

THE PREPARATION AND PROPERTIES
OF SOME PHENOXYARYLSILANES

M. ČERNÝ

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague - Suchbát*

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The synthesis of the silanes of type *o*-, *m*-, and *p*-C₆H₅—O—C₆H₄Si(C₆H₅)₂X (X = Cl, H, CH₃, OCH₃, C₂H₅, and OC₂H₅) is reported. The phenoxy group in the *meta* position substantially decreases melting points of these compounds compared to the *ortho* or *para* derivatives. The thermal and oxidation stability of the compounds was investigated by thermogravimetric analysis.

The use of thermally and oxidation stable substances that are increasingly applied as lubricants for elevated temperatures, hydraulic, heat-transfer or high-vacuum liquids *etc.*, is among others conditioned by their liquid state at ambient temperature. Within the framework of investigation of organosilicon compounds that might find this application, it was expedient to ascertain how the phenoxy group affects melting points of some arylsilanes taken as model compounds. With tetraphenylsilane (m.p. 236.5—237°C (ref.¹)), the *ortho* and *para* substitution by one phenoxy group lowers melting point to 145—146°C (ref.²) and 165—169°C (ref.³), respectively, whilst the same group when attached to the *meta* position brings melting point down to 37°C (ref.⁴). Additional phenoxy groups, both in *ortho*, *para*, and *meta* positions do not decrease melting point significantly.

The aim of this study was to ascertain how the phenoxy group in the *ortho*, *meta* or *para* position of one phenyl group of some triphenylsilanes of the type (C₆H₅)₃.SiX (X = Cl, H, CH₃, OCH₃, C₂H₅, and OC₂H₅) affects together with expected increase of their boiling point also their melting point, volatility and oxidation stability at elevated temperatures.

The compounds under study were prepared by reaction of *o*-, *m*-, and *p*-phenoxyphenylmagnesium bromides with diphenyldichlorosilane, followed by treating the products, *o*-, *m*-, and *p*-phenoxyphenyldiphenylchlorosilanes, with methylmagnesium bromide, ethylmagnesium bromide, methanol or ethanol. *o*-, *m*-, and *p*-Phenoxyphenyldiphenylsilanes were prepared by reduction of the chlorosilanes with sodium bis(2-methoxyethoxy)aluminium hydride. The compounds prepared are presented in Table I. The purity of the above compounds was verified by NMR spectroscopy.

The effect of the introduction of the phenoxy group to the *ortho*, *meta* or *para* position of the phenyl group of the parent compound, (C₆H₅)₃SiX, is demonstrated by data given in Table I. With triphenylmethylsilane, triphenylmethoxysilane, triphenylethylsilane, and triphenylethoxysilane, the *ortho* substitution by phenoxy

TABLE I
Melting Points (°C) of *o*-, *m*-, and *p*-Phenoxyphenyldiphenylsilanes Prepared

X	Ph ₃ SiX ^a	<i>o</i> -PhOC ₆ H ₄ SiPh ₂ X	<i>m</i> -PhOC ₆ H ₄ SiPh ₂ X	<i>p</i> -PhOC ₆ H ₄ SiPh ₂ X
Cl	94-95, 97, 104-5 105-8, 110-111	97-99	<i>b</i>	<i>b</i>
H	36-37, 40-43	<i>b</i>	<i>b</i>	53.5-54.5
CH ₃	67, 69.5-69.9	96-97	64-65	47-48
C ₂ H ₅	68-70, 72-74, 76 89-91	91-92	<i>b</i>	69.5-70
OCH ₃	52-55, 54, 5-55 42-43, 55	87-88	<i>b</i>	<i>b</i>
OC ₂ H ₅	63, 65	99.0-99.5	<i>b</i>	91-92

^a Data taken from refs.^{5,6}; *b* liquid at room temperature, solidifies on cooling to a glassy mass.

group brings about a melting point increase of max. 30°C. With triphenylsilane and triphenylchlorosilane, there is a slight melting point decrease. Analogous substitution in the *para* position leads to melting point increase with triphenylsilane and triphenylethoxysilane, whilst no change is observed with triphenylethylsilane; melting point decreases with triphenylmethylsilane and triphenylmethoxysilane. Melting point depression is greatest for the *meta* derivatives, *m*-phenoxyphenyldiphenylethyl-, -ethoxy-, and -methoxysilane being liquids at room temperature. Melting point decreases only slightly upon the *meta* substitution of the phenyl group of triphenylmethylsilane with phenoxy group. In the case of triphenylsilane, the introduction of phenoxy group to the *ortho*, *meta* or *para* position leads to melting point decrease, whilst with triphenylchlorosilane this decrease is observed for the *meta* and *para* derivatives.

The thermal and oxidation stability of the compounds prepared was examined by thermogravimetric analysis, following weight loss during even heating of the sample in a stream of nitrogen or air. From Table II it is seen that in a nitrogen atmosphere the most volatile compound is *p*-phenoxyphenyldiphenylsilane, followed by *p*-phenoxyphenyldiphenylmethylsilane, the least volatile being *p*-phenoxyphenyldiphenylethoxy- and -ethylsilane. In a stream of air, *p*-phenoxyphenyldiphenylsilane undergoes oxidation decomposition under formation of a large amount of distillation residue (17%). *p*-Phenoxyphenyldiphenylmethylsilane decomposes partially to both the more and less volatile components, as indicated by the course of weight loss of the sample compared to that observed on heating in a nitrogen atmosphere. *p*-Phenoxyphenyldiphenylsilane decomposes also in air (11% residue). Of the phenoxyphenyldiphenylethylsilanes, the most volatile is the *ortho* derivative, followed by the *meta* and *para* isomer (3 and 5% residue, respectively). Summarizing, the least thermally and oxidation stable are the substances containing Si—H bond, then those containing Si—OC₂H₅ bonds, and finally those with Si—C₂H₅ bonds. Of the individual isomers, the most stable one is *p*-phenoxyphenyldiphenylethylsilane that does not decompose to 240°C.

EXPERIMENTAL

In preparing the starting compounds, *p*-phenoxybromobenzene, b.p. 162–165°/14 Torr, *m*-phenoxybromobenzene, b.p. 110–115°C/0.5 Torr, and *o*-phenoxybromobenzene, b.p. 115–117°C/0.6 Torr, m.p. 43–44°C (methanol), the great attention was paid to their purity. As *p*-phenoxybromobenzene when prepared by usual bromination of diphenyl ether, contains admixture of the *ortho* derivative⁷, it was obtained by Ullmann reaction⁸ from *p*-dibromobenzene and sodium phenolate. *o*-Phenoxybromobenzene was prepared in a similar fashion from *o*-dibromobenzene. The pure *m*-phenoxybromobenzene was synthesized in the following way. Bromination of nitrobenzene afforded *m*-bromonitrobenzene⁹ which in turn was reduced to *m*-bromoaniline¹⁰. This compound was converted by Sandmeyer reaction¹¹ to *m*-dibromobenzene which by treating with sodium phenolate¹² afforded the pure *m*-phenoxybromobenzene.

TABLE II
Amounts of Compounds (%) at Various Temperatures (°C) on Their Heating in a Stream of Nitrogen^a or Air^b

Compounds	200	220	240	260	280	300	320	340	360	380	395
<i>p</i> -Phenoxyphenyldiphenylsilane	<i>a</i>	100	99	97	94	86	71	38	5	0	—
	<i>b</i>	100	100	99	97	91	78	54	31	20	17
<i>p</i> -Phenoxyphenyldiphenylmethylsilane	<i>a</i>	100	100	99	94	84	60	24	0	—	—
	<i>b</i>	100	100	96	95	90	80	63	36	3	—
<i>p</i> -Phenoxyphenyldiphenylethoxysilane	<i>a</i>	100	99	97	94	90	78	60	35	4	—
	<i>b</i>	100	98	96	94	90	81	64	40	18	11
<i>p</i> -Phenoxyphenyldiphenylethylsilane	<i>a</i>	100	100	100	97	93	82	63	38	2	—
	<i>b</i>	100	100	100	98	95	88	72	53	21	5
<i>m</i> -Phenoxyphenyldiphenylethylsilane	<i>a</i>	100	100	99	97	90	76	50	16	4	3
<i>o</i> -Phenoxyphenyldiphenylethylsilane	<i>a</i>	100	99	98	90	81	63	28	2	0	—

The purity of all compounds was verified by gas chromatography. $^1\text{H-NMR}$ spectra were recorded on Tesla B 477 spectrometer. Melting points were determined with Koeffler hot stage microscope and are uncorrected.

The instrument for thermogravimetric analysis was made according to the scheme described in the work¹³. The procedure used was the same as in the previous work¹⁴, with the exception that the sample was heated with a rate of 6°C per min. Samples weighed 70–90 mg. It was found by calibration that for such samples the quartz spiral prolongation is proportional to their weight; with 100 mg load it was 9.4 mm.

p-Phenoxyphenyldiphenylchlorosilane. The Grignard reagent prepared from 25.2 g (0.101 mol) of *p*-phenoxybromobenzene and 2.9 g of magnesium powder in 100 ml of tetrahydrofuran was added dropwise with stirring to 38.0 g (0.15 mol) of diphenyldichlorosilane in 100 ml of benzene over a period of 20 min. The reaction mixture was heated to reflux and the solvents were partially removed by distillation. After 100 ml of dry xylene were added, solvent removal was continued until the reaction mixture temperature reached a boiling point of xylene. The mixture was then refluxed for another 2 h. The inorganic salts that precipitated during solvent removal were filtered off after cooling the mixture in an inert gas atmosphere and then were washed with benzene. The filtrate was condensed. Twofold distillation afforded 26.1 g (66.6%) of *p*-phenoxyphenyldiphenylchlorosilane, b.p. $195-198^\circ\text{C}/0.3$ Torr.

o-Phenoxyphenyldiphenylchlorosilane, b.p. $190-193^\circ\text{C}/0.5$ Torr, m.p. $97-99^\circ\text{C}$, was obtained similarly in 82% yield with the exception that the Grignard reagent was added to a xylene solution of diphenyldichlorosilane.

m-Phenoxyphenyldiphenylchlorosilane, b.p. $191-195^\circ\text{C}/0.3$ Torr, was obtained in 88% yield by the procedure used to prepare the other derivative.

p-Phenoxyphenyldiphenylsilane. *p*-Phenoxyphenyldiphenylchlorosilane (3.9 g, 0.01 mol) dissolved in benzene was reduced with an excess of 70% benzene solution of $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2.\text{OCH}_3)_2$. After 15 min boiling, the reaction mixture was cooled and decomposed with 20% sulphuric acid. The benzene layer was separated, washed with aqueous sodium hydrogen carbonate and dried with calcium chloride. Distillation afforded 3.2 g (91%) of *p*-phenoxyphenyldiphenylsilane, b.p. $186-188^\circ\text{C}/0.3$ Torr; m.p. $53.5-54.5^\circ\text{C}$ (acetone). For $\text{C}_{24}\text{H}_{20}\text{OSi}$ (352.5) calculated: 81.77% C, 5.72% H; found: 81.70% C, 6.00% H. NMR spectrum: a multiplet of aromatic protons at $\delta = 7.877$ to 6.768 , a singlet (Si—H) at $\delta = 5.626$. The structure was confirmed by spectrum integration.

o-Phenoxyphenyldiphenylsilane, b.p. $180-182^\circ\text{C}/0.5$ Torr, was obtained similarly. Found 81.46% C, 5.76% H. NMR spectrum: a multiplet of aromatic protons centered at $\delta 6.77$ and a singlet (Si—H) at $\delta = 5.6$. The integrated spectrum confirmed the above structure. Cyclohexane was used as internal standard.

m-Phenoxyphenyldiphenylsilane, b.p. $176-178^\circ\text{C}/0.3$ Torr. NMR spectrum: a multiplet of aromatic protons centered at $\delta = 6.77$, a singlet (Si—H) at $\delta = 5.10$. Internal standard was cyclohexane. Integration of the spectrum confirmed the suggested structure.

p-Phenoxyphenyldiphenylmethylsilane. An excess of methylmagnesium bromide in diethyl ether was added to a solution of 2.1 g of *p*-phenoxyphenyldiphenylchlorosilane in tetrahydrofuran. After a 3 h. heating to reflux, the reaction mixture was decomposed with dilute sulphuric acid, the ether layer was shaken with aqueous sodium hydrogen carbonate solution and dried with calcium chloride. Distillation gave 1.70 g (86%) of *p*-phenoxyphenyldiphenylmethylsilane, b.p. $195-197^\circ\text{C}/0.5$ Torr, m.p. $47-48^\circ\text{C}$ (methanol). Recorded¹⁵ b.p. $212^\circ\text{C}/0.07$ Torr and the

temperature of liquidity -2°C . For $\text{C}_{25}\text{H}_{22}\text{OSi}$ (366.5) calculated: 81.92% C, 6.05% H; found: 81.84% C, 6.21% H. Its structure was confirmed by $^1\text{H-NMR}$ spectroscopy.

o-Phenoxyphenyldiphenylmethylsilane was obtained similarly in 81% yield. B.p. $170-171^{\circ}\text{C}/0.4$ Torr, m.p. $96-97^{\circ}\text{C}$ (ethanol). Recorded¹⁵ b.p. $198^{\circ}\text{C}/0.04$ Torr and m.p. 95°C . Found: 81.96% C, 6.03% H. NMR spectrum: a multiplet of aromatic protons at $\delta = 6.435-7.686$, a singlet of $\text{Si}-\text{CH}_3$ protons at $\delta = 0.780$. Hexamethyldisilane was used in capillary tube as external standard. The spectrum integration confirmed the suggested structure.

m-Phenoxyphenyldiphenylmethylsilane was obtained similarly in 85% yield. B.p. $180-182^{\circ}\text{C}/0.3$ Torr, m.p. $64.0-65.0^{\circ}\text{C}$ (methanol). Recorded¹⁵ b.p. $196^{\circ}\text{C}/0.02$ Torr, the temperature of liquidity 4°C . Found: 81.92% C, 5.97% H.

p-Phenoxyphenyldiphenylethylsilane was obtained from *p*-phenoxyphenyldiphenylchlorosilane and ethylmagnesium bromide in 80% yield. B.p. $198-201^{\circ}\text{C}/0.5$ Torr, m.p. $69.5-70^{\circ}\text{C}$. For $\text{C}_{26}\text{H}_{24}\text{OSi}$ (380.6) calculated: 82.06% C, 6.36% H; found: 81.87% C, 6.41% H. NMR spectrum: a multiplet of aromatic protons centered at $\delta = 7.59$ and unresolved multiplet of $\text{Si}-\text{C}_2\text{H}_5$ protons centered at $\delta = 1.435$. Hexamethyldisilane was used as external standard. Integration of the spectrum confirmed the suggested structure.

o-Phenoxyphenyldiphenylethylsilane was prepared similarly in 91% yield, b.p. $173-174^{\circ}\text{C}/0.4$ Torr, m.p. $91-92^{\circ}\text{C}$ (ethanol). Found: 81.92% C, 6.18% H. NMR spectrum agreed with the suggested structure. A multiplet of aromatic protons was found at $\delta = 7.235$; unresolved multiplet of $\text{Si}-\text{C}_2\text{H}_5$ protons was located at $\delta = 1.15$. External standard was hexamethyldisilane.

m-Phenoxyphenyldiphenylethylsilane. Yield 88%, b.p. $184-186^{\circ}\text{C}/0.4$ Torr. Found: 81.84% C, 6.53% H. Its structure was confirmed by NMR spectroscopy.

p-Phenoxyphenyldiphenylmethoxysilane. A solution of the Grignard reagent prepared from 39.9 g (0.16 mol) of *p*-phenoxybromobenzene and 4.28 g (0.176 mol) of magnesium in 100 ml of diphenyl ether was added slowly with stirring to a solution of 39.8 g (0.16 mol) of diphenylmethoxychlorosilane in 250 ml of benzene. After removal of the ether by distillation, light petroleum ether was added in excess to the reaction mixture. Inorganic salts were filtered off with suction and washed with benzene. The filtrate was condensed and distilled to give 31.6 g of the product, b.p. $205-210^{\circ}\text{C}/0.5$ Torr. For $\text{C}_{25}\text{H}_{22}\text{O}_2\text{Si}$ (382.5) calculated: 7.34% Si, 78.49% C, 5.80% H; found: 7.43% Si. NMR spectrum: a multiplet of aromatic protons at $\delta = 6.516-7.739$ with maximum at $\delta = 7.172$ and a singlet methoxy protons at $\delta = 3.439$. External standard was hexamethyldisiloxane. The structure was confirmed by integration.

o-Phenoxyphenyldiphenylmethoxysilane. A solution of 3.80 g (9.83 mmol) of *o*-phenoxyphenyldiphenylchlorosilane in 10 ml of benzene was mixed with a solution of 0.64 g (20 mmol) of absolute methanol and 0.80 g (10.1 mmol) of pyridine in 10 ml of benzene. Immediately after the mixing the precipitate pyridine hydrochloride appeared. This was filtered off after standing overnight and then washed with benzene. The filtrate was condensed under reduced pressure, a distillation residue was dissolved in benzene and the hydrochloride admixture was removed by filtration. The solvents were partially evaporated and the residue distilled to give 3.1 g (82.5%) of the product, b.p. $200-210^{\circ}\text{C}/0.4$ Torr (bath temperature), m.p. $87-88^{\circ}\text{C}$ (methanol). Found: 78.35% C, 5.54% H. NMR spectrum: a multiplet of aromatic protons at $\delta = 6.222-7.812$ with maximum at $\delta = 7.213$ and a singlet of methoxy protons at $\delta = 3.515$. Integration of the spectrum confirmed the suggested structure. Internal standard was 30% solution of hexamethyldisiloxane in CCl_4 .

m-Phenoxyphenyldiphenylmethoxysilane was obtained in 86% yield in a similar fashion as the *ortho* derivative, b.p. $182-184^{\circ}\text{C}/0.4$ Torr. Found: 7.45% Si. NMR spectrum: a multiplet of aro-

matic protons centered at $\delta = 7.19$, a singlet of methoxy protons at $\delta = 3.52$. Internal standard was cyclohexane. The integral agreed with the structure suggested.

p-Phenoxyphenyldiphenylethoxysilane was obtained in 63% yield by reaction of the chlorosilane with ethanol in the presence of pyridine. M.p. 91–92°C (ethanol). For $C_{26}H_{24}O_2Si$ (396.6) calculated: 78.75% C, 6.10% H; found: 78.61% C, 6.14% H. NMR spectrum confirmed the structure.

o-Phenoxyphenyldiphenylethoxysilane was obtained in 77% yield by treating the chlorosilane with ethanol in the presence of pyridine. M.p. 99–100°C (ethanol). Found 78.98% C, 6.04% H. NMR spectrum: a triplet of methyl protons of the ethoxy group centered at $\delta = 1.435$, a quadruplet of the methylene protons centered at $\delta = 4.059$ and a multiplet of aromatic protons centered at $\delta = 7.52$. Internal standard was hexamethylsilane. Integration of the spectrum confirmed the structure.

m-Phenoxyphenyldiphenylethoxysilane was prepared similarly and obtained in 87% yield. B.p. 184–186°C/0.4 Torr. Found 78.57% C, 6.08% H. NMR spectrum: a triplet of methyl protons of the ethoxy group centered at $\delta = 1.1$, a quadruplet of the methylene protons centered at $\delta = 3.77$ and a multiplet of aromatic protons at $\delta = 7.19$. The structure was confirmed by integration of the spectrum.

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