

THE PREPARATION AND THERMAL BEHAVIOUR OF SOME POLYARYLSILANES

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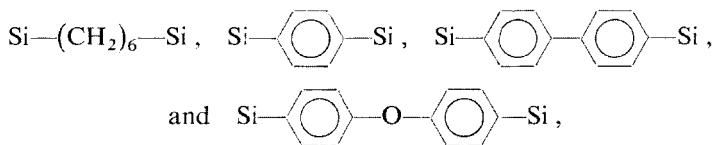
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Series of difunctional triphenylsilyl, methoxydiphenylsilyl, ethoxydiphenylsilyl, and methyl-diphenylsilyl derivatives derived from hexane, benzene, diphenyl, and diphenyl ether were prepared. Their volatility and oxidation stability on heating in an atmosphere of nitrogen or air were determined by thermogravimetric analysis. 4,4'-Bis(triphenylsilyl)biphenyl and bis(*p*-triphenylsilylphenyl) ether are more stable than some gas-chromatographic stationary phases used at elevated temperatures.

At present, organosilicon compounds are increasingly used in the industry and research as heat-transfer liquids, high vacuum liquids, lubricants, hydraulic liquids, gas chromatographic stationary phases, *etc.* One of basic conditions is their low volatility and sufficient oxidation stability at elevated temperatures. With regard to their structure, the most frequently used substances are siloxanes, alkyl- and arylsilanes, and orthosilicic acid esters¹⁻³. The application of novel compounds to this purpose is investigated also in other laboratories⁴⁻⁷.

Reported thermal properties of organosilicon compounds^{8,9} initiated us to prepare such derivatives of 1,6-bis(triorganosilyl)hexane, 1,4-bis(triorganosilyl)benzene, 4,4'-bis(triorganosilyl)biphenyl, and bis(*p*-triorganosilylphenyl) ether, *i.e.* the compounds with the linkages



silicon atoms of which are substituted with $\text{R}(\text{C}_6\text{H}_5)_2$ - groups, where R is CH_3 , C_6H_5 , OCH_3 , or OC_2H_5 .

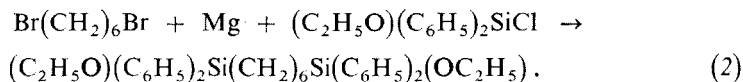
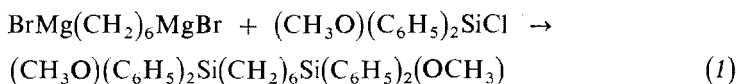
In the present study we determined *a*) the volatility and oxidation stability of these compounds and compared these properties with those of the compounds used as high-temperature gas chromatographic stationary phases; *b*) the effect of the above linkages (for compounds with identical R) and alkoxy, alkyl and aryl groups (for compounds having the linkage of the same type) on volatility and oxidation stability.

For preparing these compounds we made use of the Grignard reaction and the lithium condensation, the reaction which proved useful in the synthesis of similar organosilicon compounds. The volatility and oxidation stability of the compounds was determined by thermogravimetric analysis¹⁰⁻¹². This method rendered it possible to compare individual compounds with sufficient accuracy and reproducibility. Here, the weight loss of a compound on its heating is due to *a*) volatility of the compound (the compound does not decompose but evaporates, partially condensates on the walls of the apparatus and partially is stripped by a stream of nitrogen or air) and *b*) decomposition of the compound to more volatile substances that then evaporate. At the same time, decomposition may be accompanied by formation of non-volatile condensation products that form distillation residue. The measurements were carried out in an atmosphere of nitrogen or air, which made it possible to examine oxidation stability of the compounds.

RESULTS AND DISCUSSION

Preparation of Organosilicon Compounds

The compounds which were subjected to the volatility and oxidation stability measurements are summarized in Table I. The reaction of 1,6-hexamethylenedimagnesium bromide with diphenylethoxychlorosilane was used to prepare 1,6-bis(ethoxydiphenylsilyl)hexane. Contrary to this, the corresponding methoxy derivative, 1,6-bis(methoxydiphenylsilyl)hexane, was prepared from 1,6-dibromohexane, magnesium and diphenylmethoxychlorosilane in tetrahydrofuran by the Grignard reaction *in situ*.



1,6-Bis(triphenylsilyl)hexane was prepared such that trichlorosilane was reacted with 1,5-hexadiene to give 1,6-bis(trichlorosilyl)hexane, which in turn was treated with phenyllithium to give the expected product. The addition of triphenylsilane to 1,5-hexadiene in the presence of chloroplatinic acid has failed, likely due to steric reasons. Similarly, the reaction of 1,6-hexamethylenedimagnesium bromide with triphenylchlorosilane in ether and of 1,6-dibromohexane with magnesium and triphenylchlorosilane did not produce the required product and led predominantly to hexaphenyldisilane.

TABLE I
Amounts of Substances (in %) on Their Heating in Nitrogen or Air at Various Temperatures

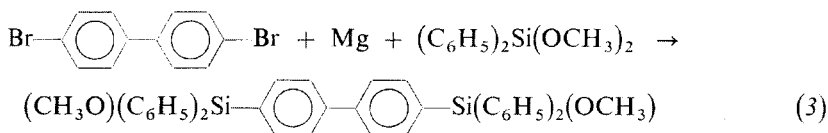
Compound	°C															
	260	280	300	320	340	360	380	400	420	440	460	480	500	520		
1,6-Bis(triphenylsilyl)hexane	a	100	100	100	97	90	82	71	51	12	0	—	—	—		
	b	100	100	99	94	82	67	50	33	18	14	13	12	11	11	
1,6-Bis(ethoxydiphenylsilyl)hexane	a	100	100	100	99	98	96	95	93	89	80	56	25	9	9	
	b	100	99	97	95	92	90	88	86	83	77	64	46	36	30	
1,6-Bis(methoxydiphenylsilyl)hexane	a	100	100	99	96	93	91	88	83	75	62	37	18	10	9	
	b	97	91	82	68	52	42	38	36	34	33	32	29	26	24	
1,4-Bis(triphenylsilyl)benzene	a	100	100	100	100	100	99	93	80	66	43	14	0	—	—	
	b	100	100	100	100	100	99	92	78	62	33	10	4	4	4	
1,4-Bis(ethoxydiphenylsilyl)benzene	a	99	97	94	86	77	62	42	20	14	13	13	12	12	11	
	b	99	96	91	80	70	65	62	60	58	56	54	53	51	50	
1,4-Bis(methoxydiphenylsilyl)benzene	a	100	100	98	89	79	65	49	32	21	16	14	11	9	9	
	b	100	100	98	94	85	74	59	48	44	41	38	37	36	35	
1,4-Bis(methylidiphenylsilyl)benzene	a	96	90	85	79	69	54	36	13	0	—	—	—	—	—	
	b	96	91	85	76	65	45	20	2	0	—	—	—	—	—	
1,3-Bis(triphenylsilyl)benzene	a	88	77	60	37	4	0	—	—	—	—	—	—	—	—	
	b	93	84	70	44	14	0	—	—	—	—	—	—	—	—	
4,4'-Bis(triphenylsilyl)biphenyl	a	100	100	100	100	100	100	99	97	95	91	88	80	64	40 ^c	
	b	100	100	100	100	100	100	99	95	91	86	75	49	12	10	
4,4'-Bis(ethoxydiphenylsilyl)biphenyl	a	100	100	100	98	95	91	85	78	70	58	45	36	29	25	
	b	100	100	100	98	92	84	77	71	67	64	61	57	53	49	

4,4'-Bis(methoxydiphenylsilyl)biphenyl	<i>a</i>	100	100	98	96	93	91	86	80	71	57	40	25	18	17
	<i>b</i>	100	100	99	98	96	92	84	76	69	65	62	58	54	50
4,4'-Bis(methyl-diphenylsilyl)biphenyl	<i>a</i>	100	100	100	100	100	98	91	83	71	47	25	7	0	—
	<i>b</i>	100	100	100	100	99	95	88	77	62	37	16	8	7	5
Bis(<i>p</i> -triphenylsilylphenyl) ether	<i>a</i>	100	100	100	100	100	100	99	97	95	91	85	78	69	57 ^d
	<i>b</i>	100	100	100	100	100	100	99	97	92	86	77	60	38	16
Bis(<i>p</i> -ethoxydiphenylsilylphenyl) ether	<i>a</i>	100	100	100	98	93	89	83	77	69	59	43	28	18	18
	<i>b</i>	100	100	97	95	91	83	76	70	65	61	59	56	53	49
Bis(<i>p</i> -methoxydiphenylsilylphenyl) ether	<i>a</i>	100	100	100	100	100	100	96	87	73	52	35	23	18	17
	<i>b</i>	100	100	99	97	94	89	78	64	54	49	45	42	38	35
Bis(<i>p</i> -methyl-diphenylsilylphenyl) ether	<i>a</i>	100	100	100	100	100	99	96	90	80	67	38	14	0	—
	<i>b</i>	100	100	100	99	96	92	86	76	60	40	16	7	5	5
<i>m</i> -Bis(<i>m</i> -phenoxyphenoxy)benzene	<i>a</i>	100	100	98	95	91	83	68	41	2	0	—	—	—	—
	<i>b</i>	100	100	98	95	90	82	68	40	1	0	—	—	—	—
Methylvinylpolysiloxane G 1 000	<i>a</i>	100	100	100	100	100	99	95	90	79	59	20	0	—	—
Methylpolysiloxane E 350	<i>a</i>	100	100	100	100	99	95	88	72	40	18	6	0	—	—
Trifluoropropylmethylpolysiloxane FS-1265	<i>a</i>	100	100	98	91	81	70	49	28	9	1	0	—	—	—
Apiezon L	<i>a</i>	100	100	100	100	99	96	90	78	55	13	1	1	1	1
Apiezon W	<i>a</i>	100	100	100	100	99	97	93	88	82	72	55	44	39	35

^a Data obtained in nitrogen, ^b data obtained in a stream of air, ^c at 530°C; 18%, ^d at 530°C; 48%.

1,4-Bis(methyldiphenylsilyl)benzene and 1,4-bis(triphenylsilyl)benzene were prepared from *p*-dibromobenzene by its conversion to *p*-dilithiumbenzene which by treatment with methyldiphenylchlorosilane or triphenylchlorosilane yielded expected products. 1,3-Bis(triphenylsilyl)benzene was obtained by the Grignard reaction from *m*-dibromobenzene and triphenylchlorosilane.

4,4'-Bis(methoxydiphenylsilyl)biphenyl was obtained by the Grignard reaction *in situ* from 4,4'-dibromobiphenyl, diphenyldimethoxysilane, and magnesium.



4,4'-Bis(ethoxydiphenylsilyl)biphenyl was obtained similarly from diphenylethoxychlorosilane. 4,4'-Bis(methyldiphenylsilyl)biphenyl and 4,4'-bis(triphenylsilyl)biphenyl were prepared by the lithium condensation from 4,4'-dibromodiphenyl, lithium, and methyldiphenylchlorosilane (or triphenylchlorosilane).

Bis(*p*-methoxydiphenylsilylphenyl) ether, bis(*p*-ethoxydiphenylsilylphenyl) ether, and bis(*p*-methyldiphenylsilylphenyl) ether were synthesized by the procedure described above (the Grignard reaction *in situ*), starting compounds being bis(*p*-bromophenyl) ether, magnesium and the appropriate silane (diphenyldimethoxysilane, diphenylethoxychlorosilane or diphenylmethylchlorosilane).

Volatility and Oxidation Stability

From the shape of obtained curves and the weight of the residue (Table I and Fig. 1) the behaviour of these compounds on heating in an atmosphere of nitrogen or air

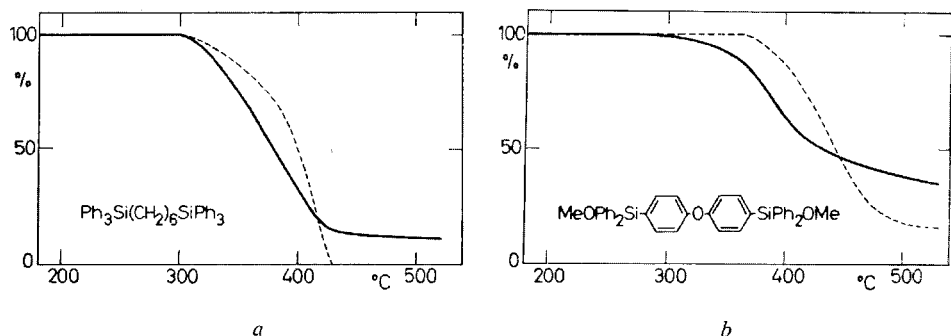


FIG. 1

Volatility of *a* 1,6-Bis(triphenylsilyl)hexane and *b* Bis(*p*-methoxydiphenylsilylphenyl) Ether in an Atmosphere of Nitrogen or Air

Full line air, dashed line nitrogen.

can be determined and their volatility and oxidation stability estimated. All the compounds under study were purified by distillation or sublimation and did not contain volatile components.

1,6-Bis(triorganosilyl)hexanes. The most stable thermally is 1,6-bis(triphenylsilyl)hexane that evaporates quantitatively in an atmosphere of nitrogen. In air, it decomposes to more volatile substances (as shown by more rapid weight loss at temperatures to 400°C) and to a distillation residue (11%). The methoxy and ethoxy derivatives are less stable. Both undergo thermal decomposition. The amount of the residue is indicative of the extent of decomposition which in air is markedly greater than in nitrogen. The ethoxy derivative is less stable than the methoxy derivative, as follows from the initial loss of the compound (230 and 280°C) and the weight of the distillation residue.

1,4-Bis(triorganosilyl)benzenes. The highest thermal stability is exhibited by the triphenylsilyl derivative that evaporates quantitatively. In air this compound partially decomposes. The distillation residue could not be determined, since even on reaching a temperature of 530°C (maximum temperature), the sample was still losing its weight. The methyldiphenylsilyl derivative quantitatively evaporates in air. However, due to the lower molecular weight its volatility is substantially greater compared to that of the triphenylsilyl derivative. Both alkoxy derivatives partially decompose on heating both in air and in nitrogen, which is indicated by the presence of non-volatile residue.

1,3-Bis(triphenylsilyl)benzene. The sample sublimed on heating and the compound flew up in the form of a white wool.

4,4'-Bis(triorganosilyl)biphenyl. The volatility of these compounds is lower than that of the corresponding 1,4-bis(triorganosilyl)benzenes. The temperature of the evaporation of the triphenylsilyl derivative is the same in nitrogen and in air. The shape of the curve for the evaporation in air, *i.e.* rapid weight loss of the sample at 460–500°C, speaks for decomposition to more volatile components. The distillation residue could not be determined accurately since even at 530°C (maximum temperature), the sample was still losing its weight. The methyldiphenylsilyl derivative evaporates quantitatively in nitrogen and decomposes partially in air. Both alkoxy derivatives decompose in nitrogen and, to a greater extent, in air.

Bis(p-triorganosilylphenyl) ethers. This group of compounds was characterized by the lower temperature of evaporation for the methoxy- and ethoxydiphenylsilyl derivatives in air, compared to nitrogen as a result of thermal decomposition. The least volatile derivative was bis(*p*-triphenylsilylphenyl) ether.

From comparison of the compounds under study it follows that with 1,6-bis(triorganosilyl)hexanes and 1,4-bis(triorganosilyl)benzenes, *i.e.* the compounds containing hexamethylene or phenylene group, phenyl, methyl, methoxy, and ethoxy

groups markedly influence volatility of these compounds by increasing their molecular weight. The least volatile, *i.e.* the most thermally stable, compounds are the triphenylsilyl derivatives, then the ethoxydiphenylsilyl and methoxydiphenylsilyl derivatives, and the most volatile (due to its lowest boiling point) is the methyl-diphenylsilyl derivative. Contrary to this, with 4,4'-bis(triorganosilyl)biphenyls and bis(*p*-triorganosilylphenyl) ethers, the relative increase in molecular weight of these compounds due to introduction of phenyl, methyl, methoxy, and ethoxy groups is smaller, and these groups affect volatility of the compounds mainly by their chemical stability and resistance toward decomposition and cleavage. Less stable are the methoxy derivatives and the least stable are the ethoxydiphenylsilyl derivatives.

Of the compounds used as gas chromatographic stationary phases (Fig. 2), the most stable one is Apiezon W. The other compounds either evaporate quantitatively, *e.g.* *m*-bis(*m*-phenoxyphenoxy)benzene whose volatility in nitrogen and in air is identical, or depolymerize to more volatile compounds at elevated temperatures, as observed with all three polysiloxanes. In comparison with these compounds, 4,4'-bis(triphenylsilyl)biphenyl and bis(*p*-triphenylsilylphenyl) ether are less volatile and could be used as gas chromatographic stationary phases for elevated temperatures.

EXPERIMENTAL

Compounds used. Diethyl ether, tetrahydrofuran, benzene, and xylene were dried by distillation with sodium bis(2-methoxyethoxy)aluminium hydride. 4,4'-Dibromobiphenyl, m.p. 167–168°C, and 4,4'-dibromodiphenyl ether, m.p. 53–54°C, were prepared in the usual way^{13,14}. Diphenylmethoxychlorosilane, b.p. 95–100°C/0.3 Torr (ref.¹⁵), diphenylethoxychlorosilane, b.p. 120 to 125°C/1.5 Torr (ref.¹⁵), methyl-diphenylchlorosilane, b.p. 156–162°C/14 Torr, triphenylchlorosilane, b.p. 210–220°C/14 Torr, diphenyldimethoxysilane, b.p. 102–105°C/0.5 Torr (ref.¹⁵), 1,4-bis(ethoxydiphenylsilyl)benzene, m.p. 163–164°C (ref.^{16,17}), and 1,4-bis(methoxydiphenylsilyl)benzene, m.p. 149–151°C, were prepared in this laboratory¹⁶. NMR spectra were recorded on Tesla BS 477 spectrometer and IR spectra were recorded on Zeiss UR 20 spectrophotometer. Nitrogen (99.9%) was dried by sulphuric acid and air was dried by calcium chloride. *n*-Butyllithium and phenyllithium were prepared by reported procedures¹⁸ and their concentrations were determined by titration^{19,20}. All syntheses were carried out in nitrogen atmosphere.

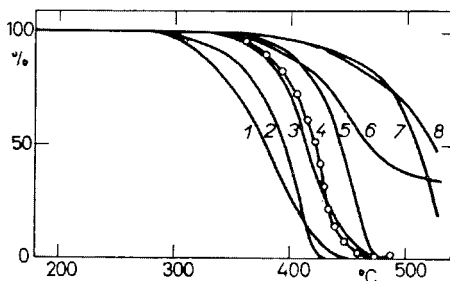


FIG. 2

Volatility of Gas Chromatographic Phases in Nitrogen Atmosphere

1 Trifluoropropylmethylpolysiloxane FS-1265, 2 *m*-bis(*m*-phenoxyphenoxy)benzene, 3 methylpolysiloxane E 350, 4 Apiezon L, 5 methylvinylpolysiloxane elastomer (Lukopren G 1000), 6 Apiezon W, 7 4,4'-bis(triphenylsilyl)biphenyl, 8 bis(*p*-triphenylsilylphenyl) ether.

Apparatus for thermogravimetric analysis was made in this laboratory according to the work¹⁰. The sample, placed in a glass basket hung on a quartz spiral, was heated in a stream of nitrogen or air such that the temperature increased by a rate of 9°C per min. Weight loss of the sample was measured by cathetometer, determining the change in the position of the sample. From the weight of the sample, the amount of distillation residue and the position of the sample at a given temperature it was possible to draw curves that characterized the weight loss of the substance (given in per cent) at a given temperature.

1,6-Bis(triphenylsilyl)hexane. Reaction mixture containing 8.2 g (0.1 mol) of 1,5-hexadiene, 27.1 g (0.2 mol) of trichlorosilane, and $2 \cdot 10^{-4}$ mol of chloroplatinic acid in isopropanol was refluxed with stirring for 8.5 h. Distillation yielded 9.7 g (27%) of 1,6-bis(trichlorosilyl)hexane, b.p. 190–195°C/50 Torr. A solution of phenyllithium, prepared from 2.9 g (0.42 mol) of lithium and 31.4 g (0.2 mol) of bromobenzene in 100 ml of dry ether, was added to a solution of 7.06 g (0.02 mol) of 1,6-bis(trichlorosilyl)benzene in 50 ml of the ether over a period of 30 min. The reaction mixture was stirred and refluxed for 1 h, then cooled and decomposed with water. The ether layer was dried over calcium chloride. The crude product (7 g) was purified by distillation and crystallization. B.p. 270–280°C/0.4 Torr, m.p. 128–129°C. NMR and IR spectra confirmed the structure of the product. For $C_{42}H_{42}Si_2$ (603.0) calculated: 83.66% C, 7.02% H, 9.32% Si; found: 83.44% C, 6.95% H, 9.61% Si.

1,6-Bis(ethoxydiphenylsilyl)hexane. Grignard reagent prepared from 1.82 g (0.075 mol) of magnesium powder, 6.1 g (0.025 mol) of 1,6-dibromohexane in 25 ml of diethyl ether was added slowly with stirring to a solution of 15.75 g (0.06 mol) of diphenylethoxychlorosilane in 25 ml of the ether. After addition of 50 ml of xylene, the ether was distilled off and the reaction mixture was refluxed for 3 h. After cooling, light petroleum was added in excess and magnesium salts that precipitated were washed with hot benzene. The reaction gave 3.2 g of the product which after crystallization from an ethanol–benzene mixture yielded 1,6-bis(ethoxydiphenylsilyl)hexane, m.p. 98–101°C. NMR spectrum confirmed the structure of this compound. For $C_{34}H_{42}O_2Si_2$ (538.9) calculated: 75.78% C, 7.86% H, 10.43% Si; found: 75.56% C, 7.62% H, 10.82% Si.

1,6-Bis(methoxydiphenylsilyl)hexane. A solution of 8.13 g (0.033 mol) of 1,6-dibromohexane in 20 ml of tetrahydrofuran was added dropwise in 20 min to a mixture of 1.94 g (0.08 mol) of magnesium powder, 18.89 g (0.076 mol) of diphenylmethoxychlorosilane and 90 ml of tetrahydrofuran. The reaction mixture was refluxed for 3 h and worked up in the usual manner. The product obtained (5 g) was distilled to give the pure 1,6-bis(methoxydiphenylsilyl)hexane, b.p. 250–253°C/0.3 Torr, n_D^{20} 1.586, d_4^{25} 1.068. Its structure was confirmed by NMR spectroscopy. For $C_{38}H_{32}O_2Si_2$ (510.8) calculated: 75.24% C, 7.50% H, 11.00% Si; found: 74.98% C, 7.29% H, 11.35% Si.

1,4-Bis(triphenylsilyl)benzene was obtained by reaction of 11.8 g (0.04 mol) of triphenylchlorosilane in 40 ml of benzene with 1,4-phenyldilithium which was prepared from 4.72 g (0.02 mol) of 1,4-dibromobenzene in 60 ml of benzene and 0.04 mol of *n*-butyllithium in 50 ml of ether. By this way 2 g of the product were obtained which after sublimation at 320–330°C/0.3 Torr melted at 350–352°C. Meston²¹ records m.p. 350–360°C without reporting the yield obtained.

1,4-Bis(methyldiphenylsilyl)benzene was prepared from methyldiphenylchlorosilane and 1,4-phenyldilithium in 14% yield. B.p. 230–240°C/0.3 Torr, m.p. 197–200°C (*n*-butanol). Ponomareva²² reports m.p. 196–197°C, Meston²¹ 205–207°C.

1,3-Bis(triphenylsilyl)benzene. The product obtained by Grignard reaction from 1,3-dibromobenzene and triphenylchlorosilane had after sublimation (210–220°C/0.3 Torr) m.p. 225–235°C. Recorded m.p. 220–230°C (ref.²³) and 237–240°C (ref.²¹).

4,4'-*Bis(triphenylsilyl)biphenyl* was prepared by reaction of 4,4'-biphenyldilithium with triphenylchlorosilane. B.p. 310—320°C/0.3 Torr, m.p. 288—289°C (CCl₄, light petroleum). Recorded m.p. 294—296.5°C (ref.²¹) and 285—286°C (ref.²⁴).

4,4'-*Bis(ethoxydiphenylsilyl)biphenyl*. A solution of 31.2 g (0.1 mol) of 4,4'-dibromobiphenyl in 150 ml of tetrahydrofuran was added to a mixture of 6 g (0.25 mol) of magnesium powder, 59.06 g (0.225 mol) of diphenylethoxychlorosilane, and 250 ml of tetrahydrofuran. The reaction mixture was refluxed for 12 h. After cooling and precipitation of magnesium salts by adding light petroleum, 40 g of product were obtained which after distillation and crystallization yielded the pure compound, b.p. 280—290°C/0.3 Torr, m.p. 152—155°C. Its structure was confirmed by NMR spectroscopy. For C₄₀H₃₈O₂Si₂ calculated: 79.16% C, 6.31% H, 9.26% Si; found: 78.94% C, 6.23% H, 9.37% Si.

4,4'-*Bis(methoxydiphenylsilyl)biphenyl* was obtained similarly as the ethoxy derivative from 16.61 g (0.053 mol) of 4,4'-dibromobiphenyl, 3.5 g (0.144 mol) of magnesium, and 30 g (0.123 mol) of diphenyldimethoxysilane in tetrahydrofuran. The reaction produced 17 g of the product which after distillation (b.p. 310—320°C/0.3 Torr) and crystallization from cyclohexane had m.p. 196—201°C. The NMR spectrum confirmed its structure. For C₃₈H₃₄O₂Si₂ (578.0) calculated: 78.85% C, 5.92% H, 9.71% Si; found: 78.86% C, 5.87% H, 9.84% Si.

4,4'-*Bis(methyldiphenylsilyl)biphenyl*. 4,4'-Biphenyldilithium was prepared from 0.022 mol of *n*-butyllithium in ether solution and 3.12 g (0.01 mol) of 4,4'-dibromobiphenyl in benzene-toluene (1 : 3). After removal of the ether by distillation, the reaction mixture was slowly added to 9.3 g (0.04 mol) of methyldiphenylchlorosilane in benzene and then refluxed with stirring for 1 h. Decomposition and work-up of the reaction mixture yielded 1 g of the product which after distillation at 270—280°C/0.4 Torr and crystallization had m.p. 175—177°C. The NMR spectrum confirmed the suggested structure. For C₃₈H₃₄Si₂ (546.9) calculated: 83.46% C, 6.27% H, 10.27% Si; found: 83.46% C, 6.17% H, 10.36% Si.

Bis(p-triphenylsilylphenyl) ether. A solution of 5.65 g (0.019 mol) of triphenylchlorosilane in 50 ml of diethyl ether were added slowly (15 min) to 4,4'-dilithiumdiphenylether prepared from 3.12 g (0.0095 mol) of 4,4'-dibromodiphenyl ether in 20 ml of diethyl ether and 0.019 mol of *n*-butyllithium in diethyl ether. The reaction mixture was refluxed for 3 h. Hydrolysis gave 2 g of the product which was distilled and crystallized from CCl₄. B.p. 300—310°C/0.4 Torr, m.p. 305—307°C. Recorded m.p. 306—308°C.

Bis(p-ethoxydiphenylsilylphenyl) ether was prepared similarly from diphenylethoxychlorosilane and the dilithium salt. B.p. 290—300°C/0.3 Torr, m.p. 153—160°C (benzene-ethanol). Its structure was confirmed by NMR spectroscopy. For C₄₀H₃₈O₃Si₂ (622.0) calculated: 77.13% C, 6.15% H, 9.02% Si; found: 76.85% C, 6.02% H, 9.32% Si.

Bis(p-methoxydiphenylsilylphenyl) ether was prepared similarly from the dilithium salt and diphenylmethoxychlorosilane. B.p. 260—170°C/0.3 Torr, m.p. 115°C (benzene-methanol). Its NMR spectrum agreed with the suggested structure. For C₃₈H₃₄O₃Si₂ (594.9) calculated: 76.73% C, 5.76% H, 9.44% Si; found: 76.53% C, 5.67% H, 9.70% Si.

Bis(p-methyldiphenylsilylphenyl) ether. A solution of 4.59 g (0.014 mol) of 4,4'-dibromodiphenyl ether in 40 ml of tetrahydrofuran was added to a mixture of 1.32 g (0.054 mol) of magnesium and 7.21 g (0.031 mol) of methyldiphenylchlorosilane in 20 ml of tetrahydrofuran. The reaction mixture was refluxed for 8 h and worked up in the usual manner to give 2.5 g of the product which after distillation (b.p. 290—300°C/0.2 Torr) and crystallization from a CCl₄-methanol mixture had m.p. 143—146°C. Its NMR spectrum confirmed the proposed structure. For C₃₈H₃₄O₂Si₂ (562.9) calculated: 81.09% C, 6.09% H, 9.98% Si; found: 80.99% C, 6.12% H, 9.95% Si.

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