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SOME DICHLORO COMPOUNDS DERIVED FROM OCTAPHENYLCYCLOTETRASILANE AND DECAPHENYLCYCLOPENTASILANE

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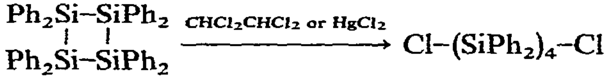
The unusual reactivity of the silicon–silicon bond of organic substituted cyclosilanes such as octaphenylcyclotetrasilane (I), decaphenylcyclopentasilane (II) and dodecamethylcyclohexasilane has provided a means of preparation of a variety of heretofore unavailable polysilanes[1–8,**]. 1,4-Dichlorooctaphenyltetrasilane (III) has been prepared from a variety of reagents. These include organic and inorganic halides of which some typical reactions are illustrated below[9,10].



$Ph_2Si-SiPh_2$ / $Ph_2Si-SiPh_2$ $\xrightarrow{CHCl_2CHCl_2 \text{ or } HgCl_2}$ $Cl-(SiPh_2)_4-Cl$

(I) (III)

This report includes the study of the reaction of (I) and (II) with reagents such as chlorine, phosphorus pentachloride and 1,1,2,2-tetrachloroethane. No previous report on the cleavage of (II) with these reagents has been made.

EXPERIMENTAL

All reactions were carried out in oven-dried glassware under atmospheres of oxygen-free, dry nitrogen. All solvents used were freshly distilled or stored over sodium wire. The temperatures reported are uncorrected. Unless specified, petroleum ether (b.p. 60–70°) was used.

*Octaphenylcyclotetrasilane and phosphorus pentachloride****

To a suspension of 44.0 g (0.06 mole) of (I) in 150 ml of benzene was added 13.6 g (0.065 mole) of phosphorus pentachloride. The mixture was refluxed with stirring for 1 h. The homogeneous reaction mixture was concentrated and petroleum ether added to precipitate the product. Recrystallization from benzene/petroleum ether gave 44.7 g (93%) of 1,4-dichlorooctaphenyltetrasilane, m.p. and mixture m.p. 186–187°

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** For a review of work prior to 1963 see ref. 1.

*** Procedure by W. H. Atwell[11].

A second reaction was made using 10.0 g (0.013 mole) of (I), 90 ml of xylene and 3.13 g (0.015 mole) of phosphorus pentachloride. The mixture was refluxed for 2 h and then cooled and filtered. The filtrate was distilled to yield 1.0 ml of phosphorus trichloride, b. range 76–80°, n_D^{20} 1.5077 (ref. sample 1.5138). An infrared spectrum of the distillate was superimposable with the spectrum of a freshly distilled sample of phosphorus trichloride. Work-up gave 1.7 g (17 %) of recovered (I), m. range 315–320° and 8.2 g (73.5 %) of 1,4-dichlorooctaphenyltetrasilane, m.p. 185–187°.

Octaphenylcyclotetrasilane with phosphorus trichloride (attempted)

Phosphorus trichloride, 2.1 g (0.015 mole), (I), 10.0 g (0.013 mole) and 90 ml of xylene were refluxed for 2 h. Upon filtering, 9.85 g (98.5 %) of the starting material was recovered, m.p. 318–322°.

Decaphenylcyclopentasilane and phosphorus pentachloride

(*a*) *In 1,1,2,2-tetrachloroethane.* Decaphenylcyclopentasilane, 20.0 g (0.022 mole), and phosphorus pentachloride, 5.0 g (0.024 mole), were added to 100 ml of 1,1,2,2-tetrachloroethane. The suspension, soluble at 80°, was refluxed for 15 min. The solvent (b.p. 65–70°/20 mm) was then removed by distillation under reduced pressure with a steam bath. The residue, dissolved in 200 ml of benzene, was poured into 200 ml of rapidly stirred petroleum ether. After stirring for 1 h, 18.6 g (86 %) of solid, m.p. 180–182°, was precipitated. Concentration of the filtrate gave no additional solids. Recrystallization gave a constant m.p. 180–181°. An infrared spectrum using KBr cells and carbon disulfide as solvent showed an Si–Cl absorption at 519 and 550 cm^{-1}. (Found: Si, 14.40, 14.37. $C_{60}H_{50}Cl_2Si_5$ calcd.: Si, 14.30 %.)

(*b*) *In carbon tetrachloride.* (II), 10.0 g (0.011 mole), phosphorus pentachloride, 4.2 g (0.02 mole), and carbon tetrachloride, 100 ml, were refluxed together for 5 h. Work-up as above gave 7.3 g (73 %) of starting material, m. range and mixture m. range 454–464°, and 2.5 g (23 %) of 1,5-dichlorodecaphenylpentasilane, m.p. and mixture m.p. 178–180°.

(*c*) *In benzene and xylene with a 2 mole excess of phosphorus pentachloride (attempted).* (II), 10.0 g (0.011 mole), phosphorus pentachloride, 4.2 g (0.022 mole), and 150 ml of benzene were refluxed together for 2.5 h. Work-up as above gave 9.6 g (96 %) of recovered (II), m. range and mixture m. range 456–464°.

A duplicate reaction using xylene as solvent was made with a reaction time of 5 h at 138°. A quantitative recovery of the starting material was made.

(*d*) *In benzene with a 5 mole excess of phosphorus pentachloride.* (II), 5.0 g (0.0069 mole), phosphorus pentachloride, 7.1 g (0.034 mole), and 100 ml of benzene were refluxed together for 16 h with stirring. Work-up as above gave 1.7 g (34 %) of crude (II), m. range 380–420°, and 2.5 g (68 %) of 1,5-dichlorodecaphenylpentasilane, m.p. and mixture m.p. 180–182°.

Decaphenylcyclopentasilane and 1,1,2,2-tetrachloroethane

Compound (II), 20.0 g (0.022 mole), in 1,1,2,2-tetrachloroethane was heated at 140° for 50 h. Work-up gave 15.2 g (70.5 %) of 1,5-dichlorodecaphenylpentasilane, m.p. and mixture m.p. 179–180°. Small amounts of lower melting solid were not identified. A similar reaction heated at reflux temperature for 36 h gave 2.7 g (13.5 %) of recovered (II) and 13.6 (63 %) of the 1,5-dichloro compound.

Decaphenylcyclopentasilane and chlorine

A series of reactions was made in which decaphenylcyclopentasilane, 10.0 g (0.011 mole), was dissolved in 100 ml of benzene, carbon tetrachloride or diethyl ether. Chlorine gas was then introduced into the rapidly stirred solution through a sintered glass gas diffusion tube at a constant rate (approximately 200 ml/min) for a specified time. The reaction was then quenched by the rapid removal of excess chlorine under reduced pressure. The products were isolated by fractional crystallization from benzene/petroleum ether mixtures.

The chlorine was metered by passing it through a 1 mm capillary 3 cm long. The pressure drop across this orifice was measured with a manometer filled with carbon tetrachloride. The calibration was based on the water displacement of air in an inverted 500 ml graduate. Excess chlorine was exhausted, via the condenser, into a hood at atmospheric pressure.

A typical example using benzene as solvent involved the addition of chlorine at 200 ml/min for 15 min. The excess chlorine and all but 30–35 ml of the solvent was then quickly removed with the use of a water aspirator and steam bath. The mixture was then added to 400 ml of petroleum ether stirred for 1 h and filtered. 1,5-Dichlorodecaphenylpentasilane, 3.5 g (30%), was obtained, m.p. and mixture m.p. 178–179°. Evaporation of the filtrate to 20 ml and addition of 50 ml of petroleum ether gave 2.0 g (29%) of solid, m. range 125–130°. Recrystallization gave a m.p. and mixture m.p. of 126–128° with 1,3-dichlorohexaphenyltrisilane. The filtrate was then evaporated to dryness and 25–30 ml of petroleum ether added hot. Upon standing overnight, 1.0 g (19%) of material, m. range 115–120°, was obtained. Recrystallization gave a constant m.p. of 116–117° which was not depressed upon admixture with

TABLE 1

REACTION OF DECAPHENYLCYCLOPENTASILANE WITH CHLORINE

Solvent	*Time* (*min*)	*Temp.* (°C)	*Starting material*	*Dichloro derivatives* (%)[a,b]		
				1,5-	1.3-	1,2-
benzene	10	18–20[c]	32%	61	0	0
benzene	15	18–20[c]	trace	76	0	0
benzene[d]	30	18–20[c]	0	33	0	10
benzene	60	18–20[c]	0	0	0	0
benzene	5	25–39	30	55	0	0
benzene	8	25–39	trace	78	0	0
benzene	10	25–44	0	53	0	0
benzene	15	25–46	0	30	30	19
benzene	20	25–46	0	trace	33	29
benzene	5	76–80	25	68	0	0
CCl_4	10	18–19[c]	73	70	0	0
CCl_4	30	21–25[c]	8.5	50	0	0
CCl_4	60[e]	25–35	0	0	trace	75
CCl_4	240	25–35	0	0	0	0
Et_2O[f]	60	18–22[c]	86	11	0	0

[a] Based on unrecovered starting material. [b] The remainder of the reaction residue was an unidentified viscous oil. [c] The temperature was regulated with a cooling bath. [d] With reactions over 20 min, mixtures of hexachlorocyclohexane isomers were isolated when using benzene. [e] The chlorine gas flow rate was not constant. [f] Diethyl ether.

1,2-dichlorotetraphenyldisilane. The results of this series of reactions are summarized in Table 1.

Octaphenylcyclotetrasilane and chlorine

A series of reactions was completed in the same manner as described with decaphenylcyclopentasilane using 10.0 g (0.014 mole) of octaphenylcyclotetrasilane and 100 ml of carbon tetrachloride, diethyl ether, petroleum ether or n-pentane with the addition of chlorine at approximately 200 ml/min for a specified time. The results are summarized in Table 2.

TABLE 2

REACTION OF OCTAPHENYLCYCLOTETRASILANE WITH CHLORINE

Solvent	*Time* (*min*)	*Temp.*[a] (°C)	*Dichloro derivatives* (%)[b,c]	
			1,4-	1,2-
CCl_4	2.5	20–29	96.7	0
CCl_4	5	25–33	89	1.7
CCl_4	10	24–31	85	8.5
CCl_4	15	25–35	71.6	25.4
CCl_4	20	25–30	56.6	33
CCl_4	30	25–30	30.6	37
CCl_4	40	28–30	0	34
CCl_4	70	26–36	0	43
Et_2O[d]	10	18–22	97.4	0
Et_2O[d]	60	18–22	98.4	0
Pet Et[e]	15	15–25	100	0
C_5H_{12}[f]	13	15–25	97.3	0

[a] Temperature control was maintained with an ice bath. [b] Based on unrecovered starting material. [c] The remainder of the reaction residue was an unidentified viscous oil. [d] Diethyl ether. [e] Petroleum ether. [f] n-Pentane.

In ether containing hydroquinone. Chlorine gas was added at approximately 200 ml/min for 3 min (0.6 l; 0.025 mole) to 5.0 g (0.007 mole) of (I) in 80 ml of diethyl ether containing 1.0 g (0.009 mole) of hydroquinone, m.p. 175–177°. The temperature was kept at 15–17° with an ice-bath. Work-up gave 4.6 g (92%) of recovered (I), 0.3 g (5.5%) of 1,4-dichlorooctaphenyltetrasilane and 0.3 g (30%) of hydroquinone all identified by mixture m.p.

Derivatives of 1,5-*dichlorodecaphenylpentasilane*

(*a*) *Decaphenylpentasilane*-1,5-*diol.* To a mixture of 75 ml of tetrahydrofuran and 20 ml of 0.1 *N* hydrochloric acid, 5.0 g (0.005 mole) of 1,5-dichlorodecaphenylpentasilane was allowed to stand two days. Removal of the liquids under reduced pressure and recrystallization of the residue in benzene/petroleum ether gave 5.0 g of crude solids, m. range 169–176°. Recrystallization gave 2.5 g (51%) of pure decaphenylpentasilane-1,5-diol, m.p. and mixture m.p. 174–176°.

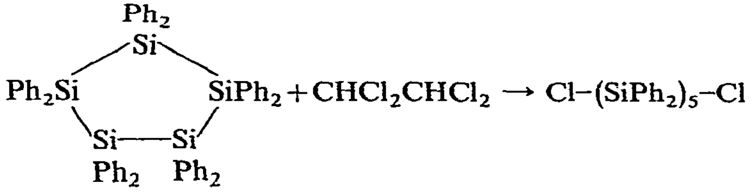
(*b*) 1,5-*Di-n-propoxydecaphenylpentasilane.* n-Propanol, 100 ml and 1,5-dichlorodecaphenylpentasilane, 3.0 g (0.003 mole), were heated together for *ca.* 4 h. The reaction was then cooled and filtered to give 2.8 g (91%) of crude products, m.p.

190–192°. Recrystallization from benzene gave 1.6 g (52.5%) of pure material, m.p. 196–197°.

An NMR spectrum of the product showed a triplet centered at 9.41 τ, a quartet centered at 8.82 τ and a triplet centered at 6.89 τ indicative of the methyl, methylene and methylene adjacent to oxygen protons, respectively. The aryl multiplet was centered at 3.13 τ. An average (3 determinations) aryl to aliphatic proton ratio of 49.9 : 14 was found (calcd. ratio: 50 : 14). (Found: Si, 13.71, 13.61, 13.62. $C_{66}H_{64}O_2Si_5$ calcd.: Si, 13.64%.)

RESULTS AND DISCUSSION

Kipping, who was the first to synthesize compounds (I) and (II), prepared (III) from the reaction of (I) and 1,1,2,2-tetrachloroethane[9], but reported that no reaction occurred with (II) in refluxing 1,1,2,2-tetrachloroethane[12]. We have found, however, that (II) does slowly react with this reagent and does provide good yields of (IV) after prolonged refluxing.



(II) (IV)

Phosphorus pentachloride reacts rapidly with (I) in refluxing benzene or xylene to provide good yields of (III)[11]. Phosphorus trichloride was obtained from the reaction of (I) with phosphorus pentachloride. Phosphorus trichloride does not react with (I) after 24 h at 80° using benzene as the solvent.

$$(I) + PCl_5 \rightarrow (III) + PCl_3$$

$$(I) + PCl_3 \rightarrow \text{No reaction}$$

We have found that (IV) can also be prepared by the cleavage of (II) with phosphorus pentachloride in good yields. However, the reaction is dependent upon the solvent used, the temperature and the reaction time. The cyclopentasilane (II) did not react with phosphorus pentachloride in refluxing benzene or xylene unless a large excess of the chlorinating agent was used. With the use of carbon tetrachloride or 1,1,2,2-tetrachloroethane as solvent, phosphorus pentachloride gave (IV) in yields of 23% and 86%, respectively, on a 1 : 1.1 molar ratio of reactants. The influence of solvent, time and temperature on the reaction of (II) with phosphorus pentachloride is summarized in Table 3.

No reaction occurred with (II) and 1,1,2,2-tetrachloroethane or with (II) and phosphorus trichloride in 1,1,2,2-tetrachloroethane after 1 h at 140°. Therefore, it is believed that the choice of 1,1,2,2-tetrachloroethane as solvent may be due to the increased solubility of chlorine in this solvent. The reaction probably proceeds via the dissociation of phosphorus pentachloride to form phosphorus trichloride and chlorine with subsequent attack of the cyclosilane by chlorine. The greater reactivity

TABLE 3

REACTION OF DECAPHENYLCYCLOPENTASILANE WITH PHOSPHORUS PENTACHLORIDE

Mole ratio	*Solvent*	*Time (h)*	*Temp. (°C)*	*Products*		
				(II)[a]	*(IV)*	*Others*[b,c]
1:2	benzene	2.5	80	92%	0%	0%
1:5	benzene	16	80	34	46	0
1:1.1	xylene	8	138	96	0	0
1:2	CCl_4	5	78	73	23	0
1:1.1	CCl_4	24	78	78	13	trace
1:1.1	$C_2H_2Cl_4$[d]	0.1	142	10	69	trace
1:1.1	$C_2H_2Cl_4$	0.25	142	0	86	trace
1:1.1	$C_2H_2Cl_4$	2	142	0	50	13
1:1.1	$C_2H_2Cl_4$	24	142	0	30	15

[a] Starting material. [b] Low melting solids, m. range 150–165°. [c] The remainder of the reaction residue consisted of an unidentified viscous oil. [d] 1,1,2,2-Tetrachloroethane.

of the cyclotetrasilane enables it to react rapidly with phosphorus pentachloride in benzene. The cyclopentasilane reacts so slowly in this solvent or at this temperature, 80°, that the chlorine is lost to the atmosphere before reaction takes place.

This large difference in the reactivity of the two cyclosilanes is attributed to a higher ground state energy of the four-membered ring, due to ring strain, and a lower transition state energy due to the geometry of the four-membered ring. An attacking species is able to form a pentacovalent addition complex with the four-membered ring resulting in less angular motion in going from a strained tetrahedral sp^3 hybrid to an essentially less strained trigonal bipyramid dsp^3 hybrid[1,13].

Compound (I) has been cleaved with iodine and bromine[9,14] and (II) with the latter reagent[3,9] to provide good yields of the corresponding α,ω-dihalopolydiphenylsilanes. No work has been previously reported on the reaction of compounds (I) and (II) with chlorine.

The reaction of (I) and (II) with chlorine is an interesting and useful reaction for the preparation of (III) and (IV) and for other shorter chain α,ω-dichloropolydiphenylsilanes as well. When (I) is suspended in diethyl ether, petroleum ether or n-pentane and chlorine is added the only reaction which takes place is cleavage of the silicon–silicon bond of the cyclosilane and quantitative yields of (III) are obtained. With the use of benzene or carbon tetrachloride as solvent the reaction of (I) with chlorine was also found to be very fast but further cleavage of the silicon chain was observed. However, initial ring-opening of the cyclosilane (I) proceeds at a much faster rate than cleavage of the resulting linear polysilanes and good product control was obtained by the addition of chlorine at a constant rate for a specified time. A series of reactions was made using a variety of solvents with varying quantities of chlorine being added. The results are given in Table 2.

$$\text{(I)} + Cl_2 \rightarrow \text{(III)} + Cl\text{–}(SiPh_2)_2\text{–}Cl$$

A possible indication that the reaction may follow a free radical mechanism was noted in that essentially no reaction occurred with (I) and chlorine in ether containing hydroquinone. Attempts to exclude light from the reaction appeared to have no effect. However, another interesting observation was made upon the addition of chlorine above the liquid surface in the reaction of chlorine with dodecamethylcyclohexasilane[15]. Small bursts of light were sometimes seen to be emitted from the surface inside the reaction vessel. Admission of chlorine below the liquid level eliminated this potentially dangerous exhibition.

Consistent with its lower reactivity, addition of chlorine to decaphenylcyclopentasilane is much slower than with the cyclotetrasilane. This was particularly noted using diethyl ether as solvent. Using benzene or carbon tetrachloride as solvents in the reaction of (II) and chlorine, a mixture of (IV), 1,3-dichlorohexaphenyltrisilane and 1,2-dichlorotetraphenyldisilane is obtained.

$$\text{(II)} + Cl_2 \rightarrow \text{(IV)} + Cl\text{–}(SiPh_2)_{2,3}\text{–}Cl$$

Careful control of the reaction time and temperature and with constant addition of the chlorine gas the desired product can be obtained as the major component. The results of a series of reactions with (II) and chlorine are found in Table 1.

It appears that cleavage of the silicon chain, subsequent to initial ring-opening, always occurs between the second and third silicon atoms. Thus addition of chlorine to (I) gave no 1,3-dichlorohexaphenyltrisilane, and addition of chlorine to (II) gave no 1,4-dichlorooctaphenyltetrasilane. Prolonged addition of chlorine to (I) or (II) in carbon tetrachloride yielded only trace amounts of dichlorodiphenylsilane and an unidentified clear viscous resin.

Infrared spectral studies in the 400–700 cm^{-1} region show that the introduction of two or more chlorine atoms into an organic substituted silane causes absorption of the silicon–chlorine bond to vary in a regular manner[16]. Our studies on the preparation of compounds in the series $Cl\text{–}(SiPh_2)_n\text{–}Cl$, where n equals 2 to 5, gave us the opportunity of studying the silicon–chlorine bond absorptions of α,ω-dichloropolydiphenylsilanes of increasing chain length. The observed absorptions are recorded in Table 4. Also included are the silicon–chlorine absorptions of 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane[8]. As a help in assigning the silicon–chlorine absorptions, a spectrum of 1,1,2,2,3,3,4,4-octaphenyltetrasilane was found to contain no absorptions in the assigned regions.

TABLE 4

SILICON–CHLORINE INFRARED ABSORPTIONS OF α,ω-DISUBSTITUTED POLYDIPHENYLSILANES[a]

Compound	*Characteristic band position (cm^{-1})*
$Cl\text{–}SiPh_2\text{–}Cl$	540, 577
$Cl\text{–}(SiPh_2)_2\text{–}Cl$	531, 584
$Cl\text{–}(SiPh_2)_3\text{–}Cl$	524, 560
$Cl\text{–}(SiPh_2)_4\text{–}Cl$	520, 544, 561
$Cl\text{–}(SiPh_2)_5\text{–}Cl$	519, 527 (shoulder), 550
$H\text{–}(SiPh_2)_4\text{–}Cl$	520, 560

[a] Infrared spectra were made with a Beckman IR-7 Spectrometer with sodium chloride optics using KBr cells with carbon disulfide as solvent.

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SUMMARY

A study of the preparation of α,ω-dichloropolydiphenylsilanes from octaphenylcyclotetrasilane (I) and decaphenylcyclopentasilane (II) with chlorinating reagents such as 1,1,2,2-tetrachloroethane, phosphorus pentachloride and chlorine is discussed. The study has led to the preparation of compounds of the general formula $Cl-(SiPh_2)_n-Cl$, where n equals 2 to 5. The conditions for the addition of chlorine to (I) and (II) with or without silicon–silicon cleavage of the polysilane after initial ring-opening are described. Some derivatives are described, and infrared absorptions are presented.

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