

PREPARATION AND PROPERTIES OF SOME *o*-, *m*-, AND *p*-PHENOXYARYLSILOXANES

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The siloxanes *o*-, *m*-, and *p*- $C_6H_5OC_6H_4Si(C_6H_5)_2OSi(C_6H_5)_3$, $C_6H_5OC_6H_4Si(C_6H_5)_2-O-Si(C_6H_5)_2C_6H_4OC_6H_5$ and $C_6H_5OC_6H_4Si(C_6H_5)_2-O-Si(C_6H_5)_2-O-Si(C_6H_5)_2C_6H_4OC_6H_5$ were synthesized and their thermal and oxidation stability was measured by thermogravimetric method.

One of important properties of unsubstituted polyphenyl ethers is their low volatility and high oxidation stability, which predetermines these compounds as lubricants, hydraulic liquids for elevated temperatures, heat-transfer or high vacuum liquids, *etc.* Typical example of these compounds are polyphenyl ethers containing 4–6 aromatic rings connected with one another in the meta positions, *e.g.* *m*-bis(*m*-phenoxyphenoxy)benzene $C_6H_5OC_6H_4OC_6H_4OC_6H_4OC_6H_5$ and similar compounds. Many other compounds have their melting points or fluidity temperatures above room temperature, which limits their practical application. One of the possibilities how to decrease their melting point (fluidity temperature) is the substitution of the aromatic ring by methyl, trifluoromethyl or alkoxy groups¹. This decreases however also their thermal and oxidation stability. Somewhat more successful is the introduction of trimethylsilyl, dimethylphenylsilyl, and methyl-diphenylsilyl groups to polyphenyl ethers^{2,3}.

Within the framework of the study of thermal and oxidation stable organosilicon compounds that along with the above-mentioned applications could also be utilized as high temperature gas chromatographic stationary phases we have prepared the compounds that in contradistinction to the polysiloxanes produced industrially were chemically well defined and could have the required properties. It was evident that this aim can be achieved by excluding all the compounds which contain thermal unstable groups, *e.g.* Si—H or Si—OR bonds or methylene chains^{4,5}. Of the compounds so far known, hexaphenyldisiloxane and octaphenyltrisiloxane exhibit such properties.

Their practical use is however limited by their high melting point^{6,7} (224–224.5 and 153°C, respectively). One of the possibilities how to decrease melting point is to substitute them with one or more thermal and oxidation stable phenoxy groups. It was expected that a decrease of melting point would be accompanied by an increase of boiling point, decreasing thus volatility which especially in the case of hexaphenyldisiloxane is relatively high.

This work describes the synthesis of *o*-, *m*-, and *p*-phenoxyphenylpentaphenyldisiloxanes, 1,3-bis(phenoxyphenyl)-1,1,3,3-tetraphenyldisiloxanes and 1,5-bis(phenoxyphenyl)-1,1,3,3,5,5-hexaphenyltrisiloxanes, *i.e.* the compounds derived from hexa-

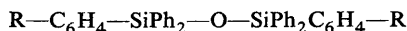
phenyldisiloxane and octaphenyltrisiloxane and containing *m*-, *o*-, or *p*-phenoxy group on one or two aromatic rings (Ph = phenyl group).



I, R = *m*-PhO

II, R = *o*-PhO

III, R = *p*-PhO



IV, R = *o*-PhO

V, R = *m*-PhO

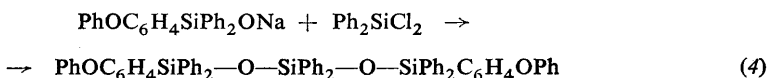
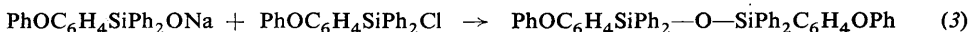
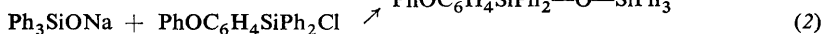
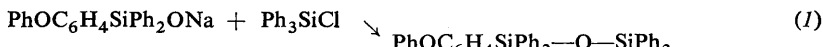
VI, R = *p*-PhO



VII, R = *m*-PhO

VIII, R = *o*-PhO

These compounds were prepared by reactions of phenoxyphenyldiphenylsilanulates with triphenylchlorosilane, phenoxyphenyldiphenylchlorosilane or diphenyldichlorosilane (equations (1)–(4)).



Thermal and oxidation stabilities were determined by the thermogravimetric analysis used earlier by us for other organosilicon compounds^{4,5}, determining the weight loss of a compound during its heating in a stream of nitrogen or air. In Table I are presented the amounts of the compounds studied in % in dependence on their heating at a given temperature in a stream of nitrogen or air. The difference due to the gas used is evident not only from the shape of the curves but also from the amount of the residue. Of the phenoxyphenylpentaphenyldisiloxanes, the *ortho* derivative is the most volatile; at 400°C 53% of the compound did not evaporate, compared to 77 and 76% in the case of *meta* and *para* derivatives, respectively. The *para* derivative was found to be the least oxidation stable (3% residue).

A similar situation has also been observed with 1,3- bis(phenoxyphenyl)-1,1,3,3-tetraphenyldisiloxanes. The most volatile was the *ortho* derivative, followed by the *para* derivative, the least volatile being the *meta* derivative, as evident from the data for temperatures above 420°C. The least oxidation stable was the *para* derivative (7% residue). 1,5-Bis(*o*- and *m*-phenoxyphenyl)-1,1,3,3,5,5-hexaphenyltrisiloxanes had similar properties. Both compounds were less volatile than the methylphenylpolysiloxane Silicone OV-17 which is recommended as a stationary phase for gas chromatography carried out at high temperatures.

Of the two trisiloxanes tested, 1,5-bis(*m*-phenoxyphenyl)-1,1,3,3,5,5-hexaphenyl-trisiloxane was more stable than the corresponding *para* derivative. As this *meta* derivative is a metastable liquid at room temperature, it can be utilized as a highly thermal stable stationary phase for gas chromatographic analyses carried out at high temperatures.

EXPERIMENTAL

The purity of the starting compounds was checked by gas chromatography. NMR spectra were measured with a Tesla BS 477 instrument. Melting points were determined with a Kofler hot stage microscope and are uncorrected.

The apparatus for thermogravimetric analysis was made in our laboratory according to the published description⁸. The procedure was the same as in our previous studies^{4,5}. The temperature was increased at a rate of 6°C per min.

m-Phenoxyphenyldiphenylsilanol. To a solution of 50 g of *m*-phenoxyphenyldiphenylchlorosilane in 100 ml of acetone, 10 ml of water and 20 ml of concentrated ammonium hydroxide solution were added. After an exothermic reaction had subsided, the reaction mixture was condensed *in vacuo* and the distillation residue was dissolved in an ether-water mixture. The ether layer was separated, dried with sodium sulphate and condensed under reduced pressure (a 50°C bath temperature). The distillation residue was dissolved in 150 ml of dry benzene and condensed at 50°C under a pressure of 0.7 Torr. A total of 46.45 g of the product were obtained which did not crystallize from any of the solvents tested and was therefore used directly in further experiments. (The sample of the silanol crystallized only after having been stored for 1 year.) After diluting 5.1 g of the sample with ethanol, 0.75 g of 1,3-bis(*m*-phenoxyphenyl)-1,1,3,3-tetra-phenylsiloxane were obtained (m.p. 158–159) which did not show melting point depression when mixed with the authentic sample. The NMR and IR spectrum of the silanol confirmed the presence of the Si—OH bonds. The *ortho* and *para* derivatives were prepared in a similar fashion.

p-Phenoxyphenyldiphenylsilanol. A total of 10.50 g (27.4 mmol) of *p*-phenoxyphenyldiphenylmethoxylane were dissolved in 25 ml of glacial acetic acid. Then 10 drops of 85% phosphoric acid were added, the solution was refluxed for 10 min and then it was diluted with 100 ml of boiling water. The oil formed was isolated by decantation, dissolved in benzene, washed with aqueous sodium hydrogen carbonate solution and dried with sodium sulphate. After solvent removal under reduced pressure, 9.4 g (95%) of the silanol were obtained as an oily compound. The NMR spectrum confirmed its structure. The band for the methoxy group was not present. After DMSO-*d*₆ was added, the OH bond disappeared.

Pentaphenyl(m-phenoxyphenyl)disiloxane (I). To 5.8 g (15.7 mmol) of *m*-phenoxyphenyldiphenylsilanol dissolved in 60 ml of absolute ether, 1.2 g of the sodium cut to small pieces were added and the mixture was refluxed under an inert atmosphere for 3 h. (After that time hydrogen evolution ceased.) Then the unreacted sodium was removed and a solution of 4.27 g (14.5 mmol) of triphenylchlorosilane in 100 ml of tetrahydrofuran was added.

The reaction mixture was freed of the ether by distillation and after addition of 100 ml of benzene the solvents were distilled-off until the temperature on the top of the column did not raise to 76°C. The mixture was then refluxed for 2 h, cooled, diluted with the ether and decomposed with water. The organic layer was separated, dried with calcium chloride and condensed. Crystallization from benzene gave 8.8 g of the product which was redistilled, b.p. 296–310°C (bath)/0.4

Torr; m.p. 157–158°C (benzene–ethanol). The IR spectrum confirmed the presence of the Si—O—Si bond. For $C_{42}H_{34}Si_2O_2$ (626.9) calculated: 80.47% C, 5.47% H 8.96% Si; found: 80.58% C, 5.62% H.

Pentaphenyl(o-phenoxyphenyl)disiloxane (II) was prepared similarly as the *meta* derivative in 91% yield. B.p. 304–310°C (bath temp.)/0.4 Torr, m.p. 143–144°C (benzene–ethanol). Found: 80.90% C, 5.61% H, 8.82% Si.

Pentaphenyl(p-phenoxyphenyl)disiloxane (III) was prepared in a similar way as the *meta* derivative, the reaction mixture was refluxed, however, for 7 h. B.p. 295–305°C (bath)/0.3 Torr, m.p. 95–96°C (benzene–ethanol). The analysis showed that this compound is not pure. The sample was subjected to gel chromatography (the solvent tetrahydrofuran, a 8 m — column packed with styrene–divinylbenzene copolymer). On using 0.1% acetic acid in tetrahydrofuran as an eluent the elution volumes of the *ortho* and *para* isomers were 237.6 and 231.8 ml, respectively.

1,3-Bis(o-phenoxyphenyl)-1,1,3,3-tetraphenyldisiloxane (IV). A solution of 3.40 g (8.79 mmol) of *o*-phenoxyphenyldiphenylchlorosilane in benzene was added to the sodium silanolate prepared from 3.46 g (9.39 mmol) of *o*-phenoxyphenyldiphenylsilanol and sodium in ether. The ether

TABLE I
Amounts of Compounds I–VIII in % at Various Temperatures on Their Heating in a Stream of Nitrogen or Air

Compound		300	320	340	360	380	400	420	440	460	480	500	520
I	^a	100	98	96	92	86	77	57	25	1	0	—	—
	^b	99	97	94	89	80	64	36	2	0	—	—	—
II	^a	96	94	90	84	73	53	26	5	0	—	—	—
	^b	98	95	92	86	77	59	39	5	0	—	—	—
III	^a	98	97	95	92	86	76	59	25	3	0	—	—
	^b	98	97	95	90	85	67	39	4	3	3	3	3
IV	^a	100	99	98	95	90	80	67	41	13	0	—	—
	^b	100	98	97	94	90	80	66	38	7	3	3	3
V	^a	100	98	97	96	94	90	84	72	52	24	0	—
	^b	98	97	97	96	93	88	82	70	46	7	3	3
VI	^a	99	98	96	95	92	86	77	62	39	1	0	—
	^b	97	96	95	93	92	88	82	71	52	25	9	7
VII	^a	100	100	100	99	98	95	90	86	78	64	31	0
	^b	100	99	97	96	95	94	92	86	78	64	41	17 ^c
VIII	^a	100	100	99	99	97	95	90	83	72	54	31	1 ^d
	^b	100	99	99	98	97	95	93	87	78	56	18	11 ^e
Silicone OV-17	^a	98	97	95	95	94	91	86	75	53	27	8	3

^a In an atmosphere of nitrogen; ^b in air; ^c at 535°C: 17%; ^d at 525°C: 0%; ^e at 510°C: 11%.

was distilled-off and the reaction mixture was heated to boiling point for 6 h. After decomposition with water, the benzene layer was separated and condensed. Crystallization of the distillation residue from a benzene-ethanol mixture afforded 5.8 g (92%) of the product which was redistilled, b.p. 325–330° (bath)/0.4 Torr. M.p. 193–194°C. For $C_{48}H_{38}O_3Si_2$ (719.0) calculated: 80.19% C, 5.33% H; found: 80.05% C, 5.33% H.

1,3-Bis(*m*-phenoxyphenyl)-1,1,3,3-tetraphenyldisiloxane (V) was obtained in 81% yield, b.p. 330–340°C (bath)/0.4 Torr, m.p. 162–163°C (benzene-ethanol). Found: 80.39% C, 5.41% H.

1,3-Bis(*p*-phenoxyphenyl)-1,1,3,3-tetraphenyldisiloxane (VI) was obtained in 82% yield, b.p. 340–350°C (bath)/0.4 Torr, m.p. 182.5–183.5°C (benzene-ethanol). Found: 80.28% C, 5.46% H.

1,5-Bis(*m*-phenoxyphenyl)-1,1,3,3,5,5-hexaphenyltrisiloxane (VII). To a solution of the sodium silanolate prepared from 10.10 g (27.4 mmol) of *m*-phenoxyphenyldiphenylsilanol and sodium in 100 ml of ether, a solution of 3.05 g (12.1 mmol) of diphenyldichlorosilane in benzene was added, the ether was removed by distillation and the mixture was refluxed for 6 h. Then 100 ml of absolute toluene were added and after removal of ether and benzene by distillation, the mixture was refluxed for another 7 h. After cooling and decomposition with water, the toluene layer was dried with calcium chloride and condensed under vacuum, giving 11.0 g of an oily product, b.p. 360–370°C (bath)/0.4 Torr. For $C_{60}H_{48}O_4Si_3$ (917.3) calculated: 78.56% C, 5.27% H; found: 78.46% C, 5.28% H.

1,5-Bis(*o*-phenoxyphenyl)-1,1,3,3,5,5-hexaphenyltrisiloxane (VIII) was prepared similarly as the meta isomer, b.p. 360°C (bath)/0.4 Torr, m.p. 114–115°C benzene-ethanol. Found: 78.58% C, 5.11% H.

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