THE REACTION OF SOME NOVEL (FORMYLPHENOXY)SILANES WITH AMINES

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Several references to alkyl- and aryl-silyl derivatives of benzaldehyde[1] and salicylaldehyde[2] occur in the literature, but only one phenoxysilane bearing a formyl group, namely, (*o*-formylphenoxy)trimethylsilane[3] (I), has so far been reported. In connection with other research we were interested in the chemical behavior of certain (formylphenoxy) compounds of silicon, and this article describes the synthesis, properties, and some reactions of (I) and eleven new formylphenoxysilanes of the following structures:

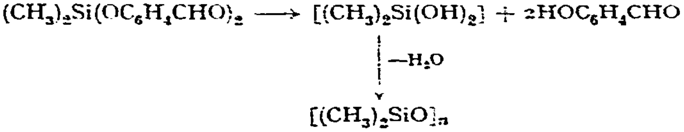
$$R_nSi(CH_3)_{4-n};\ R_2Si(CH_3)CH{=}CH_2;\ RSi(C_6H_5)_3;$$

where $R = o\text{-}, m\text{-}, p\text{-}OCHC_6H_4O\text{-}$, and $n = 1$ or 2.

(FORMYLPHENOXY)SILANES

Good yields (> 80 %) of these compounds were obtained by allowing stoichiometric amounts of the appropriate chlorosilane to react with *o*-, *m*-, or *p*-hydroxybenzaldehyde in benzene solution containing pyridine. The methyl- and methylvinylsilanes were colorless or pale straw-colored liquids which became noticeably yellow on exposure to light for several days. The corresponding phenyl-substituted silanes were colorless crystalline solids which did not discolor on exposure to light.

The methyl- and methylvinyl-silanes were rapidly hydrolyzed by moist air or water to the parent hydroxybenzaldehyde and silicon-containing oils. This behavior is similar to the cleavage reaction which occurs when (*p*-bromophenoxy)trimethylsilane is exposed to moist air[4]. The hydrolysis products were identified by determining their infrared spectra, and by forming the azines of the hydroxybenzaldehydes. The infrared spectra of the oils showed them to be methylsilicones, presumably formed as in the following example:



$$\begin{tikzcd} (CH_3)_2Si(OC_6H_4CHO)_2 \arrow[r] & {[(CH_3)_2Si(OH)_2]} + 2HOC_6H_4CHO \arrow[d, "-H_2O"] \\ & {[(CH_3)_2SiO]_n} \end{tikzcd}$$

Qualitative observations showed that the alkyl compounds were more readily cleaved

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by water than the aryl derivatives. Moreover, the ease of hydrolysis was in the order: *ortho-* $\gg$ *para-* $>$ *meta-*.

REACTIONS WITH AMINES

Although both the methyl- and phenyl-substituted formylphenoxysilanes reacted readily with hydrazine, and a wide variety of aliphatic and aromatic mono- and diamines, no silicon-containing azines or Schiff bases could be isolated. Reactions were conducted in anhydrous benzene, isopropanol, and occasionally pyridine, but the products in every case were the azines or Schiff bases of the hydroxybenzaldehydes rather than of the (formylphenoxy)silanes. Attempts to prepare phenylhydrazones, and 2,4-dinitrophenylhydrazones, of the (formylphenoxy)silanes resulted in the formation of hydroxybenzaldehyde derivatives. Even the most feebly basic amines [*e.g.* (4-aminophenyl)triphenylmethane] cleaved these silanes. It is evident, therefore, that cleavage of the Si–O–R linkage in these compounds occurs extremely readily.

EXPERIMENTAL

Bis(o-formylphenoxy)dimethylsilane

The procedure employed in the preparation of this compound is typical of that used in the synthesis of other (formylphenoxy)silanes.

A stirred mixture of salicylaldehyde (244.2 g; 2.0 moles), pyridine (158.2 g; 2.0 moles), and sodium-dried benzene (250 ml) was cooled to 5° in an ice-bath, and a solution of dimethyldichlorosilane (129.0 g; 1.0 mole) in benzene (100 ml) was added during a 30-min period at such a rate that the temperature did not exceed 20°. After the mixture had been stirred for one hour the pyridinium chloride which had separated was filtered and washed twice with dry benzene (125 ml aliquots). The benzene was then removed using a rotary evaporator, and the residual deep yellow liquid was distilled *in vacuo* using a Wood's metal bath. The fraction of b.p. 155–170°/0.25 mm was collected as 269 g (89.7 %) of straw-colored liquid which was redistilled and 210 g (70.0 %) of very pale straw-colored liquid, b.p. 162°/0.18 mm, was obtained. Prolonged exposure to light caused this compound [and other *liquid* (formylphenoxy)silanes] to turn yellow, and contact with moist air resulted in cleavage of the siloxy group.

(o-Formylphenoxy)triphenylsilane

Salicylaldehyde (12.2 g; 0.10 mole), benzene (30 ml), and pyridine (9.9 g; 0.125 mole), were added to a stirred solution of triphenylchlorosilane (29.5 g; 0.10 mole) in hot benzene (100 ml). The mixture was heated at reflux for 2 h, then cooled to room temperature. The precipitated pyridinium chloride was removed by filtration, and the filtrate was washed with water (4 × 60 ml aliquots). The solution was dried over anhydrous sodium sulfate and the benzene was removed using a rotary evaporator. An orange-colored oil remained. A few ml of isopropanol were added to this oil and, after stirring for 2–3 min, 35.0 g (92 %) of white crystals separated. This product was recrystallized from isopropanol and yielded 28.0 g (74 %) of white needles, m.p. 101° (uncorr.).

Analytical and infrared spectral data[5] on the formylphenoxysilanes are reported in Tables 1 and 2.

TABLE I

PHYSICAL DATA ON (FORMYLPHENOXY)METHYLSILANES

Structural formula	*B.p. °C/mm*	*Yield, %*	*Carbon, %*		*Hydrogen, %*		*Infrared absorption bond assignments (cm⁻¹)*							
			Calcd.	*Found*	*Calcd.*	*Found*	*-CHO*				*-CHO*	*Si–CH₃*		*Si–O–Ph*
							C–H STR	*C=O STR*	*C–H STR*	*C=C STR*	*C–C*	*C–H STR*	*Si–C STR*	
o-OCHC$_6$H$_4$OSi(CH$_3$)$_3$	62°/0.30	90	61.81	61.60	7.26	7.45	2880	1695	3080	1605 1490 1465	1398 1192 1157	2980	1258	1102
m-OCHC$_6$H$_4$OSi(CH$_3$)$_3$	62°/0.26	83	61.81	62.03	7.26	7.46	2825 2735	1703	3060	1601 1588 1489	1390 1168 1145	2970	1257	1078
p-OCHC$_6$H$_4$OSi(CH$_3$)$_3$	66°/0.20	90	61.81	62.14	7.26	7.56	2825 2735	1697	3050	1600 1512	1393 1209 1158	2970	1258	1100
(o-OCHC$_6$H$_4$O)$_2$Si(CH$_3$)$_2$	162°/0.18	88	63.97	64.09	5.37	5.55	2875	1694	3080	1606 1488 1463	1397 1192 1157	2980	1238	1102
(m-OCHC$_6$H$_4$O)$_2$Si(CH$_3$)$_2$	156°/0.25	82	63.97	63.75	5.37	5.47	2840 2755	1708	3070	1590 1490 1454	1392 1168 1147	2985	1263	1079
(p-OCHC$_6$H$_4$O)$_2$Si(CH$_3$)$_2$	171°/0.20	86	63.97	63.74	5.37	5.53	2845 2765	1702	3080	1603 1513	1393 1212 1159	2990	1256	1104
(o-OCHC$_6$H$_4$O)$_2$Si(CH$_3$)CH=CH$_2$	168°/0.18	84	65.36	65.54	5.16	5.14	2875	1696	3080	1602 1483 1461	1395 1192 1157	2980	1234	1100
(m-OCHC$_6$H$_4$O)$_2$Si(CH$_3$)CH=CH$_2$	156°/0.18	86	65.36	65.17	5.16	5.01	2840 2755	1700	3080	1588 1480 1452	1390 1166 1146	2980	1260	1080
(p-OCHC$_6$H$_4$O)$_2$Si(CH$_3$)CH=CH$_2$	177°/0.18	88	65.36	65.18	5.16	5.00	2840 2750	1702	3070	1601 1512	1391 1210 1162	2970	1252	1103

TABLE 2

PHYSICAL DATA ON (FORMYLPHENOXY)PHENYLSILANES

			Carbon, %		*Hydrogen, %*		*Infrared absorption bond assignments (cm^{-1})*				
Structural formula	*M.p. °C**	*Yield, %*	*Calcd.*	*Found*	*Calcd.*	*Found*	*-CHO* *C=O* *STR*	 *C=C* *STR*	 *-CHO* *C–C* *STR*	*Si-C_6H_5*	*Si-O-C_6H_5*
o-$OCHC_6H_4OSi(C_6H_5)_3$	101	92.0	78.91	78.85	5.30	5.27	1690	1600 1583 1485 1455	1397 1300 1188	1431 1122 698	1109 912
m-$OCHC_6H_4OSi(C_6H_5)_3$	73	87.0	78.91	79.03	5.30	5.35	1705	1590 1582 1485 1450	1389 1315 1172	1430 1117 697	1105 842
p-$OCHC_6H_4OSi(C_6H_5)_3$	117	94.0	78.91	78.72	5.30	5.31	1700	1602 1581 1508 1460	1388 1297 1210	1430 1118 696	1108 917

* Uncorrected.

Infrared spectra

Infrared spectral data in the 2.5–15.0 μ region were obtained using a Perkin-Elmer, Model 21, double-beam spectrophotometer. Spectra were determined using capillary films of liquid (formylphenoxy)silanes and Nujol mulls of (*o*-, *m*-, and *p*-formylphenoxy)-triphenylsilanes.

Hydrolysis studies

All of the liquid (formylphenoxy)silanes were hydrolyzed on contact with water or atmospheric moisture. Hydrolysis studies were conducted by exposing 25 g samples of each silane to the atmosphere for 48 h. The (*o*-formylphenoxy)silanes yielded liquid products containing salicylaldehyde which was identified by forming the azine, m.p. 213°. The (*m*- and *p*-formylphenoxy)silanes yielded white crystalline solids which were recrystallized from benzene and shown by their melting points (*m*-derivative, m.p. 106°; *p*-derivative, m.p. 116°), infrared spectra, and formation of the azines (*m*-azine, m.p. 162°; *p*-azine, m.p. 240°), to be *m*- and *p*-hydroxybenzaldehydes. Shaking the (*m*- or *p*-formylphenoxy)methylsilanes with water yielded a colorless oil which was separated and dried over anhydrous sodium sulfate. The infrared spectrum of this oil showed C–H stretch at 2970, Si–CH_3 at 1265, and Si–O at 1088–1044 cm^{-1}, indicating a methylsilicone[7]. The infrared spectrum of the oil obtained in this manner compared closely with that of an authentic methylsilicone (Dow Corning 703 Fluid).

Hydrolysis of the solid (*o*-, *m*-, and *p*-formylphenoxy)triphenylsilanes yielded the hydroxybenzaldehydes, and triphenylsilanol which was characterized by its melting point[8], 152°, and infrared spectrum (OH stretch at 3210, Si–phenyl at 1429 and 1118, and Si–OH at 852 cm^{-1})[7].

Reactions with amino compounds

(*a*) *Phenylhydrazones.* Phenylhydrazine (2.16 g; 0.02 mole) in isopropanol (5.0 ml) and (*o*-formylphenoxy)trimethylsilane (1.94 g; 0.01 mole) were heated at reflux for 30 min then refrigerated overnight. The resulting pale-yellow crystals were recrystallized from isopropanol and melted[6] sharply at 143°. Infrared and analytical data confirmed that this compound was salicylaldehyde phenylhydrazone. All other formylphenoxysilanes behaved similarly when treated with phenylhydrazine, or 2,4-dinitrophenylhydrazine, in alcohol.

(*b*) *Azines.* (*o*-Formylphenoxy)trimethylsilane (1.94 g; 0.01 mole) and hydrazine (0.15 g; 0.005 mole) in alcohol (5.0 ml) were mixed and refrigerated overnight. Salicylaldehyde azine, m.p. 215° (lit.[6] value 214°), was obtained. The azines of *m*-hydroxybenzaldehyde, m.p.[6] 162° and *p*-hydroxybenzaldehyde, m.p.[6] 240°, were similarly obtained from the (*m*- and *p*-formylphenoxy)trimethylsilanes.

(*c*) *Schiff bases.* Each of the (formylphenoxy)silanes was reacted with a variety of aliphatic and aromatic mono- and di-amines* in an attempt to produce silicon-containing Schiff bases. In every case the products isolated were the Schiff bases of the parent hydroxybenzaldehydes. Yields of products were theoretical (95–98 %).

The preparation of *N*,*N'*-bis(*o*-hydroxybenzylidene)ethylenediamine illustrates the procedure employed. Ethylenediamine (0.60 g; 0.01 mole) in isopropanol (15.0

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* Ethylenediamine, benzidine, *o*-, *m*-, and *p*-phenylenediamine, 4,4'-diaminodiphenylmethane, and 4,4'-diaminodiphenyl ether.

ml) was added to (*o*-formylphenoxy)trimethylsilane (3.88 g; 0.02 mole). The solution became bright yellow and almost immediately a yellow crystalline solid separated. The product, after recrystallizing from alcohol, melted sharply at 125° (lit.[6] value: 126–7°).

SUMMARY

The syntheses and physical properties of (*o*-formylphenoxy)trimethylsilane and eleven new methyl-, methylvinyl-, and phenyl-substituted (formylphenoxy)silanes are described. Although these compounds react readily with hydrazine, substituted hydrazines, and a number of aliphatic and aromatic mono- and di-amines, no silicon-containing azines or Schiff bases could be isolated in this study due to cleavage of the Si–O–C bond.

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