$-63.7°$, 10.25 mm) upon hydrolysis in a 35% aqueous solution of sodium hydroxide containing alcohol (2 ml) and piperidine (2 ml), after warming to approximately 50° upon four occasions, yielded 21.8 ml of hydrogen at STP (calcd 21.88 ml).

A sample of pure $SiH_3SiH_2CH_3$ melted sharply at $-134.9 \pm 0.2°$ and was spontaneously inflammable in air. The vapor pressure of $SiH_3SiH_2CH_3$ (mol wt found 76.1, calcd 76.25) was measured in a glass tensimeter connected to a mercury manometer which had previously been pretreated with $SiH_3SiH_2CH_3$ for 5.5 hr. Vapor pressures at various temperatures are given in Table I.

TABLE I

VAPOR PRESSURES OF $SiH_3SiH_2CH_3$[a,b]

Temp, °C	P, mm		Temp, °C	P, mm	
	Obsd	Calcd		Obsd	Calcd
−83.5	1.85	2.15	−16.1	184.65	184.83
−76.6	3.90	3.90	−8.4	266.05	266.14
−63.5	10.45	10.86	0.0	382.60	386.94
−56.4	17.80	17.97	−46.0	36.20[c]	35.50
−45.8	35.50	35.94	−63.7	10.80[c]	10.70
−38.4	56.50	56.19	−196	0.00[c]	0.00

[a] Duration of experiment 10 hr. [b] The molecular weight of the whole sample at the conclusion of the experiment was 76.2 (calcd 76.25). The infrared spectrum of the sample at the conclusion of the experiment was identical with that of the pure material. [c] Pressure observed on decreasing the temperature.

Vapor pressures in the range -83.5 to $-8.4°$ are represented by the equation

$$\log P_{\mathrm{mm}} = -\frac{1399.46}{t + 273.16} + 7.71087$$

Additional values to those given in Table I were used to derive the above relationship. The extrapolated boiling point is 16.6°, the heat of vaporization is 6.40 kcal mole^{-1}, and Trouton's constant is 22.1 cal deg^{-1} mole^{-1}. The fact that the vapor pressure curve is reproducible on increasing and decreasing the temperature indicates that little, if any, thermal decomposition of the compound had occurred during the experiment.

The mass spectrum of $SiH_3SiH_2CH_3$ was consistent with its proposed structure. Possible assignments of the major fragments observed are, in decreasing order of abundance; $SiH_2CH_3^+$ (100.0%), $SiHCH_3^+$ (38.3%), $SiCH_3^+$ (35.9%), $SiH_3SiH_2CH_3^+$ (32.1%), $Si_2HCH_3^+$ (26.1%), $Si_2H_3CH_3^+$ (25.7%), $Si_2H_4CH_3^+$ (22.7%), Si_2CH^+ (20.3%). It should be noted that a strong parent ion peak was observed.

The proton nuclear magnetic resonance spectrum of $SiH_3SiH_2CH_3$ (mol wt found 76.4, calcd 76.25; vapor pressure at $-64.0°$, 10.2 mm) was determined on a 17.8% (by volume) solution in cyclohexane. The data obtained for the essentially first-order spectrum are listed with reference to cyclohexane as internal standard: δSiH_3, -1.73 ppm; δSiH_2, -2.23 ppm; δCH_3, 1.20 ppm; $J_{HH'}(SiH_3SiH_2)$, 2.5 cps; $J_{HH'}(CH_3SiH_2)$, 4.2 cps; $J_{^{29}SiH}(SiH_3)$, 191.0 cps; $J_{^{29}SiH}(SiH_2)$, 189.0 cps. The high-field ^{29}Si satellites of both the SiH_2 and SiH_3 protons could not be observed since they were obscured by the solvent resonance peak. The corresponding $J_{^{29}SiH}$ values were therefore obtained by doubling the value between the observed satellite and its parent peak. Since in those cases where both satellites of a given peak in a SiH_3SiH_2 compound have been observed there is no isotope shift,[3] $\delta SiH(^{29}Si–^{28}Si)$, it appears likely that the error introduced by the above procedure will not affect the significance of the results. Integration of the spectrum gave the proton abundance ratios, $SiH_3:CH_3:SiH_2 = 1.5:1.5:1.0$, as expected for the postulated structure.

The absorption maxima in the infrared spectrum of $SiH_3SiH_2CH_3$ (P = 4.0 and 85.0 mm) are: 2990 w, 2160 vs, 1420 w, 1268 w, 1254 w, 954 m, 940 m, 856 vs, 848 vs, 840 vs, 731 m, 723 m cm^{-1}.

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Preparation and Properties of Some Aryloxysilane Compounds

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Studies[1,2] of the preparation methods and thermal stabilities of several poly(aryloxysilanes) in this laboratory emphasized the need to examine methods of synthesis and properties of low molecular weight compounds of similar structure. Reported below are the preparation methods, composition, melting points, molecular weights, infrared absorption, and thermal properties of eight compounds, listed in Table I, representing the structures: $R'OSi(R)_2OR'$, $R_3SiOR'OSiR_3$, and R_3SiOR', in which R is methyl, ethyl, or phenyl and R′ is a biphenylene or a substituted biphenylene group. The materials were obtained in high yields. Five of the compounds are new to the literature.

Experimental Section

Materials.—All of the reactants, except the two aminosilanes, were obtained from commercial sources. The two phenols, *p*-phenylphenol and 3,3′-dimethyl-4,4′-biphenol, Eastman Grade, were obtained from Distillation Products Industries, Rochester, N. Y. Diphenyldichlorosilane was obtained from Dow Corning Corp., Midland, Mich. The other chlorosilanes, diphenyldiethoxysilane and hexamethylcyclotrisilazane, were procured from Peninsular ChemResearch, Inc., Gainesville, Fla. The bis(anilino)diphenylsilane was prepared by the reaction of 1.0 mole 253.2 g) of diphenyldichlorosilane and 4.0 moles (372.5 g) of freshly distilled aniline with excess 2,4,6-trimethylpyridine in boiling benzene by the procedure of Dunnavant, *et al.*,[2] which is a modification of the methods of Curry and Byrd,[1] Anderson,[3] and Larsson and Smith.[4] The anilinotrimethylsilane was prepared by the reaction of trimethylchlorosilane and aniline as described by Osthoff and Kantor.[5]

Methods of Analysis.—The number-average molecular weights were measured in benzene solution at 25° by use of a Mechrolab Model 302 vapor pressure osmometer. The melting points were determined by use of a Mel-Temp Apparatus, Laboratory Devices, Cambridge, Mass. The thermometer was calibrated against an ASTM standard thermometer, and melting point data are believed to be accurate to within 1°.

The thermal properties of the materials were observed over the range of 24–485° by use of a Du Pont Model 900 differential thermal analyzer. The infrared absorption spectra were obtained by use of Perkin-Elmer Model 521 grating infrared spectrophotometer.

Synthetic Methods.—Four reaction methods were employed in the synthesis of the eight compounds listed in Table I. In the first three cases, the *p*-phenylphenol was condensed with the appropriate alkyl or aryl ethoxy-, anilino-, or chlorosilane compound with the elimination of ethanol, aniline, or hydrogen chloride, respectively. In the fourth reaction, the *p*-phenylphenol reacted with the cyclic silazane, hexamethylcyclotrisilazane, with the formation of the monosilyl compound and the elimina-

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TABLE I
ARYLOXYSILANE COMPOUNDS

Compd	Name	Formula	Synthesis method	Mp, °C	Dta endotherm, °C	Mol wt		Calcd, %			Found, %		
						Calcd	Found	C	H	Si	C	H	Si
I	Bis(*p*-phenylphenoxy)-diphenylsilane	$(C_6H_5)_2Si(OC_6H_4C_6H_5)_2$	B, D, A[a]	195–197	185–195	521	522	83.0	5.4	5.4	82.8	5.6	6.5
II	Bis(*p*-phenylphenoxy)-methylphenylsilane	$(CH_3)(C_6H_5)Si(OC_6H_4C_6H_5)_2$	D	93–95	85–93	459	435	81.2	5.7	6.1	80.7	5.4	5.8
III	Bis(*p*-phenylphenoxy)-dimethylsilane	$(CH_3)_2Si(OC_6H_4C_6H_5)_2$	D	92–94	80–85	396	393	78.7	6.1	7.1	78.3	5.8	7.2
IV	Bis(*p*-phenylphenoxy)-diethylsilane	$(C_2H_5)_2Si(OC_6H_4C_6H_5)_2$	A	49–60	46–68	377	381	76.5	7.5	7.5	78.1	7.0	7.3
V	4,4′-Bis(triphenyl-siloxy)biphenyl	$(C_6H_5)SiOC_6H_4C_6H_4OSi(C_6H_5)_3$	C	211.5–213.5	185–203	703	686	82.0	5.4	8.0	81.8	5.9	7.1
VI	4,4′-Bis(triphenyl-siloxy)-3,3′-dimethyl-biphenyl	$(C_6H_5)_3SiOC_6H_3(3\text{-}CH_3)C_6H_3(3\text{-}CH_3)OSi(C_6H_5)_3$	C	238–240	228–235	731	*b*	82.1	5.8	7.7	81.7	6.0	7.1
VII	*p*-Phenylphenoxy-triphenylsilane	$(C_6H_5)_3SiOC_6H_4C_6H_5$	C[a]	111–114	90–112	429	436	84.1	5.6	6.5	84.4	6.3	6.4
VIII	*p*-Phenylphenoxy-trimethylsilane	$(CH_3)_3SiOC_6H_4C_6H_5$	B, D[c,d]	100–103[e]	...	242	231	74.3	7.5	11.6	74.3	8.1	11.4

[a] Prepared by Kuznetsova and Sobolevskii,[6] by method A. [b] Insoluble in benzene. [c] Prepared by Ismail,[8] by a method similar to method D. [d] Prepared by Martin,[7] by a method similar to route C. [e] Boiling point (°C) at 0.2 mm; refractive index n_D 1.5588 at 29°.

tion of ammonia. Typical examples of these processes are recorded.

Method A. Bis(*p*-phenylphenoxy)diphenylsilane (I) from Diphenyldiethoxysilane.—In dry glass apparatus fitted with an effluent condenser, a mixture of 0.1 mole (27.2 g) of diphenyldiethoxysilane, 0.3 mole (51.3 g) of *p*-phenylphenol, and 0.1 g of sodium was heated with stirring to 150° during a period of 3 hr, at which time the evolution of ethanol ceased. The reaction product was extracted with benzene and compound I was recovered in 87% yield from the benzene solution by the addition of ethanol. Compound IV was also prepared by this procedure. This method is equivalent to that of Kuznetsova and Sobolevskii.[6]

Method B. *p*-Phenylphenoxytrimethylsilane (VIII) from Anilinotrimethylsilane.—In apparatus similar to that described above a mixture containing 0.056 mole (13.5 g) of anilinotrimethylsilane and 0.056 mole (9.5 g) of *p*-phenylphenol was heated during a 6-hr period to 190°. Fractional distillation of the reaction products gave compound VIII, bp 100–103° (0.2 mm), in 90% yield. Triphenylanilinosilane was employed to form compound I in 90% yield. Method B is similar to the reaction employed by Curry and Byrd[1] for the preparation of polymeric aryloxysiloxanes.

Method C. 4,4′-Bis(triphenylsiloxy)3,3′-dimethylbiphenyl (VI) from Triphenylchlorosilane.—In similar dry apparatus, with a continuing stream of dry nitrogen, 0.1 mole (29.5 g) of triphenylchlorosilane was added dropwise over a period of 2 hr to a refluxing benzene solution containing 0.05 mole (10.7 g) of 4,4′-dihydroxy-3,3′-dimethylbiphenyl and 0.1 mole (10.1 g) of triethylamine. The mixture was held at the refluxing temperature for an additional 24-hr period. After separation of the solid triethylamine hydrochloride, compound VI crystallized on cooling the benzene solution and was obtained in 89% yield after recrystallization from benzene. Compound V was also prepared by this method, and Martin[7] used the procedure for the preparation of compound VIII.

Method D. Bis(*p*-phenylphenoxy)dimethylsilane (III) from Hexamethylcyclotrisilazane.—A mixture of 0.0173 mole (3.8 g) of hexamethylcyclotrisilazane and 0.14 mole (23.8 g) of *p*-phenylphenol was heated with mixing until a homogenous melt was obtained and then held at 165–175° for 30 hr. The reaction products were poured into benzene and the insoluble, unreacted *p*-phenylphenol removed. Benzene was removed by distillation under reduced pressure and the product, compound III, was obtained in 64% yield after crystallization from petroleum ether. Compounds I, II, and VIII were also prepared by this method. Method D is similar to that described by Ismail,[8] who prepared compound VIII by the reaction of hexamethyldisilazane and *p*-phenylphenol using the sodium salt of the phenol as a catalyst.

Results and Discussion

The four reaction schemes led to the formation of desired products in rather high yields, and, considered together, the four processes provide some freedom of choice in the selection of a method for the preparation of a particular aryloxysilane. Five of the eight compounds described in Table I are new to the literature.

The infrared spectra of the several materials appeared to be normal and generally similar to those observed for the related polymeric structures described by Curry and Byrd[1] and Dunnavant, *et al.*,[2] with one exception, namely, compound II, $(CH_3)(C_6H_5)Si(OC_6H_4C_6H_5)_2$, containing one CH_3 group, did not show the expected absorption in the 2900–3000 cm^{-1} region for the C–H aliphatic stretching. The C–H absorption was rather weak for compound III, and relatively strong for compound VIII, containing two and three CH_3 groups, respectively.

The differential thermal analysis of the solids showed no indication of instability up to 485°. The endotherms reported in Table I correspond to the melting points.

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