silicon is believed to be more easily deformed than that of carbon<sup>22</sup>.

A possible explanation for the greater reactivity of octaphenylcyclotetrasilane, compared to the other perphenylated cyclosilanes and hexaphenyldisilane, is due to the tetracyclic geometry of I. This enables it to more easily achieve a pentacovalent transition state. There is a lack of data concerning the reactivity of the silicon-silicon bond in strained ring systems, such as might be found in 1,2-disilacyclobutanes. It has been found that silacyclobutane<sup>22-25</sup> and 1,3-disilacyclobutane<sup>26-29</sup> derivatives undergo facile ring opening reactions with a variety of reagents. The reactivities of 1,1,2-triphenyl-1-silacyclobutane and 1,1,2-triphenyl-1-silacyclopentane have been compared with respect to ring-opening and the ease of formation of a pentacovalent silicon intermediate<sup>30</sup>. As has been observed with cyclosilanes, the five-membered ring was found to be much less reactive.

Therefore, the high reactivity of octaphenylcyclotetrasilane can be attributed to the geometry of the compound which allows easy approach of a reacting molecule. A pentacovalent state is attained in which angular strain of the tetracovalent silicon atoms has been relieved. There is also less added steric strain due to compression of phenyl groups in such an intermediate of a four-membered ring than in a larger one. These factors are discussed more fully in a recent review<sup>1</sup>.

## EXPERIMENTAL

In general, the apparatus consisted of an appropriately sized standard taper flask, provided with a condenser, stirrer, and, as required, an addition funnel, gas inlet tube or thermometer. All temperatures are °C and are uncorrected. Melting points were obtained with a Mel-Temp apparatus. Reagents, gases, and solvents were used as they were obtained commercially. Except where noted, petroleum ether (b.p. 60-70° or 70-115°) was used. Reactions involving organometallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. Yields of unidentified solids are based on the weight of the starting material and therefore are not precise. The attempted pressure reaction was made in a stirred one liter Parr Pressure Reaction Apparatus, Item No. 4511.

### *Reactions of octaphenylcyclotetrasilane (I)*

*I with anhydrous hydrogen bromide.* Anhydrous hydrogen bromide was bubbled at a moderate rate through a mildly refluxing stirred suspension of 7.29 g (0.01 mole) of I in 150 ml of sodium-dried benzene. After four hours only a small amount of suspended material remained and the solution had become slightly yellow in color. The benzene solution was concentrated and 100 ml of sodium-dried petroleum ether was added. A fine white precipitate, melting with decomposition above 475°, was removed by filtration. This operation was repeated until no more high melting precipitate formed upon concentration of the solution.

Final concentration of the petroleum ether solution provided 6.89 g (85.0%)

of crude 1-bromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane, melting over the range 161–168°. Recrystallization (decolorizing charcoal) from petroleum ether gave 5.68 g (70%) of pure product, m.p. 166–167°. (Found: Si, 13.76, 13.72; hydrogen value, 109 ml/g.  $C_{48}H_{41}BrSi_4$  calcd.: Si, 13.86%; hydrogen value<sup>31</sup>, 111 ml/g.)

*I with anhydrous hydrogen iodide.* Anhydrous hydrogen iodide was prepared by the dropwise addition of a solution of 125 g of iodine in 70.5 g of 47% hydriodic acid to an excess of red phosphorus in a two-necked flask provided with a gas outlet tube. Between the hydrogen iodide flask and the reaction flask was a drying tube containing phosphorus pentoxide. The gas generated in this manner was bubbled through a suspension of 7.29 g (0.010 mole) of I in 150 ml of refluxing benzene. Within one hour all of the cyclosilane had gone into solution. Dry nitrogen was passed through the cooled solution. Removal of the benzene by distillation left a gray gummy mass to which chloroform was added. A small amount of white insoluble material was filtered off. Dry ether was added to the chloroform solution which was then cooled to 0°. Only a small quantity of white solid precipitated which melted over a wide range above 400°.

Because the iodo compound appeared to be decomposing (depositing of iodine) in solution, it was hydrolyzed. Work-up of the hydrolysis product afforded 3.50 g (47%) of a white crystalline material, m.p. 177–183°. Recrystallization from benzene/petroleum ether gave 2.00 g (27%) of pure 1-hydroxy-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 183–185°. The infrared spectrum possessed absorption bands at 3570 and 2090  $cm^{-1}$  indicative of SiOH and SiH, respectively. (Found: Si 15.0, 14.9.  $C_{48}H_{42}OSi_4$  calcd.: Si, 15.0%.)

*I with anhydrous hydrogen chloride.* Octaphenylcyclotetrasilane was treated with anhydrous hydrogen chloride under a variety of conditions with regard to solvent, temperature and duration of reaction (Table 2). Depending on the conditions the

TABLE 2

REACTIONS OF OCTAPHENYLCYCLOTETRASILANE (I) WITH HYDROGEN CHLORIDE

Solvent (ml)	I (mole)	Temp. (°C)	Time (h)	Recovered I (%)	Product (%)
Benzene <sup>a</sup> (450)	0.02	78	12	89	2
Xylene (300)	0.02	138	6	62	33
Xylene (350)	0.04	138	13	55	33
Xylene (750)	0.04	138	17	70	21
<i>o</i> -Dichlorobenzene (300)	0.04	175	2.0	1.4	81
<i>o</i> -Dichlorobenzene (300)	0.04	175	1.0		91
<i>o</i> -Dichlorobenzene (300)	0.04	175	1.5	3	88
<i>o</i> -Dichlorobenzene (400)	0.08	175	1.75	1.2	91
<i>o</i> -Dichlorobenzene (400)	0.08	175	3	1.3	93

<sup>a</sup> With the exception of the reaction in benzene the hydrogen chloride was admitted below the liquid level at all times.

yield of 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane ranged from 2 to 92%. Details of the reaction in benzene are given and the work-up of the products given as a general procedure.

A mixture of 14.6 g (0.02 mole) of I and 250 ml of benzene was heated to the reflux temperature and anhydrous hydrogen chloride was added continuously above the liquid level for 6 h. An additional 200 ml of benzene was introduced and the admission of gas continued for 6 h. After standing overnight at room temperature the reaction mixture was filtered to give 12.6 g (86.3%) of crude starting material, m.p. 308–320°. Concentration of the filtrate gave in two crops an additional 1.9 g (13.4%) of recovered octaphenylcyclotetrasilane.

The final filtrate was then evaporated to dryness at reduced pressure with the aid of a steam bath. The residue was dissolved in 2 ml of benzene and the addition of 20 ml of petroleum ether caused the precipitation of 0.30 g of solid, m.p. 156–158°. Recrystallization of this material provided 0.28 g (2.0%) of pure 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 161–163°. Mixture melting point determinations of this compound with 1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 160–161°, and with 1-bromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 161–162°, were not depressed. However, an infrared spectrum of the product (in carbon disulfide) using potassium bromide cells showed a silicon–hydrogen absorption at  $795\text{ cm}^{-1}$  as well as absorptions at 560 and  $523\text{ cm}^{-1}$  attributable to the silicon–chlorine bond<sup>32</sup>. (Found: Si, 14.58, 14.48.  $\text{C}_{48}\text{H}_{41}\text{ClSi}_4$  calcd.: Si, 14.68%.)

*1-Hydroxy-1,1,2,2,3,3,4,4-octaphenyltetrasilane.* A mixture containing 15.3 g (0.02 mole) of 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane, 100 ml of tetrahydrofuran and 50 ml of 1 *N* hydrochloric acid was stirred at room temperature for 6 h. The organic layer was separated from the aqueous layer and was washed several times with distilled water.

The solvent was stripped from the organic soluble material and the residue was dissolved in 50 ml of benzene. The resulting solution was dried with anhydrous sodium sulfate and after filtration was treated with 100 ml of petroleum ether to give 13.1 g (87%) of crude 1-hydroxy-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 188–190°. Partial evaporation of the filtrate provided an additional 1.6 g (10.7%) of product, m.p. 184–189°. Recrystallization gave 13.35 g (89.5%) of the pure product, m.p. 185–187°. Identification of the compound was made by comparison of its infrared spectrum with that of the product of hydrolysis of the material obtained from the addition of hydrogen iodide to I. A mixed melting point determination also indicated the identity of the two compounds.

A sample of 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane treated in a similar manner in a mixture of benzene, ether and water showed no hydrolysis after 8 h of stirring at 30°.

*1-Methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane.* 1-Chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane, 4.8 g (0.063 mole) dissolved in 60 ml of tetrahydrofuran was added slowly to a mixture of 7 ml of a 0.81 *M* methylmagnesium iodide/ether (0.006 mole) solution and 40 ml of tetrahydrofuran. Color Test I<sup>33</sup> was negative after 15 min and 10 ml more (0.008 mole) of the 0.81 *M* methylmagnesium iodide was added. After 1 h the color test was negative and an additional 5 ml (0.004 mole) of the Grignard reagent provided a positive color test after 30 h of stirring. The reaction was then left standing for three days after which a solution of ammonium chloride in water was

added and the two layers separated. The aqueous layer was washed several times with ether. After distillation of the organic layer under reduced pressure the residue was dissolved in 25 ml of benzene to which 50 ml of petroleum ether was added. Upon standing overnight, 3.1 g (66.5%) of solid, m.p. 172–174° was obtained. Evaporation of the solvent mixture provided an additional 0.7 g (15%), m.p. 171–173°. The melting point of the first fraction when mixed with an authentic sample of 1-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane was not depressed. 1-Methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane was previously prepared and characterized from the reaction of methyl lithium with I followed by acid hydrolysis<sup>34</sup>. An infrared spectrum (CS<sub>2</sub>) of the product was very similar to the spectrum of the starting material with the exception of an absorption at 1240 cm<sup>-1</sup> which is due to the silicon-methyl bond.

*I with 2,2'-dichloroethyl ether.* A mixture of 14.6 g (0.02 mole) of I and 100 ml of 2,2'-dichloroethyl ether was refluxed for 1.5 h. After standing overnight, 2.2 g (15%) of starting material, m.p. 318–330° was obtained. The solvent was removed by distillation under reduced pressure with a steam bath and the residue dissolved in 10–15 ml of benzene. Addition of 30–40 ml of petroleum ether provided 4.2 g (29%) of solids, m.p. 173–176°. Evaporation of the filtrate to approximately 20 ml provided an additional 0.6 g (4.1%) of solid, m.p. 153–155°. Repeated recrystallization provided no pure products. An infrared spectrum in CS<sub>2</sub> using KBr cells of the lowest melting fraction showed strong absorption at 790, 560 and 523 cm<sup>-1</sup> superimposable with the spectrum of 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane. A spectrum of the higher melting fraction, m.p. 170–175°, showed weak absorption at 790 cm<sup>-1</sup> and strong absorption at 523, 545 and 560 cm<sup>-1</sup> superimposable with the spectrum of 1,4-dichlorooctaphenyltetrasilane.

*I with tert-butyl chloride. In xylene.* A mixture of 22 g (0.03 mole) of I, 200 ml of xylene and 5 ml (0.046 mole) of tert-butyl chloride was heated for 24 h at 133–138°. tert-Butyl chloride, 5 ml (0.046 mole), was then added and heating continued 23 h at 132°. Upon cooling, 7.0 g (31%) of starting material, melting over the range 327–332°, was obtained. Partial distillation of the xylene and the addition of increasing amounts of petroleum ether provided the following solid fractions: 12.3 g (53%) of 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. and mixed m.p. 161–162°; 1.0 g (4.3%), m.p. 156–160°; and 0.3 g (1.4%), m.p. 158–176°. A vapor trap immersed in a dry ice/acetone bath attached to the condenser trapped a mixture of liquids and solids. This mixture was slowly warmed and placed in a gas cell. An infrared spectrum showed absorptions, which differed from the spectrum of the tert-butyl chloride used, at 1660 and 888 cm<sup>-1</sup>. This is believed to be due to isobutylene formed by dehydrohalogenation of the tert-butyl chloride.

*In decalin.* A mixture of I, 22 g (0.03 mole), tert-butyl chloride, 28 g (0.3 mole), and 100 ml of freshly distilled decalin was heated at reflux temperature (83–95°) for 72 h. Concentration of the solvent gave a 21.8 g (99%) recovery of I, m.p. 332–334°.

To a second reaction mixture containing 22 g (0.03 mole) of I in 100 ml of decalin was added 5 ml (4.35 g, 0.046 mole) of tert-butyl chloride. The mixture was then heated to a reflux temperature of 144°, which slowly rose to 170° after 12 h of heating. Addition of 5 ml (4.35 g, 0.046 mole) of tert-butyl chloride brought the temperature down to 148°. After 11 h of heating, the temperature was 173° and the reaction was cooled and allowed to stand overnight. Work-up as above provided 18.6 g (80.6%) of crude 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 157–159°.

An infrared spectrum of the material was superimposable with that of an authentic sample.

*In o-dichlorobenzene.* A mixture of I, 40 g (0.055 mole), and tert-butyl chloride, 5 ml (4.35 g, 0.046 mole), were heated in 150 ml of *o*-dichlorobenzene at 161–167° for 1.75 h. An additional 4 ml (0.037 mole) of tert-butyl chloride was added and heating continued at 157° to 180° for 7.5 h. Work-up as above gave 11.0 g (27%) of starting material, m.p. and mixture m.p. 229–231°, and 29.4 g (70%) of 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. and mixture m.p. 164–166°.

*Pyrolysis of tert-butyl chloride in decalin.* Decalin, 75 ml, and tert-butyl chloride, 10 ml, were refluxed together for 24 h. A dry ice/acetone trap connected to the condenser collected a small amount of tert-butyl chloride but no olefinic material was indicated in its infrared spectrum.

*I with tert-butyl bromide.* A mixture of octaphenylcyclotetrasilane, 7.3 g (0.01 mole), tert-butyl bromide, 5 ml (0.044 mole) and 100 ml of decalin was heated for 1 h at 166°. An additional 2 ml (0.018 mole) of the bromide was then added and heating continued for 0.5 h at 162°. Upon cooling and standing for 36 h 6.25 g (77%) of solid, m.p. 174–177° precipitated. Several recrystallizations in cyclohexane provided 0.1 g of a white solid, m.p. 216–217°, whose melting point was not depressed by an authentic sample of 1,4-dibromooctaphenyltetrasilane. Concentration of the filtrate by distillation and the addition of petroleum ether provided 1.3 g (16%) of crystals, m.p. 161–163°. It was not possible to determine if this fraction was 1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 160–161°, or 1-bromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 162–163°, or a mixture of both as they give a mixture m.p. which is not depressed. An infrared spectrum of the last fraction obtained indicated the presence of octaphenylloxatetrasilacyclopentane with a strong Si–O–Si absorption at 1045 cm<sup>-1</sup> (ref. 32).

*Reaction of 1-bromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane with tert-butyl bromide.* A mixture of 8.1 g (0.01 mole) of 1-bromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane, 8 ml (0.07 mole) of tert-butyl bromide and 100 ml of decalin was heated at 154° for 12 h. An additional 5 ml (0.044 mole) of tert-butyl bromide was added and heating was continued 4 h at 145°. The solvent was removed by distillation under reduced pressure and the residue dissolved in benzene. The addition of petroleum ether provided 4.4 g (55%) of crude product, m.p. 200–202°. Three recrystallizations in cyclohexane provided 1.9 g of white solid, m.p. 219–221°, the melting point of which was not depressed by an authentic sample of 1,4-dibromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane. Distillation of the filtrate and treatment with petroleum ether provided an additional 3.0 g of a solid (37%), m.p. 147–150° which was not characterized. Benzene was found to be unsuitable for the recrystallization of 1,4-dibromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane due to entrapment of the solvent in the crystal structure giving a m.p. of 200–204° instead of 223–224° as obtained with the use of cyclohexane or petroleum ether.

*I with a hexachlorocyclohexane.* Decalin (100 ml) containing 80 g (0.11 mole) of I and 11.7 g (0.04 mole) of 1,2,3,4,5,6-hexachlorocyclohexane, m.p. 111–113°, was heated at 185° for 5 h. The solvent was then removed with a rotary evaporator under reduced pressure and the residue, except for 18.9 g (24%) of I, m.p. 328–332°, was dissolved in hot benzene. Concentration of the solvent and addition of petroleum ether provided 41.7 g (52%) of solids melting over the range 175–180° and 2.4 g (3%) of solids, m.p. 150–154°. Repeated recrystallization from benzene/petroleum ether



mixtures gave no pure fractions. Mixture melting points and infrared spectra comparisons with high melting, 178–180°, fractions and low melting, 160–162°, fractions as in the previous reaction indicated the products to be mixtures of 1,4-dichloro- and 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane. Infrared spectra studies of hydrocarbon fractions obtained indicated they were a mixture of chlorocyclohexenes.

*I with 2-chlorobutane.* 2-Chlorobutane (10 ml, 8.7 g, 0.095 mole) was added slowly to 100 ml of *o*-dichlorobenzene containing 7.3 g (0.01 mole) of I preheated to 180°. The mixture was refluxed at 147–155° for 7 h after which time an additional 4 ml (3.5 g, 0.04 mole) of 2-chlorobutane was added. Heating was continued at 146–150° for an additional 9 h. Work-up of the products as described gave a 6.2 g (85%) recovery of I and a 0.5 g (6.8%) yield of crude 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 156–159°. Recrystallization gave a m.p. and mixture m.p. 164–166°.

*I with n-butyl chloride (attempted). In xylene.* A mixture containing 7.3 g (0.01 mole) of I in 100 ml of xylene was heated under reflux. Over a 70-h period, 8.0 ml (0.074 mole) of *n*-butyl chloride was added in 2 ml aliquots. The boiling point ranged from 129–133°. Work-up gave a 99% recovery of I, m.p. and mixture m.p. 329–333°.

*In o-dichlorobenzene.* A similar reaction was carried out with 7.3 g (0.01 mole) of I in 100 ml of refluxing *o*-dichlorobenzene. Over a period of 67 h, 9 ml (0.085 mole) of *n*-butyl chloride was added. The temperature ranged from 157–168°. Work-up gave 7.2 g (98%) of recovered I, m.p. and mixture m.p. 328–331°.

### Reactions of decaphenylcyclopentasilane (II)

*II with hydrogen halides (attempted).* The reaction of II was attempted with hydrogen chloride and hydrogen bromide using a variety of conditions with regard to solvent, temperature and time. In only two instances was there any appreciable reaction and in these cases a secondary cleavage of the polysilane occurred to give intractable products. The attempted reactions, the conditions used, and their results are tabulated in Table 3.

TABLE 3

REACTION OF DECAPHENYLCYCLOPENTASILANE (II) WITH HYDROGEN CHLORIDE AND HYDROGEN BROMIDE

II (mole)	Solvent (ml)	Gas used	Temp. (°C)	Time (h)	Recovered II (%)
0.018	<i>o</i> -Dichlorobenzene (250)	HCl	170	10	84
0.019	<i>o</i> -Dichlorobenzene (200)	HCl	175	45	83
0.016	<i>o</i> -Dichlorobenzene (200)	HBr	170	7	37.5
0.022	Xylene (200)	HBr	138	48	91
0.022	Bromobenzene (200)	HBr	153	31	92.5
0.011	<i>m</i> -Dibromobenzene (70)	HBr	210	16	
0.022	Triethylbenzene (150)	HBr	205	19	71

*II with hydrogen chloride at high pressure.* A 68 g sample of II (0.0745 mole) was placed in a stainless steel autoclave and hydrogen chloride gas was added to a pressure of 300 psi (0.83 mole, a 11-fold excess) at 27°. Over a period of 4 h, the autoclave was slowly heated to 143° (pressure 320 psi). At 85°, the pressure was 380 psi.

Upon cooling and release of the excess gas from the autoclave through a trap immersed in a dry ice/acetone bath, a mixture of liquids and solids was obtained. Distillation provided 32 g of benzene, b.p. 79–80°,  $n_D^{20}$  1.5085 (ref. sample  $n_D^{20}$  1.5090). This accounts for 54.7% of the available phenyl groups. No further attempt to isolate or identify the products was made.

*II with alkyl halides (attempted).* Attempted reactions of II were carried out with tert-butyl chloride, tert-butyl bromide, 1,2,3,4,5,6-hexachlorocyclohexane and 2,2'-dichlorodiethyl ether under conditions for which I reacted readily. There was a high recovery of starting material with small amounts of viscous oils being isolated in each instance. The results and the conditions used are given in Table 4.

TABLE 4

REACTION OF DECAPHENYLCYCLOPENTASILANE (II) WITH ORGANIC HALIDES

II (mole)	Solvent (ml)	Halide used	Temp. (°C)	Time (h)	Recovered II (%)
0.011	"Neat" (100)	(CICH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O	170	11	86
0.036	Decalin (80)	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	150–160	24	95
0.0296	Decalin (100)	tert-BuCl	150	22	98
0.066	<i>o</i> -Dichlorobenzene (100)	tert-BuCl	158	70	77 <sup>a</sup>
0.066	Decalin (75)	tert-BuBr	153–166	48	91

<sup>a</sup> An infrared spectrum of vapors in a cold-trap connected to the condenser indicated a small amount of olefin had been formed.

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## REFERENCES

- 1 H. GILMAN AND G. L. SCHWEBKE, *Advan. Organometal. Chem.*, 1 (1964) 89.
- 2 F. S. KIPPING AND J. E. SANDS, *J. Chem. Soc.*, 119 (1921) 830.
- 3 F. S. KIPPING, *J. Chem. Soc.*, 123 (1923) 2590.
- 4 A. W. P. JARVIE, H. J. S. WINKLER, D. J. PETERSON AND H. GILMAN, *J. Amer. Chem. Soc.*, 83 (1961) 1921.
- 5 H. GILMAN AND D. R. CHAPMAN, *J. Organometal. Chem.*, 8 (1967) 451.
- 6 H. GILMAN AND A. W. P. JARVIE, *Chem. Ind. (London)*, (1960) 965.
- 7 H. GILMAN AND W. H. ATWELL, *J. Org. Chem.*, 28 (1963) 2905.
- 8 H. GILMAN AND D. R. CHAPMAN, unpublished studies.
- 9 H. GILMAN AND G. SCHWEBKE, *J. Amer. Chem. Soc.*, 85 (1963) 1016.
- 10 H. J. S. WINKLER, A. W. P. JARVIE, D. J. PETERSON AND H. GILMAN, *J. Amer. Chem. Soc.*, 83 (1961) 4089.
- 11 C. EABORN, *Organosilicon Compounds*, Butterworths, London, 1960, pp. 146–152.
- 12 R. A. BENKESER, W. SCHROEDER AND O. H. THOMAS, *J. Amer. Chem. Soc.*, 806 (1958) 2283.
- 13 (a) G. FRITZ AND D. KUMMER, *Chem. Ber.*, 94 (1961) 1143.  
(b) G. FRITZ AND D. KUMMER, *Z. Anorg. Allg. Chem.*, 308 (1961) 105.

- 14 H. GILMAN AND D. R. CHAPMAN, *Chem. Ind. (London)*, (1965) 1788.
- 15 See ref. 8.
- 16 H. WESTERMARK, *Acta Chem. Scand.*, 8 (1954) 1086.
- 17 H. GILMAN AND W. H. ATWELL, *J. Organometal. Chem.*, 4 (1966) 176.
- 18 H. SAKURAI AND M. KUMADA, *Bull. Chem. Soc. Jap.*, 37 (1964) 1894.
- 19 H. GILMAN AND G. L. SCHWEBKE, *J. Organometal. Chem.*, 3 (1965) 382.
- 20 A. YA. YAKUBOVICH AND G. V. MOTSAREV, *Zh. Obshch. Khim.*, 25 (1955) 1748; *Chem. Abstr.*, 50 (1956) 5550.
- 21 H. GILMAN AND D. R. CHAPMAN, unpublished studies.
- 22 R. WEST, *J. Amer. Chem. Soc.*, 77 (1955) 2339.
- 23 L. H. SOMMER AND G. A. BAUM, *J. Amer. Chem. Soc.*, 76 (1954) 5002.
- 24 L. H. SOMMER, O. F. BENNETT, F. G. CAMPBELL AND D. R. WEYENBERG, *J. Amer. Chem. Soc.*, 79 (1957) 3295.
- 25 H. GILMAN AND W. H. ATWELL, *J. Org. Chem.*, 29 (1964) 237.
- 26 G. FRITZ, H. J. BECKER, E. A. V. EBSWORTH, J. GROBE, W. KEMMERLING AND G. SONTAG, *Z. Anorg. Allg. Chem.*, 321 (1963) 10.
- 27 R. MÜLLER, R. KÖHNE AND H. BEYER, *Chem. Ber.*, 95 (1962) 3030.
- 28 R. MÜLLER AND W. MÜLLER, *Chem. Ber.*, 97 (1964) 1111.
- 29 W. H. KNOTH JR. AND R. V. LINDSAY JR., *J. Org. Chem.*, 23 (1958) 1392.
- 30 H. GILMAN AND W. H. ATWELL, *J. Amer. Chem. Soc.*, 86 (1964) 2687.
- 31 H. J. S. WINKLER AND H. GILMAN, *J. Org. Chem.*, 26 (1961) 1265.
- 32 A. L. SMITH, *Spectrochim. Acta*, 16 (1960) 87.
- 33 H. GILMAN AND F. SCHULZE, *J. Amer. Chem. Soc.*, 47 (1925) 2002.
- 34 H. GILMAN AND K. Y. CHANG, unpublished studies.

*J. Organometal. Chem.*, 14 (1968) 267-277