mixture poured on ice. The mixture was filtered to remove arsenic trioxide and the organic layer was separated and washed with water and dilute sodium bicarbonate solution. Evaporation of the methylene chloride left pentaerythritol acetate trinitrate, 5.7 g. (97%), m.p. 86–87°. One recrystallization from ethanol gave 5.0 g. of product, m.p. 87–88°, reported 87–88°.[4]

Preparation of pentaerythritol p-toluenesulfonate trinitrate. The procedure outlined for the nitration of pentaerythritol arsenite acetate was followed using 0.3 g. of urea, 30 ml. of nitric acid, and 3.0 g. of pentaerythritol *p*-toluenesulfonate arsenite. Two recrystallizations of the product from methanol gave pentaerythritol *p*-toluenesulfonate trinitrate, 2.97 g., m.p. 96–98°, reported 97–100°.[4]

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, SCIENTIFIC LABORATORY OF THE FORD MOTOR COMPANY]

Preparation, Properties, and Infrared Spectra of 2,6-Disubstituted Phenoxysilanes

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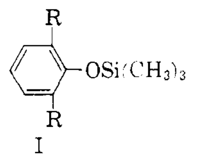
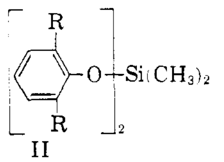
Two series of 2,6-disubstituted-phenoxy di- and trimethylsilanes in which the 2,6-substituents are H—, CH_3—, and $(CH_3)_2$-CH— groups are reported. Attention is called to the intense absorption band in the 10–11 μ region of the infrared absorption spectra of these compounds that appears to be characteristic of the Si-O-phenyl linkage.

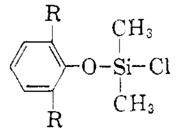
In conjunction with studies on improving the thermal and hydrolytic stability of some organosilicon compounds, two series (I and II) of 2,6-disubstituted-phenoxy silanes were prepared. An additional chloro-derivative, IIIc, was also prepared as an intermediate for conversion to a disiloxane derivative. Only two of the compounds reported here, Ia[1] and IIa[2,3] have been reported in the literature.



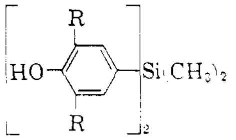
I



II



III



IV

a. R = H—
b. R = CH_3—
c. R = $(CH_3)_2CH$—

The phenoxy silanes were prepared by first converting the respective phenol to its bromomagnesium salt (reacting the phenol with methylmagnesium bromide in tetrahydrofuran) followed by treating this intermediate with dimethyldichlorosilane or trimethylchlorosilane. For laboratory-scale preparations this procedure was found more expedient than the conventional methods of preparing the alkali metal phenoxides, especially in the case of the more hindered phenols.

Di-*tert*-butylphenol, when subjected to this sequence of reactions, failed to yield a silicon derivative and the starting materials were recovered. Due to steric factors it was initially anticipated that the product would have structure IV rather than II in accord with the work of Coffield, Filbey, Ecke, and Kolka[4] on 2,6-disubstituted phenoxides. Very recently, however, Kornblum and Lurie[5] have shown that a new factor, homogeneity *vs.* heterogeneity, is of paramount importance in this type reaction. Oxygen alkylation is obtained in homogeneous solutions and the truly heterogeneous reaction gives exclusively carbon alkylation. This factor correlates well with Coffield's[4] work and also the findings reported here. Our reaction mixtures were homogeneous and we obtained only oxygen alkylation.

Several attempts were made to hydrolyze IIIc to the corresponding silanol for subsequent conversion to the disiloxane; however, hydrolytic cleavage of the 2,6-diisopropylphenoxy group occurred simultaneously.

The physical properties of the various derivatives reported here are summarized in Table I.

Infrared absorption spectra. The infrared spectra of the derivatives reported here were recorded on a Perkin-Elmer Infracord, Model 137 in the 2.5–15.0 μ region. All spectra were taken from capillary films between sodium chloride windows with the exception of bis(2,6-diisopropylphenoxy)dimethylsilane (IIc), which was prepared as a Nujol mull. The spectra are reproduced in Figs. 1 and 2.

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[1] S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

[2] P. D. George and A. E. Newkirk, U. S. Patent 2,837,552 (1958).

[3] E. Larsson, *Chem. Ber.*, **86**, 1382 (1953).

[4] T. H. Coffield, A. H. Filbey, G. G. Ecke, and A. J. Kolka, *J. Am. Chem. Soc.*, **79**, 5019 (1957).

[5] K. Kornblum and A. P. Lurie, *J. Am. Chem. Soc.*, **81**, 2705 (1959).

TABLE I

PHYSICAL PROPERTIES OF 2,6-DISUBSTITUTED-PHENOXYSILANES

Silane	M.P. (°C.)	B.P. (°C.)/mm.	d_4^{25}	n_D^{20}	Yield, %
Ia	-55^a	113/94	0.9209	1.4782	58
Ib	-44^a	127/50	0.9228	1.4862	74
Ic	-12.4^a	154/50	0.9015	1.4838	74
IIa	-23^a	104–106/0.8	$1.0599^{27.5}$	1.5330	79.9
IIb	37.0–38.0	130–131/0.2–0.3	. . .	1.5320^b	80.1
IIc	89.0–89.5	142–146/0.15	. . .	. . .	74.4
IIIc	. . .	66–67/0.4–0.45	. . .	1.4925	20.3

[a] Freezing point from cooling curves. [b] Supercooled liquid.

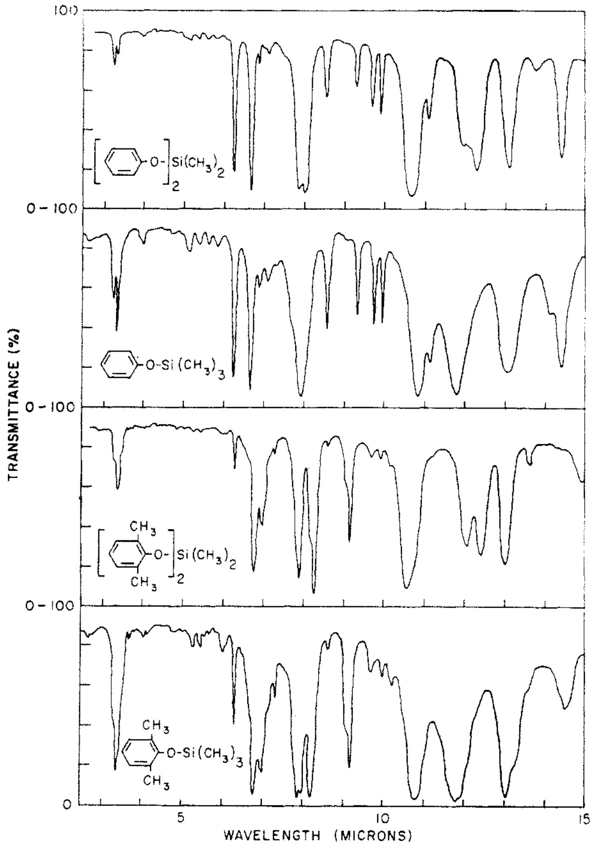

Fig. 1. Absorption spectra of phenoxy silanes

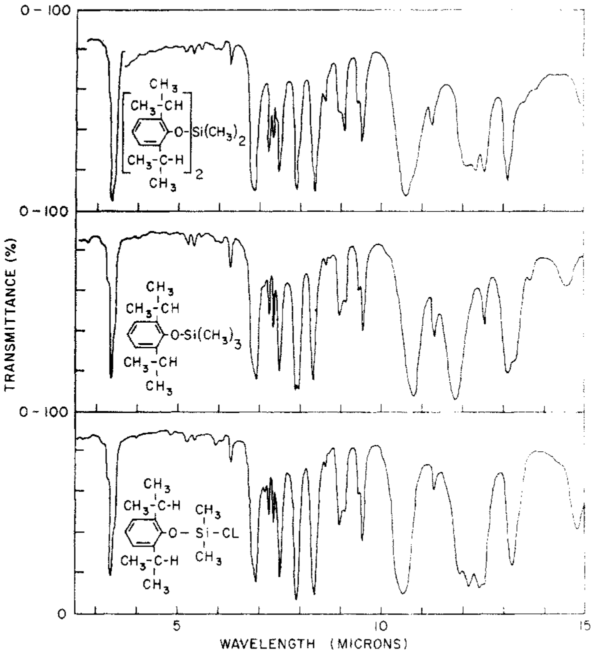

Fig. 2. Absorption spectra of phenoxy silanes

The spectra are somewhat complicated by the fact that absorptions characteristic of organosilicon bonds occur in the same regions as those characteristic of the parent phenols. One exception, however, is noted in the 10.0–11.0 μ region where a very intense and slightly broadened band appears in all the spectra reported here. The intensity of this band is the same in all these derivatives but varies in wave length, depending upon the substitution—the dimethylsilyl derivatives absorb at somewhat shorter wave lengths than the respective trimethylsilyl derivatives. This same intense band also occurs in the spectrum of phenyl silicate at 10.3 μ. In view of the paucity of spectra of phenoxy silanes in the literature, we are wondering if this strong absorption band is characteristic of the Si—O—phenyl linkage. The absorption band often associated with the Si—O—C linkage has been assigned to the 9.2 μ region by Stuart, laLau, and Breederveld[6] from their investigations of alkoxytrichlorosilanes and to the 9.5–9.65 region by Kreshkov, Mikhailenko, and Yakimovich[7] from their investigations of alkyl silicates and phenyl silicate—unfortunately the latter investigators studied only the 2–10 μ region. Certain alkoxy silanes, such as ethyl silicate, diethoxydimethylsilane, ethoxytrichlorosilane, and the ethoxy- and methylethoxysilicones also exhibit strong absorptions in the 10.0–11.0 μ region, however; Okawara[8] has assigned these absorptions to the ethyl group.

The 8.0 μ region of the spectra (characteristic of the Si—CH_3 linkage) of these derivatives is complicated by the equally intense and sharp absorption of the phenyl—O linkage. In several derivatives this band appears as equally intense doublets depending upon the degree of substitution. A similar phenomenon was also noted by Dahlgard

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(6) A. A. V. Stuart, C. laLau, and H. Breederveld, *Rec. trav. chim.*, **74**, 747 (1955).

(7) A. P. Kreshkov, Yu. Ya. Mikhailenko, and G. F. Yakimovich, *Zhur. Fiz. Khim.*, **28**, 537 (1954).

(8) R. Okawara, *Bull. Chem. Soc., Japan*, **31**, 154 (1958).

and Brewster[9] in their studies on *ortho*-substituted diphenyl ethers.

The 11.6–14.3 μ region of the spectra (characteristic of the Si—C linkage) is equally complicated by aromatic absorption bands.

The absence of hydroxy absorptions in the 2.7–3.0 μ region of these spectra supports the fact that these derivatives are phenoxy-substituted silanes and not hydroxyphenyl-substituted silanes.

EXPERIMENTAL

General procedure. All reactions were carried out under a dry nitrogen atmosphere and the sequence of reactions was the following:

A molar solution of the phenol in tetrahydrofuran was prepared in a flask equipped with a stirring assembly, condenser, dropping funnel, and a nitrogen inlet. To the solution was added an equivalent molar quantity or slight excess of ethereal three molar methylmagnesium bromide. After a short reflux period, the appropriate chlorosilane, dimethyldichloro- or trimethylchlorosilane, was added.

The reaction mixture was then refluxed for a short time, cooled, diluted with benzene, toluene, or a hydrocarbon, concentrated to remove any unreacted chlorosilane and ethereal solvent, then filtered to remove the magnesium halides formed. The filtrate was then fractionated at reduced pressures.

Due to the almost identical boiling points of the phenols and their trimethylsilyl derivatives, these filtrates were treated with metallic sodium or methylmagnesium bromide in order to retain the phenol present during the distillation.

Phenoxytrimethylsilane (Ia). The yield of Ia from 94.1 g. (1 mole) of phenol, 1.29 moles of methylmagnesium bromide, and 1.43 moles of trimethylchlorosilane was 96.6 g. (58% yield): b.p. 110° (90 mm.); f.p. −55°; d_4^{25} 0.9209, n_D^{20} 1.4782. (Langer[1] lists b.p. 181.9–182.4; d_4^{25} 0.9209; n_D^{20} 1.4782.)

Anal. Calcd. for $C_9H_{14}SiO$: C, 65.01; H, 8.49; Si, 16.88. Found: C, 64.95; H, 8.44; Si, 16.92.

2,6-Dimethylphenoxytrimethylsilane (Ib). The yield of Ib from 122.2 g. (1 mole) of 2,6-dimethylphenol, 1.33 moles of methylmagnesium bromide, and 200 ml. (1.58 moles) of trimethylchlorosilane was 144.2 g. (74% yield): b.p. 120° (43 mm.); f.p. −44°; d_4^{25} 0.9228; n_D^{20} 1.4862.

Anal. Calcd. for $C_{11}H_{18}SiO$: C, 67.99; H, 9.34; Si, 14.44. Found: C, 68.25; H, 9.22; Si, 14.74.

2,6-Diisopropylphenoxytrimethylsilane (Ic). The yield of Ic from one mole quantities of 2,6-diisopropylphenol, methylmagnesium bromide, and trimethylchlorosilane was 184 g. (74% yield): b.p. 154° (50 mm.); f.p. −12.4°; d_4^{25} 0.9015; n_D^{20} 1.4838.

Anal. Calcd. for $C_{15}H_{26}SiO$: C, 71.94; H, 10.47; Si, 11.20. Found: C, 72.14; H, 10.46; Si, 11.30.

Diphenoxydimethylsilane (IIa). The yield of IIa from 226 g. (2.4 moles) of phenol, 800 ml. of 3*M* methylmagnesium bromide, and 154.9 g. (1.2 moles) of dimethyldichlorosilane was 234.3 g. (79.9% yield): b.p. 104–106° (0.8 mm.) and 93–94° (0.15 mm.); f.p. −23°; d_4^{25} 1.0599; n_D^{20} 1.5330. (George and Newkirk[2] list b.p. 206° (100 mm.); d_{20} 1.063; n_D^{20} 1.5335.)

Anal. Calcd. for $C_{14}H_{16}O_2Si$: C, 68.82; H, 6.60; Si, 11.48. Found: C, 68.92; H, 6.20; Si, 11.60.

Bis(2,6-dimethylphenoxy)dimethylsilane (IIb). The yield of IIb from 293.3 g. (2.4 moles) of 2,6-dimethylphenol, 2.4 moles of methylmagnesium bromide, and 159.9 g. (1.2 moles) of dimethyldichlorosilane was 288.7 g. (80.1% yield): b.p. 130–131° (0.2–0.3 mm.); m.p. 37–38°; n_D^{20} 1.5320 (supercooled).

Anal. Calcd. for $C_{18}H_{24}O_2Si$: C, 71.96; H, 8.05; Si, 9.34. Found: C, 71.91, 72.14; H, 7.99, 8.19; Si, 9.24, 9.11.

Bis(2,6-diisopropylphenoxy)dimethylsilane (IIc). The yield of IIc from 178.3 g. (1.0 mole) of 2,6-diisopropylphenol, 1.05 moles of methylmagnesium bromide, and 64.5 g. (0.50 mole) of dimethyldichlorosilane was 154.0 g. (74.7% yield) after recrystallizing from denatured ethanol: b.p. 142–146° (0.15 mm.); m.p. 89.0–89.5°.

Anal. Calcd. for $C_{22}H_{40}O_2Si$: C, 75.76; H, 9.77; Si, 6.80. Found: C, 76.10, 75.95; H, 9.71, 9.89; Si, 6.60, 6.52.

2,6-Diisopropylphenoxydimethylchlorosilane (IIIc). A solution of bromomagnesium-2,6-diisopropylphenoxide, prepared from 178.3 g. (1.0 mole) of 2,6-diisopropylphenol and 1.05 moles of methylmagnesium bromide in tetrahydrofuran, was added to a second solution of 258 g. (2.0 moles) of dimethyldichlorosilane in tetrahydrofuran. The yield of IIIc was 55.0 g. (20.3% yield): b.p. 66–67° (0.4–0.45 mm.); n_D^{20} 1.4925.

Anal. Calcd. for $C_{14}H_{23}OSiCl$: C, 62.08; H, 8.56; Si, 10.36; Cl, 13.09. Found: C, 61.76; H, 8.48; Si, 10.59; Cl, 13.58.

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[9] M. Dahlgard and R. Brewster, *J. Am. Chem. Soc.*, **80**, 5861 (1958).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, SMITH KLINE AND FRENCH LABORATORIES AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS]

Reaction of Epoxides with 2-Aminobenzenethiol

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Reaction of ethylene oxide, cyclopentene oxide, and styrene oxide with 2-aminobenzenethiol anion has been found to give the corresponding 2-aminophenyl-2-hydroxyethyl sulfides. With styrene oxide, the product is a mixture of 2-aminophenyl-2-hydroxy-1-phenylethyl sulfide and 2-aminophenyl-2-hydroxy-2-phenylethyl sulfide. 2-Aminobenzene thiol in basic solution effects debromination of *trans*-1,2-dibromocyclohexane to give an almost quantitative yield of cyclohexene.

In 1949, Culvenor and co-workers[2] reported that the reaction of 2-aminobenzenethiol anion with ethylene oxide, cyclohexene oxide, styrene oxide, and benzoylphenylethylene oxide, respectively, afforded in every case the corresponding dihydrobenzo-1,4-thiazine [2,3-dihydrobenzo-1,4-thiazine

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(1) Smith Kline and French Laboratories.

(1a) University of Kansas.

(2) C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 278 (1949).