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DIFUNCTIONAL DERIVATIVES OF HEXAPHENYLDISILOXANE

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Summary

Difunctional organosiloxane derivatives containing only aromatic substitution on silicon were prepared and characterized. The series include compounds with the structure, $O[Si(C_6H_5)_2C_6H_4X]_2$, where X is *p*-Cl, *p*-Br, *p*-CH_3, *m*-CH_3, *p*-CO_2H, *p*-COCl, *p*-$CO_2C_6H_5$, *m*-$CO_2C_6H_5$, *p*-$CO_2C_6Cl_5$, *m*-$CO_2C_6Cl_5$, *p*-CN, *p*-$CONH_2$, *p*-NH_2, and *m*-NH_2 as well as various intermediates in their preparation.

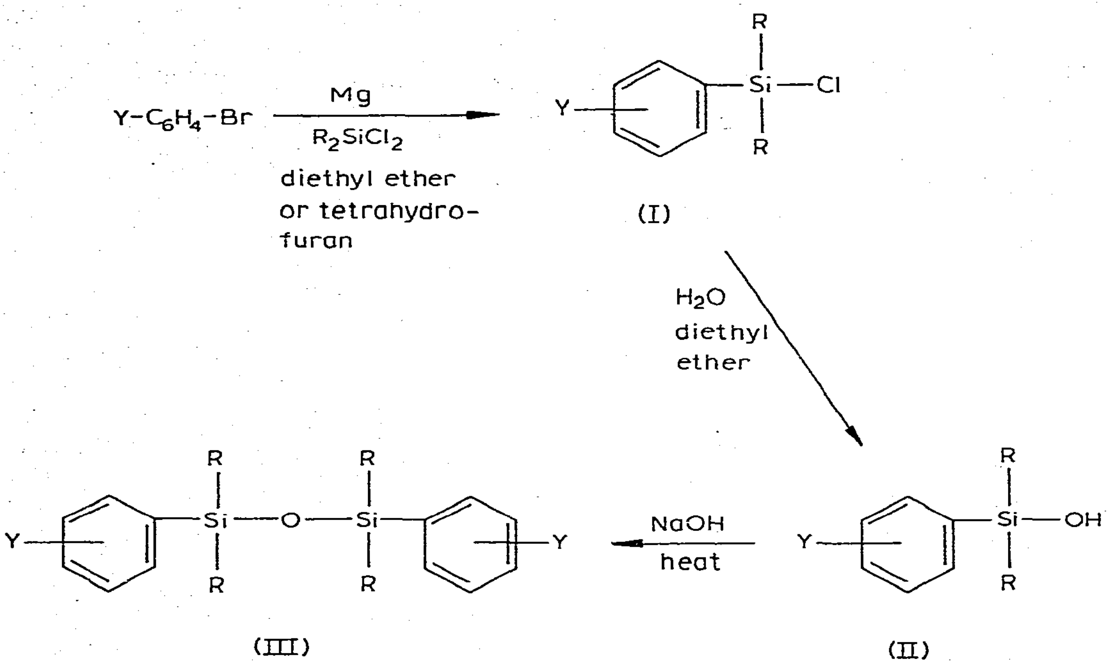
Introduction

Only a few examples of the synthesis of difunctional derivatives of wholly aromatic silicon compounds capable of undergoing chemical conversion to other derivatives are reported in the literature. These reports include the synthesis of bis(*p*-hydroxyphenyl)diphenylsilane [1]. Some silane and disiloxane derivatives with multiple *p*-chlorophenyl substitution [2]; bis-(*p*-carboxyphenyl)-diphenylsilane, its acid chloride, hydrazine, and esters [3-5]; bis-(*p*-carboxyphenyl)diphenylsilane, di-*p*-tolyldiphenylsilane, and 1,3-di-*p*-tolyltetraphenyldisiloxane [6]; and the bis(trimethylsilyl) derivative of di(*p*-anilino)diphenylsilane [7]. This study, which was concerned with the synthesis of some difunctional derivatives of hexaphenyldisiloxane, provided information on the preparation and properties of a number of new compounds in the series, as well as their intermediates.

Results

Chloro-*p*-chlorophenyldiphenylsilane (Ia), *p*-bromophenylchlorodiphenylsilane (Ib), chlorodiphenyl-*p*-tolylsilane (Ic), and chlorodiphenyl-*m*-tolylsilane (Id), which were prepared by the Grignard method, were hydrolyzed with moist ether to *p*-chlorophenyldiphenylsilanol (IIa), *p*-bromophenyldiphenylsilanol (IIb), diphenyl-*p*-tolylsilanol (IIc), and diphenyl-*m*-tolylsilanol (IId), respectively. Base catalyzed dehydration of the silanols afforded 1,3-bis(*p*-chlorophenyl)tetraphenyldisiloxane (IIIa), 1,3-bis(*p*-bromophenyl)tetraphenyldisiloxane (IIIb), tetraphenyl-1,3-di-*p*-tolyldisiloxane (IIIc), and tetraphenyl-1,3-di-*m*-tolyldisiloxane (IIId).

SCHEME 1



a, Y = *p*-Cl ; b, Y = *p*-Br ; c, Y = *p*-CH_3 ; d, Y = *m*-CH_3

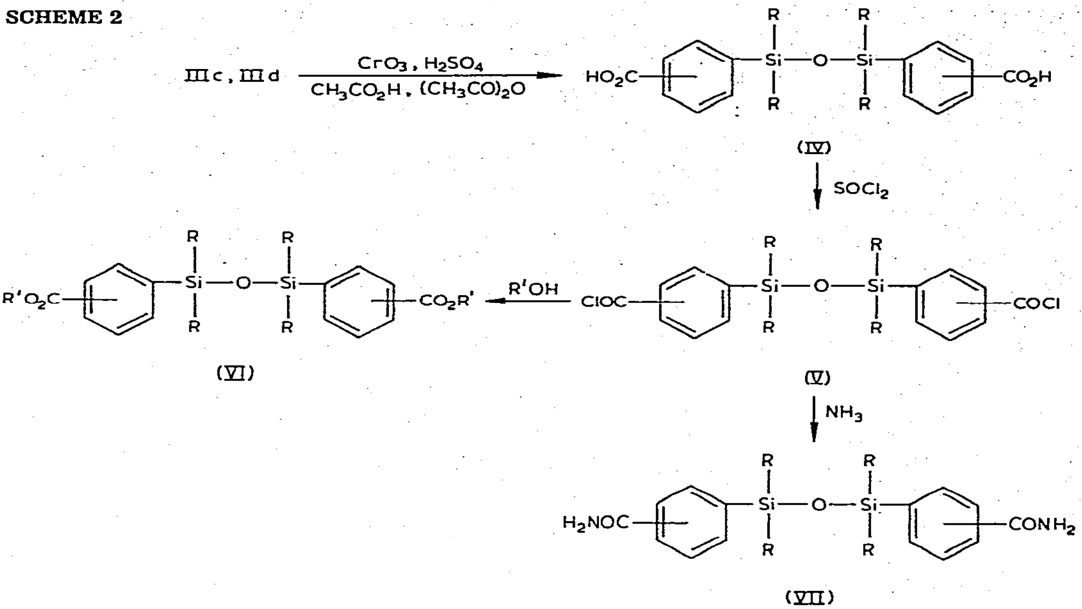
R = C_6H_5 throughout

Compounds IIIc and IIId were oxidized with chromic acid to 4,4′-(1,1,3,3-tetraphenyldisiloxanylene)dibenzoic acid (IVa) and 3,3′-(1,1,3,3-tetraphenyldisiloxanylene)dibenzoic acid (IVb). Acid chlorides were prepared with thionyl chloride (only 4,4′-(1,1,3,3-tetraphenyldisiloxanylene)dibenzoyl chloride (Va) was isolated) and converted with phenol or pentachlorophenol to diphenyl 4,4′-(1,1,3,3-tetraphenyldisiloxanylene)dibenzoate (VIa), diphenyl 3,3′-(1,1,3,3-tetraphenyldisiloxanylene)dibenzoate (VIb), bis(pentachlorophenyl 4,4′-(1,1,3,3-tetraphenyldisiloxanylene)dibenzoate (VIc), and bis(pentachlorophenyl) 3,3′-(1,1,3,3-tetraphenyldisiloxanylene)dibenzoate (VId). Treatment of the acid chloride (Va) with ammonia gave 4,4′-(1,1,3,3-tetraphenyldisiloxanylene)dibenzamide (VII). 4,4′-(1,1,3,3-Tetraphenyldisiloxanylene)dibenzonitrile (VIII) was obtained directly from IIIb and cuprous chloride in dimethylacetamide.

Minimal quantities of aniline derivatives were obtained from *N*,*N*-bis(trimethylsilyl)-*p*-bromoaniline (IXa) and *N*,*N*-bis(trimethylsilyl)-*m*-bromoaniline (IXb). Treatment of the Grignard reagent of these compounds with dichlorodiphenylsilane and subsequent cleavage of the trimethylsilyl blocking groups with methanol afforded 4,4′-(1,1,3,3-tetraphenyldisiloxanylene)dianiline (Xa)

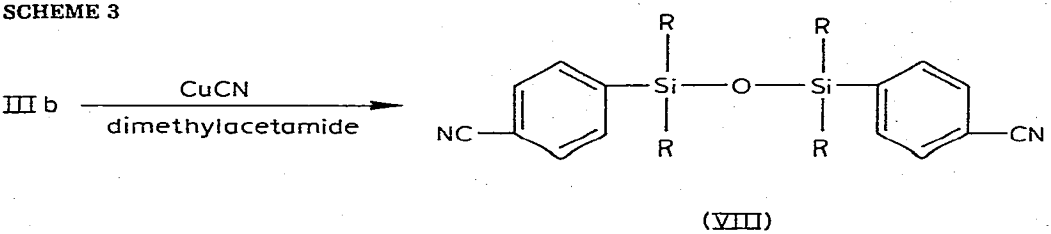
(continued on p. 33)

SCHEME 2

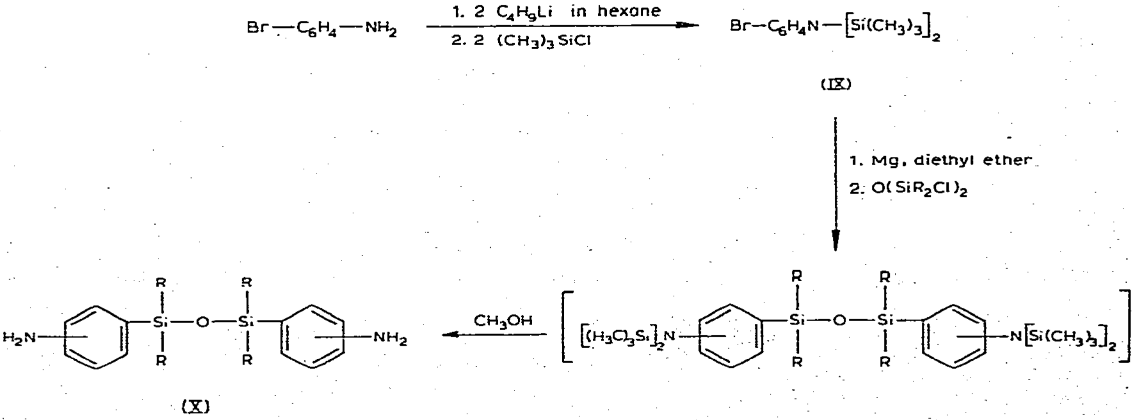


a, *p*-CO_2H , *p*-CO_2Cl , *p*-$CO_2C_6H_5$, *p*-CO_2NH_2 ; b, *m*-CO_2H , *m*-$CO_2C_6H_5$; c, *p*-$CO_2C_6Cl_5$; d, *m*-$CO_2C_6Cl_5$

SCHEME 3



SCHEME 4



a, *p*-N-$[Si(CH_3)_3]_2$, *p*-NH_2
b, *m* -N-$[Si(CH_3)_3]_2$, *m*-NH_2

TABLE 1

PHYSICAL PROPERTIES AND ANALYSES

Compound No.	M.p. (°C)	B.p. [°C/mm Hg]	Yield (%)	Analyses Found (Calcd.) (%)					
				C	H	Cl	Br	N	Si
Ia[a]	68-69	174/0.2	39						
Ib		198-200/0.5	23[b]	58.06	4.05	9.67	21.51		7.27
			55[c]	(57.84)	(3.78)	(9.49)	(21.38)		(7.52)
Ic[d]	66-70	178-180/0.4	77	73.23	5.61	11.65			9.38
				(73.88)	(5.55)	(11.48)			(9.09)
Id[e]	36-39	178-179[f]/0.4	62						
IIa	75-77		81	69.65	4.81	11.83			9.34
				(69.54)	(4.86)	(11.41)			(9.04)
IIb	87-89		72	60.92	4.23		22.16		7.97
				(60.84)	(4.26)		(22.49)		(7.91)
IIc[g]	93-94		92						
IId	91-92		88	78.08	6.70				9.75
				(78.57)	(6.25)				(9.67)
IIIa	195-196		75	71.81	4.74	11.90			9.63
				(71.62)	(4.67)	(11.75)			(9.31)
IIIb	191-192		67	62.20	4.25		23.30		8.09
				(62.43)	(4.07)		(23.07)		(8.11)
IIIc[h]	161-162		94						
IIId	183-184		91	81.17	6.26				10.03
				(81.09)	(6.09)				(9.98)
IVa	240-241		84[i]	73.22	5.09				11.08[j]
				72.59	4.57				9.48[k]
				(73.28)	(4.86)				(9.02)
IVb	236-241		67[l]	73.05	4.91				9.37[j]
				72.49	4.65				9.36[k]
				(73.28)	(4.86)				(9.02)
Va	190-191		55[m]	69.92	4.24	11.31			9.20
				(69.18)	(4.28)	(10.75)			(8.52)
VIa	162-163		88[n,o]	77.03	4.98				7.20
				(77.49)	(4.94)				(7.25)
VIb	148-149		90[p,o]	77.27	4.91				7.44
				(77.49)	(4.94)				(7.25)
VIc	268-269		91[q]	53.87	2.58	30.45			4.86
				(53.64)	(2.52)	(31.67)			(5.02)
VId	248			54.45	2.75	29.82			4.80
				(53.64)	(2.52)	(31.67)			(5.02)
VIIa	272-274		86[r]	73.21	5.47			4.51	9.08
				(73.51)	(5.20)			(4.51)	(9.05)
VIII	229-230		71	78.54	4.93			4.49	9.25
				(78.04)	(4.83)			(4.79)	(9.61)
IXa[s]		102-104[t]/1	89	45.77	6.79		25.23	4.46	17.58
				(45.55)	(7.01)		(25.26)	(4.43)	(17.76)
IXb[u]		106/1	94						
Xa	207-209		5	76.49	5.81			4.95	9.93
				(76.55)	(5.71)			(4.96)	(9.95)

continued

TABLE 1 (continued)

Compound No.	M.p. (°C)	B.p. [°C/mm Hg]	Yield (%)	Analyses Found (Calcd.) (%)					
				C	H	Cl	Br	N	Si
Xb	259-261		3	76.69 (76.55)	5.48 (5.71)			5.03 (4.96)	9.89 (9.95)
XI[v]	39-40	198-200/0.01	57						
XII[w]	173-174		67						
XIII	170-174		29	82.49 (82.00)	5.69 (6.02)			3.86 (3.98)	7.76 (8.00)

[a] Lit. [8] b.p. 149-150°C/0.3 mm Hg. [b] From the Grignard reagent. [c] From the organolithium reagent. [d] Lit. [8] b.p. 147-148°C/0.2 mm Hg. [e] Lit. [8] b.p. 150-151°C/0.5 mm Hg. [f] n_D^{25} 1.6120. [g] Lit. [6] m.p. 94-95°C. [h] Lit.[6] m.p. 156-158°C. [i] Impure, m.p. 233-235°C and 237-239°C. [j] Toluene insoluble. [k] Toluene soluble. [l] Impure, including some material, m.p. 233-237°C. [m] Impure, m.p. 176-185°C. [n] Impure, m.p. 146-150°C. [o] From the acid. [p] Impure, m.p. 145-146°C. [q] Impure, m.p. 247-250°C. [r] Impure, m.p. 264-267°C. [s] Lit. [9] b.p. 106°C/1 mm Hg, n_D^{25} 1.5140. [t] n_D^{25} 1.5140. [u] Identified by infrared analysis [v] Lit. [10] b.p. 238-241°C/1 mm Hg, m.p. 38°C. [w] Lit. [11] m.p. 167-168°C.

and 3,3'-(1,1,3,3-tetraphenyldisiloxanylene)dianiline (Xb).
In an attempt to prepare X by an alternate procedure, compound VII was recovered quantitatively when it was treated with sodium hypochlorite solution at 80°C.

The properties of these compounds and certain intermediates, the yields in their preparation, and elemental analyses to verify their structure are summarized in Table 1.

Discussion

On the basis of the literature for the preparation of various derivatives of 1,3-diphenyltetramethyldisiloxane, the preferred method for synthesis of the hexaphenyldisiloxane derivatives appeared to be the condensation of various organolithium or Grignard intermediates with 1,3-dichlorotetraphenyldisiloxane (XI). Among other reagents, *N,N*-bis(trimethylsilyl)-*p*-anilinolithium [12] and *p*-bromophenyllithium [13] are reported to condense smoothly with 1,3-dichlorotetramethyldisiloxane at low temperature and provide good conversions to the condensation products. All attempts to condense these same reagents under the same conditions with XI gave oils which could not be further purified. Gilman has observed that aryllithium reagents cleave phenyl-substituted silicon—oxygen bonds more readily than methyl-substituted groups and explains that the nucleophilic attack takes place more readily at the silicon atom which is less electronegative [14]. Silicon—oxygen cleavage in the structure sequence Cl—Si-$(C_6H_5)_2$—O— must indeed have been a factor in the failure to obtain the hexaphenyldisiloxane derivatives since *p*-bromophenyltriphenylsilane (XII) and *p*-anilinotriphenylsilane (XIII) were readily obtained when the same reagents were condensed with chlorotriphenylsilane. Very small quantities of IIIb, Xa, and Xb were obtained when the Grignard reagents of *p*-dibromobenzene, IXa, and IXb in tetrahydrofuran were condensed with XI. The yields in these condensations were so low that the methods are of no preparative value.

The first approach failing, the sequence described in Scheme 1 was followed. The Grignard method proved satisfactory for Ia, Ic, and Id, but provided only low yields of (23%) Ib, either in diethyl ether or tetrahydrofuran. Condensation of *p*-bromophenyllithium with dichlorodiphenylsilane increased the yield of Ib to 55%.

The chlorotriarylsilanes were hydrolyzed in ether with water in high yield. It was essential that these silanols be purified by recrystallization before proceeding to dehydration to the silanols for two reasons: Impurities, particularly in IIb, if not removed before that dehydration to the siloxane, were extremely difficult to separate from the siloxane; last traces of silyl chlorides are difficult to hydrolyze in chlorotriarylsilanes, and it these acidic impurities were not removed or neutralized, disproportionation rather than dehydration occurred when the silanols were treated thermally to obtain siloxanes. In practice, the latter conversion was accomplished by establishing the stoichiometry on a small scale prior to large scale dehydration. Small quantities of the recrystallized silanols were treated with various concentrations of sodium hydroxide and the mixtures were heated under conditions of differential thermal analysis to determine the proper ratio of reactants that would insure dehydration rather than disproportionation. Silanol IIb proved to be the most difficult to purify since crystallization occurred from oils rather than from solution.

The oxidation and esterification procedures emphasize the stability of the silicon—phenyl and silicon—oxygen linkages in these compounds against certain acidic reagents. Both procedures had been used previously for the preparation of 4,4′-(tetramethyldisiloxanylene)dibenzoic acid [15] and its phenyl ester [16]. An alternate procedure for the preparation of the acid, carbonation of the organolithium derivative of IIIb, afforded only 44% of the unpurified acid, thus proving to be a less advantageous approach to this compound.

Two forms of the acid IVa could be separated on the basis of the difference in their solubility in toluene. The less soluble form converted to the more soluble form at 140°C with a mild exotherm. A similar change took place when the sodium salt of the more soluble form was acidified and the free acid precipitated. The reverse conversion could be accomplished by heating the acid in polyphosphoric acid at 120°C and precipitating it with water. The two forms were differentiated by their infrared spectra which were identical except for a strong band at 1055 cm^{-1} in the more soluble form that shifted to 1110 cm^{-1} in the less soluble form. These bands were too strong and broad to be characteristic of the aromatic in plane hydrogen rocking vibrations usually found in this region. Although no assignment was made for this band, a similar band is present in a number of *ortho* substituted aromatic polycarboxylic acids, including phthalic acid, trimellitic acid, and prehnitic acid, and no similar band in acids in which carboxy groups cannot interact through internal hydrogen bonding, such as isophthalic acid, 4,4′-(dimethylsilylene)dibenzoic acid, terephthalic acid, or *p*-triphenylsilylbenzoic acid.

The difference between these two forms is not clearly understood. Clathrate formation is unlikely since thermal conversion occurs above the boiling point of toluene. The difference may reflect the mode of aggregation of the hydrogen-bonded difunctional carboxylic acid and possible intramolecular interactions. It is also possible that the two compounds may be rotational isomers which exist as a consequence of restricted rotation about the siloxane bond. Such isomers of tetraphenyldisiloxanediols have been studied [17].

Infrared spectra

The Si_2O asymmetric stretch frequency was observed as a strong, sharp band with little variation in frequency (1090-1105 cm^{-1}) from the same absorption band in hexaphenyldisiloxane. The sharpness of these bands contrasts with the broad bands reported for derivatives of tetramethyldiphenyldisiloxane [13], but can perhaps be accounted for in that all data obtained in this work was for compounds in the solid state, whereas the other work was concerned chiefly with liquids. Compound XI, dichlorotetraphenyldisiloxane, which melts at 40°C, absorbs sharply at 1110 cm^{-1} as a solid, but shows a much broader absorption centered at 1080 cm^{-1} as a melt.

Two frequencies that were particularly useful in the characterization of the *p*-halophenyl derivatives were the in-plane hydrogen bending in the benzene ring at about 1020 cm^{-1} and the C_6H_4—X stretch at 1070-1090 cm^{-1}. Both were strong sharp bands. The former, which is customarily a rather weak absorption, and was so observed in other compounds in this series, was considerably strengthened with halogen substitution.

With few exceptions, little unusual was observed for other characteristic absorptions: the C=O stretch in the *meta*-substituted diphenyl ester (VIb) occurred as a doublet at 1725 and 1750 cm^{-1}, but as a singlet in the other esters; frequencies for the carboxylic acids corresponded well for the dimer structure; a band at 1070-1080 cm^{-1} in the esters remains unassigned, but is presumably associated with a C—O stretch frequency.

Experimental

Melting points were determined with a Thomas Hoover melting point apparatus or a Du Pont 900 Differential Scanning Calorimeter. Infrared spectra were obtained on a Beckman Infracord spectrophotometer. The molecular weights of IIIb, IVa, and Va were verified from their parent ion mass spectrum using a Varian MAT CH-4B Mass Spectrometer. Elemental analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Michigan.

All procedures involving the use of organometallic reagents or silicon chlorides were carried out under a positive pressure of nitrogen in a flask previously flushed with nitrogen and flame-dried. The starting material, XI, was prepared according to a reported procedure by the controlled hydrolysis of dichlorodiphenylsilane [18]. Other reagents were commercially available.

Preparation of chlorotriphenylsilane derivatives

P-Bromophenylchlorodiphenylsilane (Ib). A solution of 47.2 g (0.20 mol) of *p*-dibromobenzene and 50.6 g (0.20 mol) of dichlorodiphenylsilane in 75 ml of tetrahydrofuran was added over a 1.5 hr period to 5.4 g (0.22 mol) of previously activated magnesium. The mixture was refluxed for 3 h, 100 ml of toluene was added, the tetrahydrofuran was distilled out, and heating was continued for 3 h. After the magnesium salts were filtered off, and the filtrate was concentrated, fractional distillation gave 17.0 g (23%) of Ib. With diethyl ether as the solvent, the yield was 15%.

The following were similarly prepared: Ia (in ether); Ic (in tetrahydrofuran); and Id (in tetrahydrofuran).

Alternately Ib was prepared by rapidly treating a solution of 9.5 g (0.040 mol) of *p*-dibromobenzene in 80 ml of dry ether at room temperature with 25.5 ml (0.040 mol) of 1.6 *M* n-butyllithium in hexane. The resulting solution was transferred to an addition funnel and 30 min after the addition of the butyllithium solution was initiated, the aryllithium solution was added to a rapidly stirred solution of 10.1 g (0.040 mol) of dichlorodiphenylsilane in 80 ml of dry ether. After the mixture was refluxed 2 h, filtered to remove the lithium salts, concentrated, and distilled, 8.2 g (55%) of Ib was obtained. Similarly, *p*-bromophenyllithium and chlorotriphenylsilane afforded XII.

Preparation of triphenylsilanol derivatives

P-Bromophenyldiphenylsilanol (IIb). After 98.4 g (0.26 mol) of Ib dissolved in 300 ml of ether was washed with water until the washings were neutral, the ether solution was dried over sodium sulfate and concentrated on a rotary evaporator. When the residual oil was dissolved in 400 ml of boiling hexane and stored at 4°C for 6 days, 71 g of material oiled from the solution, then crystallized. These crystals dissolved in 250 ml of boiling hexane and stored at 4°C for 4 days again oiled and crystallized to give 67 g (72%) of IIb.

The other silanols were similarly prepared but could be crystallized from solution: IIa (from toluene); IIc (from hexane); and IId (from hexane).

Preparation of derivative of hexaphenyldisiloxane from silanols

1,3-Bis(p-bromophenyl)-1,1,3,3-tetraphenyldisiloxane (IIIb). After 45.0 g (0.127 mol) of IIb was mixed with 50 ml of 0.1 *N* sodium hydroxide on a rotary evaporator heated with boiling water under vacuum for 1 h, the flask containing the mixture was placed in a Wood's metal bath at 180°C. Within 2 min an exothermic reaction was initiated and heating was continued for an additional 10 min. Recrystallization of the cooled, crystallized mass from toluene gave 29.9 (67%) of IIIb.

In the preparation of the other siloxanes, the quantity of sodium hydroxide was adjusted to completely neutralize any residual acidity in the silanols. The following were prepared: IIIa (from toluene); IIIc (from heptane—toluene); and IIId (from toluene).

Preparation of carboxylic acid derivatives of hexaphenyldisiloxane

4,4'-(1,1,3,3-Tetraphenyldisiloxanylene)dibenzoic acid (IVa). To a rapidly stirred solution of 1554 ml of glacial acetic acid, 504 ml of acetic anhydride, and 126 ml of sulfuric acid cooled to 10°C was added 107.5 g (0.19 mol) of IIIc (in 27 g portions) and 192 g of chromium trioxide (in 50 g portions). The portions of chromium trioxide were added at 0.5 h intervals followed in 10 min by a portion of the disiloxane with the temperature maintained at 10-14°C during the additions. After the additions were complete, stirring was continued for 3 h at 12-17°C and the mixture was poured over crushed ice. The precipitated acid was washed thoroughly with water and dried, mixed with 1050 ml of boiling toluene, and 38.4 g (32%) of "toluene-insoluble" IVa, m.p. 237-239°C, was filtered off. From the cooled toluene solution separated 61.7 g (52%) of "toluene-soluble" IVa, m.p. 233-235°C. The purity of the acid could be improved by repeated reprecipitations of the sodium salt. Thus, 38.4 g of the "toluene-insoluble" fraction in 800 ml of water was neutralized with sodium hydroxide, and the sodium salt was filtered off and dried under vacuum. Upon acidification with 85 ml of 12 *N* hydrochloric acid, 28.9 g of acid precipitated, which upon recrystallization from toluene gave 10.1 g of the toluene-insoluble product and 12.1 g of the toluene-soluble acid, m.p. 237-239°C. The two forms were differentiated by their infrared spectra.

In the preparation of IVb by the same method toluene-soluble and toluene-insoluble forms were separated, but they could not be differentiated by their infrared spectra.

Preparation of chlorocarbonyl and phenoxycarbonyl derivatives of hexaphenyldisiloxane

Diphenyl 4,4'-(1,1,3,3-tetraphenyldisiloxanylene)dibenzoate (VIa) and 4,4'-(1,1,3,3-tetraphenyldisiloxanylene)dibenzoyl chloride (V). After 40.0 g (0.064 mol) of IVa and 160 ml of thionyl chloride were refluxed for 4 h, the excess thionyl chloride was distilled under reduced pressure leaving a cream-colored residue of the acid chloride. After the residue was mixed with 24.0 g (0.26 mol) of phenol and heated on a steam bath for 2.5 h (under vacuum for the last 0.5 h to remove residual hydrochloric acid) it was dissolved in ether, filtered, washed with 10% aqueous sodium hydroxide, concentrated on a rotary evaporator, and crystallized from acetone—acetonitrile to obtain 43.6 g (88%) of VIa, m.p. 146-150°C. Pure VIa could be obtained after repeated crystallizations from acetone-acetonitrile with charcoal treatment. In a similar preparation, the intermediate Va was purified by crystallization from toluene.

With the same procedure IVb gave VIb (from acetone—acetonitrile).

Bis(pentachlorophenyl) 4,4'-(1,1,3,3-tetraphenyldisiloxanylene)dibenzoate (VIc). An intermediate acid chloride, similarly prepared from 31.5 g (0.051 mol) of IVa and 50 ml of thionyl chloride, dissolved in 250 ml of methylene chloride, was mixed overnight at room temperature with a solution of 30.4 g (0.114 mol) of pentachlorophenol and 10.2 g (0.109 mol) of triethylamine in 400 ml of methylene chloride. After the mixture was concentrated on a rotary evaporator, the residue was treated with a boiling mixture of 200 ml of acetonitrile and 200 ml of acetone, filtered hot, and 51.6 g (91%) of bis(pentachlorophenyl) 4,4'-(1,1,3,3-tetraphenyldisiloxanylene)dibenzoate crystallized from the filtrate. The pure compound was obtained after two recrystallizations from toluene.

A similar procedure was satisfactory for the preparation of VId.

4,4'-(1,1,3,3-tetraphenyldisiloxanylene)dibenzamide (VII). Impure Va, prepared from 14.4 g (0.024 mol) of IVa, and dissolved in 150 ml of dioxane, was added to 6.3 ml (0.095 mol) of concentrated ammonium hydroxide cooled to 10-15°C. Filtration gave 12.7 g (86%) of VII, m.p. 264-267°C, which after recrystallization from ethanol melted at 272-274°C.

4,4'-(1,1,3,3-tetraphenyldisiloxanylene)dibenzonitrile (VIII). After a mixture of 14.0 g (0.020 mol) of IIIb, 4.5 g (0.035 mol) of cuprous cyanide, and 20 ml of dimethyl acetamide was refluxed and stirred for 7 h, the hot mixture was poured into a solution of 4 g of sodium cyanide in 24 ml of water. The precipitated solids were filtered off, washed with three 50 ml portions of 10% aqueous sodium cyanide and dried under vacuum. After the remaining material was dissolved in hot toluene and filtered, 8.3 g (71%) of VIII crystallized.

Preparation of aniline derivatives

N,N-Bis(trimethylsilyl)-p-bromoaniline (IXa). To a solution of 34.4 g (0.20 mol) of *p*-bromoaniline in 600 ml of tetrahydrofuran, which was cooled to —70°C, was added 240 ml (0.40 mol) of 1.6 *M* solution of n-butyllithium in hexane. After the solution was stirred for 1 h, 43.3 g (0.40 mol) of chlorotrimethylsilane was added over a 1 h period and stirring was continued an additional 2 h at —70°C. The mixture was warmed to room temperature, filtered, concentrated on a rotary evaporator, and fractionally distilled to obtain 54.6 g (89%) of IXa.

The same method gave IXb from *m*-bromoaniline.

4,4'-(1,1,3,3-Tetraphenyldisiloxanylene)dianiline (Xa). A Grignard reagent, prepared from 1.1 g (0.044 mol) of magnesium and 12.6 g (0.040 mole of IXa in 50 ml of tetrahydrofuran, was treated with 9.0 g (0.20 mol) of XI and the mixture was refluxed for 18 h. After the cooled mixture was concentrated on a rotary evaporator, the silylamine product was extracted successively with petroleum ether, b.p. 60-90°C, and ether. The trimethylsilyl groups were cleaved from the resulting oil by treatment with 100 ml of methanol. After the solution was concentrated, the residue was extracted with hot toluene from which 1.4 g (8%) of Xa precipitated. The pure compound was obtained after three additional recrystallizations from toluene.

The same method provided Xb from IXb. Similarly, XIII was prepared by treating 3.2 g (0.010 mol) of *N,N*-bis(trimethylsilyl)-*p*-bromoaniline in 50 ml ether with 6.3 ml (0.010 mol) of 1.6 *M* n-butyllithium in hexane, condensing the interconversion product with 2.9 g (0.010 mol) of chlorotriphenylsilane, cleaving the trimethylsilyl groups with methanol, and recrystallizing the product from hexane and toluene.

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