

A Preparative, Refractometric and Spectrophotometric Investigation of Some Phenoxysilanes

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The synthesis of phenoxyalkoxysilanes by various methods was studied. The refractometric properties and ultraviolet absorption spectra of the compounds prepared were measured. From the results obtained it was possible to draw certain conclusions concerning the charge distribution in the phenoxysilanes.

As an extension of previous studies of various types of silanes and siloxanes¹ an investigation of some phenoxysilanes, including phenoxyethoxysilanes, phenoxyethoxysilanes and tetraphenoxysilane from a preparative, refractometric, and spectrophotometric point of view is now reported.

PREPARATION OF PHENOXYSILANES

Several methods were tried. The first one involved the reaction between a phenoxychlorosilane and an alcohol, the second a controlled disproportionation of a phenoxyalkoxysilane, and in the third a tetraalkoxysilane was allowed to react with phenol in the presence of sodium phenoxide as a catalyst.

Method 1. Chlorosilanes usually react easily with alcohols with the exchange of alkoxy groups for chlorine. Thus the principal reaction product between a phenoxychlorosilane and an alcohol might be expected to be the corresponding phenoxyalkoxysilane. However, if the synthesis is made in the absence of an acceptor for hydrogen chloride this is by no means the case. Table 1 summarizes some preparations according to method 1. In run No. 1, mainly phenoxytrimethoxysilane and tetraphenoxysilane were formed in a reaction between diphenoxydichlorosilane and methyl alcohol. Thus a considerable disproportionation took place.

The effect of a base is demonstrated in run No. 2. Here the synthesis in No. 1 was repeated using pyridine as an acceptor for the hydrogen chloride. Disproportionation was diminished appreciably and the yield of the required diphenoxydimethoxysilane increased from 5 to 47 %. To obtain a reasonable yield of triphenoxymethoxysilane from triphenoxychlorosilane and methyl

Table 1. Preparation of phenoxymethoxysilanes and tetraphenoxysilane from phenoxychlorosilanes and methyl alcohol.

No.	Starting material (mole)	Products **				Conditions
		$C_6H_5OSi(OCH_3)_2$	$(C_6H_5O)_2Si(OCH_3)_2$	$(C_6H_5O)_3SiOCH_3$	$(C_6H_5O)_4Si$	
1*	$(C_6H_5O)_2SiCl_2(0.14) + CH_3OH(0.31)$	51	5	2	33	Without solvent. Refluxing for 20 min. after addition of the alcohol.
2*	$(C_6H_5O)_2SiCl_2(0.14) + CH_3OH(0.31) + C_2H_5N(0.31)$	12	47	4	8	Solvent carbon tetrachloride. Temp. 50–60°.
3	$(C_6H_5O)_3SiCl(0.10) + CH_3OH(0.12) + C_2H_5N(0.12)$	5	30	12	40	As in No. 2.
4	$(C_6H_5O)_3SiCl(0.10) + CH_3OH(0.12) + C_2H_5N(0.12)$	2	16	54	22	Solvent carbon tetrachloride. Temp. 0–4°.

* Some tetramethoxysilane was also formed in these syntheses.

** Mol.-% calculated on the chlorosilane used as starting material.

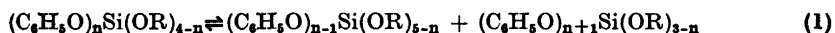
Table 2. Preparation of phenoxymethoxysilanes and tetraphenoxysilane from tetraalkoxysilanes or phenoxymethoxysilanes and phenol.

No.	Starting material (mole)	Products *					Conditions
		$(RO)_4Si$	$C_6H_5OSi(OR)_2$	$(C_6H_5O)_2Si(OR)_2$	$(C_6H_5O)_3SiOR$	$(C_6H_5O)_4Si$	
1	$(CH_3O)_4Si(0.5) + C_6H_5OH(0.5)$	61	16	4	1	18	Sodium phenoxide as catalyst
2	$(C_2H_5O)_4Si(0.5) + C_6H_5OH(0.5)$	26	56	4	0	7	—
3	$C_6H_5OSi(OC_2H_5)_2(0.2) + C_6H_5OH(0.2)$	0	34	33	1	25	—
4	$(C_2H_5O)_4Si(0.3) + C_6H_5OH(0.1)$	10	71	13	0	0	—
5	$(C_2H_5O)_4Si(0.3) + C_6H_5OH(0.1)$	80	13	0	0	0	Without catalyst

* Mol.-% calculated on the silane used as starting material. In Nos. 4 and 5 the yield was calculated on 0.1 mole of the silane. R denotes methyl or ethyl depending on the starting material.

alcohol, however, it was not sufficient to absorb the hydrogen chloride but also necessary to carry out the reaction at a low temperature (*cf.* runs Nos. 3 and 4). A possible explanation of this fact will be given later in this paper.

Method 2. To examine the cause of the disproportionation of the phenoxyalkoxysilanes in the syntheses above some experiments were carried out. It was found that phenoxyalkoxysilanes could be heated, without appreciable change, in the presence of dry hydrogen chloride or small amounts of an alcohol or water. The simultaneous presence of hydrogen chloride and a hydroxylic compound, however, caused a disproportionation*. Furthermore it was found that the disproportionation could be controlled by using suitable conditions (see the experimental part). Thus it was possible from one phenoxyalkoxysilane to prepare the two "neighbours".



Method 3. The reaction between tetramethoxysilane and tetraethoxysilane, respectively, and phenol in equimolecular quantities and in the presence of sodium phenoxide is demonstrated by runs Nos. 1 and 2 of Table 2. The fact that a considerable part of the tetraalkoxysilanes remains after completion of the reaction and the formation of substantial amounts of tetraphenoxy silane indicates a ready reaction of the phenoxyalkoxysilanes with the phenoxide ion under the prevailing conditions. The same conclusion may be drawn from run No. 3, where phenoxytriethoxysilane and phenol were allowed to react in the molar ratio 1:1. Furthermore from the figures in runs Nos. 1, 2, and 3 it is evident that the reactivity of a silane $(C_6H_5O)_nSi(OR)_{4-n}$ increases when n increases from 1 to 3 and is greater for $R = CH_3$ than for $R = C_2H_5$. The low yield of triphenoxyalkoxysilanes in all instances is noteworthy. Obviously these compounds, when formed, immediately react with phenoxide ion to tetraphenoxy silane.

To get a good yield of a particular phenoxyalkoxysilane from the alkoxy silane with one phenoxy group less, and phenol, it was necessary to use the alkoxy silane in excess (*cf.* run No. 4). A suitable inert diluent should also serve. In this way the formation of higher phenoxyalkoxysilanes was suppressed to a great extent. In the absence of a catalyst the exchange of phenoxy groups for alkoxy groups proceeded slowly and with a low yield of phenoxyalkoxysilanes (*cf.* run No. 5)**.

The boiling points and analyses of the compounds prepared in this investigation are given in Table 3.

* Similar experiences were made by Peppard *et. al.*³ with mixed tetraalkoxysilanes.

** A new procedure for the alkoxylation of halosilanes using alkyl orthoformates was recently described by Shorr². An attempt was made to prepare diphenoxydiethoxysilane by this method. However, an impure product was obtained (see the experimental part).

EXPERIMENTAL

Phenoxy-methoxysilanes from phenoxychlorosilanes and methyl alcohol (Method 1).

Phenoxychlorosilanes. Jörg and Stetter⁴ prepared diphenoxydichlorosilane and triphenoxychlorosilane by adding silicon tetrachloride to molten phenol and then heating the mixture. They attempted, without success, to prepare phenoxytrichlorosilane by this method. Thompson and Kipping⁵ added a solution of phenol in benzene to boiling silicon tetrachloride whereupon the mixture was heated to 200° for three to four hours. By this method all three of the phenoxychlorosilanes were obtained. The diphenoxy- and triphenoxychlorosilanes were obtained by Vol'nov⁶ in a reaction between phenyl acetate and silicon tetrachloride. A modification of the Thompson and Kipping procedure was used in the work described in this paper.

Phenol (23.5 g, 0.25 mole) was dissolved in 60 ml of dry toluene and the solution added to 42.5 g (0.25 mole) of silicon tetrachloride with rapid stirring. The mixture was heated to 100° for one hour, the toluene and some unchanged silicon tetrachloride were removed and the residue fractionated in vacuum. There was obtained 25.0 g (44 %) of phenoxytrichlorosilane, 10.5 g (15 %) of diphenoxydichlorosilane and 6.3 g (7 %) of triphenoxychlorosilane. The yield of the various phenoxychlorosilanes is dependent on the ratio of phenol to silicon tetrachloride, the amount of solvent used, and the heating time. By using suitable conditions it is possible to obtain any of the phenoxychlorosilanes as the principal product.

The boiling points of the phenoxychlorosilanes were: phenoxytrichlorosilane 70° (9 mm), diphenoxydichlorosilane 156–157° (13 mm), and triphenoxychlorosilane 210–212° (9 mm). Their purity was ascertained by chlorine analyses.

Phenoxy-methoxysilanes (Table 1). In run No. 1 the methyl alcohol was dropped into diphenoxydichlorosilane and the mixture heated to 60–70° for 20 minutes. Fractionation yielded tetramethoxysilane, phenoxy-methoxysilanes and a residue of tetraphenoxy-silane which was recrystallized from petroleum ether.

When pyridine was used as hydrogen chloride acceptor (runs Nos. 2 and 3) the phenoxychlorosilane was dissolved in carbon tetrachloride and the mixture of methyl alcohol and pyridine then added by stirring. The temperature rose to 50–60° during the addition. The precipitate of pyridine hydrochloride was filtered with the exclusion of moisture and washed with carbon tetrachloride; the solvent was distilled off at atmospheric pressure and the residue treated as above. In run No. 4 the heat of reaction was dissipated by cooling the reaction mixture with icewater during the addition of the methyl alcohol-pyridine mixture and the removal of the solvent was carried out at 30–35° (180 mm).

Disproportionation of phenoxyalkoxysilanes (Method 2).

As an example of the application of this method the preparation of phenoxytrimethoxysilane and triphenoxy-methoxysilane from diphenoxydimethoxysilane is described.

To 27.6 g (0.1 mole) of diphenoxydimethoxysilane was added one drop of methyl alcohol. A stream of dry hydrogen chloride was bubbled through the mixture with simultaneous refluxing for one hour. Fractionation furnished 4.3 g (0.02 mole) or 20 % of phenoxytrimethoxysilane, 13.8 g (0.05 mole) or 50 % of diphenoxydimethoxysilane, and 7.1 g (0.021 mole) or 21 % of triphenoxy-methoxysilane. A small residue of tetraphenoxy-silane remained in the distillation flask. If the conversion of the diphenoxydimethoxysilane is restricted to about 50 % almost no tetramethoxysilane and tetraphenoxy-silane are obtained.

Phenoxy-silanes from alkoxysilanes and phenol (Method 3)*.

The alkoxysilane and phenol were mixed and a small amount of sodium added which dissolved as sodium phenoxide. Slow distillation, about 8 hours per mole of alcohol,

* This method was previously used by Malatesta⁷ for the preparation of tetraphenoxy-silane from tetraethoxysilane and phenol.

Table 3. Boiling points and analyses.

Compound *	B. p. °C (mm)	% H		% Si	
		Found	Calcd.	Found	Calcd.
$C_6H_5OSi(OCH_3)_2$	102 (12)	6.61	6.59	13.2	13.11
$C_6H_5OSi(OC_2H_5)_2$	121 (12)	7.86	7.86	11.1	10.96
$(C_6H_5O)_2Si(OCH_3)_2$	160 (9)	5.89	5.84	10.2	10.16
$(C_6H_5O)_2Si(OC_2H_5)_2$	170 (9)	6.55	6.62	9.23	9.23
$(C_6H_5O)_3SiOCH_3$	140 (0.2)	5.41	5.36	8.23	8.30
$(C_6H_5O)_4Si$ **	—	5.10	5.03	6.94	7.01

* All compounds except tetraphenoxysilane are new.

** M. p. 52—53°.

Table 4. Densities, refractive indices and molar refractions.

Compound	Mol. wt	d_4^{20}	n_D^{20}	n_F^{20}	n_g^{20}	MRC	MR_D	MR_F	MRg
$C_6H_5OSi(OCH_3)_2$	214.29	1.1056	1.45767	1.46944	1.47631	52.85	53.19	54.02	54.70
$C_6H_5OSi(OC_2H_5)_2$	256.37	1.0283	1.44943	1.46027	1.46655	66.93	67.33	68.32	69.12
$(C_6H_5O)_2Si(OCH_3)_2$	276.36	1.1420	1.51018	1.52562	1.53474	72.40	72.92	74.24	75.31
$(C_6H_5O)_2Si(OC_2H_5)_2$	304.41	1.0937	1.49999	1.50409	1.52300	81.86	82.43	83.86	85.02
$(C_6H_5O)_3SiOCH_3$	338.42	1.1626	1.54340	1.54833	1.57112	91.81	92.50	94.31	95.66
$(C_6H_5O)_4Si$	400.49	—	—	—	—	112.92	113.92	116.35	118.32

afforded an amount of alcohol equivalent to the amount of phenol used. The tetraalkoxysilanes and phenoxyalkoxysilanes were fractionated and the residual tetraphenoxysilane recrystallized from petroleum ether (see also Table 2).

Diphenoxydiethoxysilane from diphenoxydichlorosilane and ethyl orthoformate.

A mixture of 14.3 g (0.05 mole) of diphenoxydichlorosilane and 22.2 g (0.15 mole) of ethyl orthoformate was heated to 70° for one hour. Ethyl chloride was evolved. The ethyl formate formed and the excess of ethyl orthoformate were slowly distilled from the reaction mixture at atmospheric pressure and the residue fractionated in vacuum. There was obtained 2.2 g (17 %) of phenoxytriethoxysilane, b. p. 102–104° (5 mm), 9.5 g (62 %) of diphenoxydiethoxysilane, b. p. 152–154° (5 mm) and 3.0 g (17 %) of presumably triphenoxyethoxysilane, b. p. 196–197° (5 mm), $n_D^{20} = 1.535$. All of the products contained small amounts of chlorosilanes. Thus it appears that the alkoxylation of diphenoxydichlorosilane using this method is incomplete, at least under the conditions used here.

REFRACTOMETRIC INVESTIGATION

The phenoxyalkoxysilanes were redistilled to constant density and refractive index (n_D^{20} , Abbe-refractometer). For the samples thus obtained the refractive indices for the sodium D-line ($\lambda = 5892.6 \text{ \AA}$), hydrogen c- and F-lines ($\lambda = 6562.8 \text{ \AA}$ and 4861.3 \AA , respectively), and mercury g-line ($\lambda = 4358.3 \text{ \AA}$) were measured using a Bellingham and Stanley "Critical Angle Refractometer". These values together with densities and molar refractions (Lorenz-Lorentz-formula) are listed in Table 4. This Table also gives the molar refractions of tetraphenoxysilane. Since tetraphenoxysilane is a solid the molar refractions were determined using an indirect method.

Solutions of tetraphenoxysilane in *n*-heptane were made up and the refractive indices and densities of the solutions measured. From these values the specific refractions of the solutions (r_s) were calculated. The density and refractive indices of pure *n*-heptane were also measured and the specific refractions (r_h) calculated. The specific refractions of pure tetraphenoxysilane (r_x) were then obtained using the formula *

$$r_x = \frac{100r_s - (100-p)r_h}{p} \quad (2)$$

assuming the specific refractions of tetraphenoxysilane and *n*-heptane to be additive * (p is the weight-% of tetraphenoxysilane in the solution). Multiplication of the r_x -values by the molar weight of tetraphenoxysilane gave the molar refractions.

For example, a solution of 0.5443 g of tetraphenoxysilane in 6.7968 g of *n*-heptane had $n_C^{20} = 1.39434$, $n_D^{20} = 1.39647$, $n_F^{20} = 1.40167$, $n_g^{20} = 1.40557$, and $d_4^{20} = 0.7064$. From these data the following specific refractions were calculated by the L.L.-formula: $r_C = 0.33888$, $r_D = 0.34050$, $r_F = 0.34445$, and $r_g = 0.34740$. Pure *n*-heptane had $n_C^{20} = 1.38599$, $n_D^{20} = 1.38787$, $n_F^{20} = 1.39274$, $n_g^{20} = 1.39633$, $d_4^{20} = 0.68387$, $r_C = 0.34346$, $r_D = 0.34495$, $r_F = 0.34879$, and $r_g = 0.35161$. Using eqn. 2 the following specific refractions were obtained for tetraphenoxysilane: $r_C = 0.2816$, $r_D = 0.2849$, $r_F = 0.2903$, and $r_g = 0.2948$.

* Several measurements at different concentrations indicated the validity of this assumption.

Table 5. Molar dispersions, specific refractions, specific dispersions and Abbe numbers.

Compound	$MR_F - MR_C$	$MR_g - MR_C$	r_d	r_{F-C}	A
$C_6H_5OSi(OCH_3)_3$	1.168	1.843	0.2482	106.5	39.2
$C_6H_5OSi(OC_2H_5)_3$	1.392	2.192	0.2626	105.4	41.7
$(C_6H_5O)_2Si(OCH_3)_2$	1.838	2.913	0.2639	135.2	33.4
$(C_6H_5O)_2Si(OC_2H_5)_2$	1.997	3.163	0.2708	132.5	34.8
$(C_6H_5O)_3SiOCH_3$	2.504	3.851	0.2733	154.5	30.5
$(C_6H_5O)_4Si$	3.43	5.40	—	—	—

In Table 5 the molar dispersions of the F—C and g—c lines are collected together with the specific refractions [r_D (L.L.-formula)], specific dispersions ($r_{F-C} = \frac{n_F - n_C}{d^{20}} \cdot 10^4$) and Abbe numbers ($A = \frac{n_D - 1}{n_F - n_C}$). The bond refractions and bond dispersions of a phenoxy group bonded to silicon in various types of phenoxysilanes are listed in Table 6.

In a previous communication⁹ an identification scheme for organosilicon compounds, utilizing some refractometric constants, was proposed. Although it might be possible to identify phenoxyalkoxysilanes by chemical or spectrophotometric means it is considered of interest to include them in the refractometric identification system. As seen from the figures in Table 5 it is easy to distinguish between the mono-, di- and triphenoxyalkoxysilanes using the specific dispersions or Abbe numbers. The specific refractions are of less use

Table 6. Bond refractions and bond dispersions of the phenoxy group bonded to silicon.

Compound	$r\lambda(Si-OC_6H_5)$				$d\lambda, -\lambda_2(Si-OC_6H_5)$	
	c	D	F	g	F-C	g-c
$C_6H_5OSi(OCH_3)_3$	28.10	28.34	28.92	29.41	0.820	1.304
$C_6H_5OSi(OC_2H_5)_3$	28.11	28.34	28.93	29.42	0.824	1.310
$(C_6H_5O)_2Si(OCH_3)_2$	27.95	28.18	28.75	29.23	0.803	1.277
$(C_6H_5O)_2Si(OC_2H_5)_2$	27.99	28.22	28.80	29.28	0.809	1.287
$(C_6H_5O)_3SiOCH_3$	27.85	28.07	28.65	29.08	0.796	1.224
$(C_6H_5O)_4Si$	28.23	28.48	29.09	29.58	0.86	1.35

Table 7. Differences between observed and calculated molar refractions and molar dispersions.

Compound	Δ_D	Δ_{F-C}
$C_6H_5OSi(OCH_3)_2$	-0.14	-0.040
$C_6H_5OSi(OC_2H_5)_2$	-0.14	-0.036
$(C_6H_5O)_2Si(OCH_3)_2$	-0.60	-0.114
$(C_6H_5O)_2Si(OC_2H_5)_2$	-0.52	-0.102
$(C_6H_5O)_3SiOCH_3$	-1.23	-0.192

Table 8. Molar extinction coefficients per phenoxy group.

λ (approx.) m μ max	$C_6H_5OSi(OC_2H_5)_2$	$C_6H_5OSi(OCH_3)_2$	$(C_6H_5O)_2Si(OC_2H_5)_2$	$(C_6H_5O)_2Si(OCH_3)_2$	$(C_6H_5O)_3SiOCH_3$	$(C_6H_5O)_4Si$
273	890	860	835	790	765	710
265	1 080	1 025	1 010	950	900	860
260	810	755	745	700	680	660

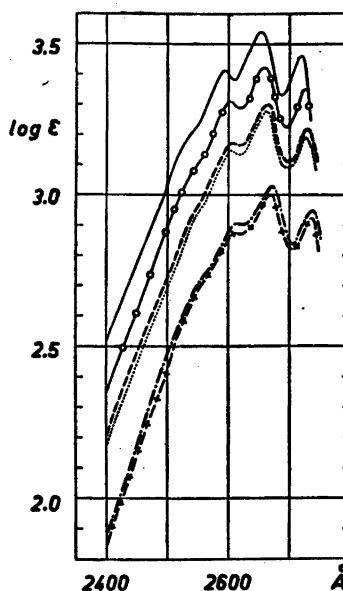


Figure 1. Absorption spectra of tetraphenoxysilane (—), triphenoxymethoxysilane (—○—○—○—), diphenoxydiethoxysilane (---), diphenoxydimethoxysilane (.....), phenoxytriethoxysilane (-·-·-·-), and phenoxytrimethoxysilane (-+-+-).

for this purpose. It is also possible to differentiate between the phenoxyalkoxysilanes and the eleven types of organosilicon compounds to which the refractometric identification method was previously applied (*cf.* Table 1, Ref⁹).

The bond refractions and bond dispersions of a phenoxy group bonded to silicon which are listed in Table 6 were, in the case of tetraphenoxysilane, obtained by dividing the molar refractions and molar dispersions of this compound by four and in the case of the phenoxyalkoxysilanes by subtracting the normal bond values of the alkoxy groups from the molar refractions and molar dispersions*. From the figures in Table 6 it is evident that in the phenoxyalkoxysilanes either the bond values of the phenoxy group or alkoxy groups or, which is most likely, of both of them are different from the normal ones. On that account the discrepancies between the observed molar refractions and molar dispersions and those calculated from the normal bond values are considerable (*cf.* Table 7).

When calculating molar refractions and molar dispersions of phenoxyalkoxysilanes the bond values of the phenoxy groups in Table 6 should be used together with the normal bond values of the alkoxy groups taken from Ref.¹ (*cf.* Tables 37, 38, 39, 48, 49, and 50 of this reference). Although Table 6 only

* The bond refraction of a group X bonded to silicon is written $r(\text{Si}-\text{X})$ and means the sum of the refraction of the group X and the bond Si-X. The normal value of the bond refraction $r(\text{Si}-\text{X})$ is defined as the bond refraction of the group in the silane SiX_n , where n equals 4 in the present case. The normal bond refraction is obtained by dividing the molar refraction of the silane SiX_4 by 4. Thus the normal bond refractions of the phenoxy group bonded to silicon are tabulated in the last row of Table 6. Concerning the bond dispersions $d(\text{Si}-\text{X})$ the same applies as to the bond refractions. The normal bond values of the alkoxy groups used in the calculation were taken from Ref.¹.

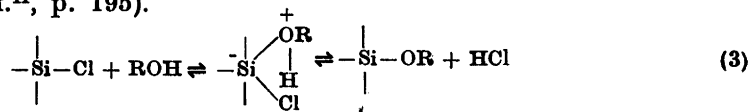
lists bond values of phenoxy groups in phenoxymethoxy- and phenoxyethoxysilanes it is believed that these values may also be used in calculating molar refractions and molar dispersions of phenoxyalkoxysilanes with other types of alkoxy groups.

SPECTROPHOTOMETRIC INVESTIGATION

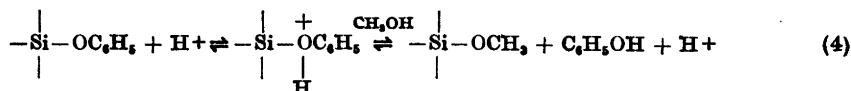
The ultraviolet absorption of the phenoxysilanes was measured in *n*-heptane solution in the range 240—275 $m\mu$ using a Hilger UVISPEK spectrophotometer (see Fig. 1). The molar extinction coefficients per phenoxy group are given in Table 8. It is seen that in the series tetraphenoxysilane-triphenoxyalkoxysilane-diphenoxydialkoxysilane-phenoxytrialkoxysilane there is a bathochromic shift. Likewise a bathochromic shift exists between the corresponding phenoxymethoxysilanes and phenoxyethoxysilanes. The shifts are accompanied by hyperchromic effects as shown by the figures of the molar extinction coefficients per phenoxy group. The significance of the spectra will be further discussed below.

DISCUSSION

The reaction between a chlorosilane and an alcohol may be assumed to proceed in the same way as the reaction between an acid chloride and an alcohol * (*cf.* Ref.¹¹, p. 195).



A proof of the formation of intermediate addition compounds between chlorosilanes and alcohols has been given by Troost¹² who isolated adducts between silicon tetrachloride and alcohols at a low temperature. Similar addition compounds between silicon tetrafluoride and alcohols were reported by Gierut *et al.*¹³ In the absence of reactive groups other than chlorine at the silicon atom the only disturbance of the above reaction that may occur is hydrolysis of the chlorosilane or alkoxy silane by water formed in a side reaction between hydrogen chloride and the alcohol (*cf.* Ref.¹). However, if other reactive groups are present (in the case of the phenoxychlorosilanes phenoxy groups) complications may arise as exemplified by synthesis No. 1 of Table 1. As pointed out previously the disproportionation is originated by the simultaneous presence of hydrogen chloride and an alcohol. This fact indicates that the cause of the disproportionation is an acid-catalyzed re-esterification of the phenoxychlorosilane and/or phenoxyalkoxysilane.



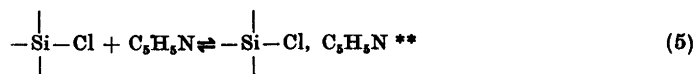
If the phenol then reacts with another silane molecule than that from which it was formed, for instance by the exchange of a phenoxy group for a methoxy

* A similar mechanism was proposed by Swain *et al.*¹⁰ for the hydrolysis of halogenosilanes which reaction was shown to proceed by a S_N2 attack by a water molecule on the halogenosilane.

group or a chlorine atom, this molecule gains one phenoxy group and the transference of a phenoxy group from one silane molecule to another is explained.

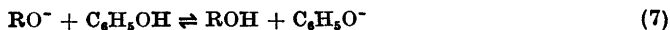
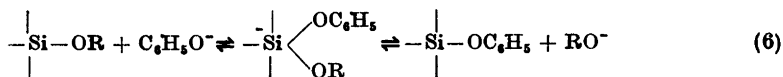
In the reactions between phenoxychlorosilanes and methyl alcohol using pyridine as a hydrogen chloride acceptor it was observed that the extent to which pyridine hindered the disproportionation in the case of the triphenoxychlorosilane was dependent on the temperature. A low temperature was necessary to obtain a reasonable yield of triphenoxyethoxysilane. No such temperature dependence was observed in the case of diphenoxydichlorosilane (*cf.* syntheses Nos. 2, 3, and 4, Table 1).

The function of pyridine or other tertiary amines in the reaction between halogenosilanes and alcohols has generally been considered to be merely that of a hydrogen chloride acceptor in spite of the fact that addition compounds between halogenosilanes and tertiary amines have been known to exist for a long time.^{14, 15} It is very likely, however, that the tertiary amine takes a more active part in the reaction and that the real "acylating" reagent is an addition compound between the amine and the chlorosilane*.



Such an assumption is supported by the observations made in this work and elsewhere***. The stability of the addition compound should, among other things, be dependent on the structure of the chlorosilanes. From steric considerations the addition compound between pyridine and triphenoxychlorosilane might be expected to be less stable than that between pyridine and diphenoxydichlorosilane (*cf.* F-strain in amine salts²¹). If it be assumed that the extent to which pyridine hinders the disproportionation reaction is a function of the stability of its addition compound with the chlorosilane the influence of the temperature on the reaction between the phenoxychlorosilanes and methyl alcohol in the presence of pyridine is understandable.

The nucleophilic displacement of an alkoxy group by a phenoxy group was utilized in the third method used in this work for the preparation of phenoxyalkoxysilanes.

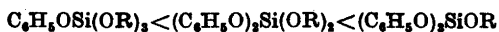


* It has been proposed that the promoting action of pyridine in benzoylation reactions is due to the formation of quaternary addition compounds between pyridine and benzoyl chloride (Ref. 11, p. 198). Furthermore acetylpyridinium chloride is a well known analytical reagent for the determination of active hydrogen in the hydroxyl groups of alcohols and phenols¹⁶.

** The nature of the addition compounds is not definitely established. They have been formulated as co-ordination compounds in which use is made of vacant silicon orbitals, but also a quaternary salts¹⁷⁻²⁰.

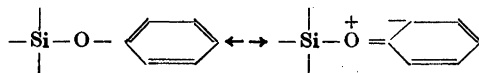
*** In the preparation of dimethyldialkoxysilanes and diphenyldialkoxysilanes from the corresponding chlorosilanes and alcohols, the reaction was incomplete in the absence of a tertiary amine. In the presence of pyridine, however, all of the chlorine atoms were replaced by alkoxy groups. The effect of pyridine can hardly be attributed to its salt formation with hydrogen chloride only, as other means of removing the hydrogen chloride *e. g.* boiling or blowing an inert gas through the reaction mixture were without effect¹.

From the figures of Table 2 it is apparent that the reactivity of phenoxyalkoxysilanes for phenoxide ion increases in the series



and is greater for $\text{R} = \text{CH}_3$ than for $\text{R} = \text{C}_2\text{H}_5$. This means that the positive charge on the silicon atom also increases in the mentioned series and is greater in the phenoxymethoxysilanes than in the corresponding phenoxyethoxysilanes. Such a charge distribution might be anticipated in view of the greater electron attraction of the phenoxy group in comparison with the alkoxy groups and the difference in inductive effects of the methyl and ethyl groups.

It is of interest that the difference in charge on silicon is also manifested in the absorption spectra of the phenoxysilanes. The ultraviolet absorption of these compounds originates from the aromatic part of the molecule. Mulliken²² and others have stated from wave-mechanical considerations that absorption of light takes place predominantly through transitions to charge-resonance structures. Accordingly the transition energy is dependent on the resonance in the molecule. In the present case resonance occurs between such forms as *



The difference in energy between the ground state and the excited states is diminished with increased contribution of polar structures as a result of the lowering of the potential energy of the excited states. At the same time there is an increase in the molar extinction coefficients and bathochromic shifts take place²⁴.

The resonance in the phenoxysilane is dependent on the charge on the silicon atom in such a way that the contribution of polar structures decreases with increased positive charge**. Consequently from the study of the absorption curves in Fig. 1 and the molar extinction coefficients per phenoxy group in Table 8 it is apparent that the silicon atom in tetraphenoxysilane has the greatest positive charge which then decreases as alkoxy groups are exchanged for phenoxy groups. The greater positive charge on the silicon atom of the phenoxymethoxysilanes as compared with the corresponding phenoxyethoxysilanes is also clearly shown.

The differences between the molar refractions, calculated for the phenoxyalkoxysilanes from the normal bond refractions of the phenoxy and alkoxy groups and the molar refractions found, are appreciable*** (cf. Table 7). In

* To explain the acidity of the silanols R_3SiOH the participation of resonance structures such as $\begin{array}{c} - \\ \text{Si}=\text{O}^+ \\ | \end{array} \text{---} \text{H}^-$ have been proposed²³. In view of this resonance structures such as $\begin{array}{c} - \\ \text{Si}=\text{O}^+ \\ | \end{array} \text{---} \text{C}_6\text{H}_5^-$ and $\begin{array}{c} - \\ \text{Si}=\text{O}^+ \\ | \end{array} \text{---} \text{R}^-$ might contribute to the state of the phenoxyalkoxysilanes. At present there is no evidence, however, of the existence of such forms. While it seems unlikely that the contribution of the first type should be significant, the existence of the second might explain the variation of the apparent bond refraction of the phenoxy group bonded to silicon (see Table 6).

** Disturbances may arise, however, if steric hindrance is present²⁵.

*** Similar deviations were previously shown to exist for the alkylalkoxysilanes¹ [$\text{RSi}(\text{OR})_3$ (−0.10 ml), $\text{R}_2\text{Si}(\text{OR})_2$ (−0.20 ml) and R_3SiOR (−0.10 ml)].

all probability this result has to be ascribed to the variation in charge on silicon. The differences increase as alkoxy groups are successively replaced by phenoxy groups indicating that a tightening of the Si—O bond of the alkoxy group is the main cause of the deviations (*cf.* note p. 1348).

REFERENCES

1. Smith, B. *Kiselorganiska Studier* (Diss.) Gothenburg, 1951.
2. Peppard, D. F., Brown, W. G. and Johnson, W. C. *J. Am. Chem. Soc.* **68** (1946) 70.
3. Shorr, L. M. *J. Am. Chem. Soc.* **76** (1954) 1390.
4. Jörg, H. and Stetter, J. *J. prakt. Chem.* [2] **117** (1927) 305.
5. Thompson, R. A. and Kipping, F. S. *J. Chem. Soc.* **1929** 1176.
6. Vol'nov, Y. N. *J. Gen. Chem. (U.S.S.R.)* **9** (1939) 2269.
7. Malatesta, L. *Gazz. chim. ital.* **78** (1948) 747.
8. Bauer, N. and Fajans, K. in Weissberger, A. (Ed.) *Physical Methods of Organic Chemistry*, Part II, 2nd Ed., Interscience Publishers, New York 1949, p. 1160.
9. Smith, B. *Svensk Kem. Tidskr.* **64** (1952) 330.
10. Swain, C. G., Esteve, R. M. and Jones, R. H. *J. Am. Chem. Soc.* **71** (1949) 965.
11. Day, A. R. *Electronic Mechanisms of Organic Reactions*, American Book Company, 1950.
12. Trost, W. R. *Nature* **169** (1952) 289.
13. Gierut, J. A., Sowa, F. J. and Niewland, J. A. *J. Am. Chem. Soc.* **58** (1936) 786.
14. Harden, A. *J. Chem. Soc.* **51** (1887) 40.
15. Reynolds, J. E. *J. Chem. Soc.* **95** (1909) 512.
16. Smith, D. M. and Bryant, W. M. D. *J. Am. Chem. Soc.* **57** (1935) 61.
17. Trost, W. R. *Can. J. Chem.* **29** (1951) 877; **30** (1952) 835, 842.
18. Emeléus, H. J. and Miller, N. *J. Chem. Soc.* **1939** 819.
19. Burg, A. B. *J. Am. Chem. Soc.* **76** (1954) 2674.
20. Piper, T. S. och Rochow, E. G. *J. Am. Chem. Soc.* **76** (1954) 4318.
21. Ferguson, L. N. *Electron Structures of Organic Molecules*, Prentice-Hall Inc., New York 1952, p. 111 ff.
22. Mulliken, R. S. *J. Chem. Phys.* **7** (1939) 20.
23. Gilman, H. and Dunn, G. E. *Chem. Revs.* **52** (1953) 104.
24. Ferguson, L. N. *Chem. Revs.* **43** (1948) 385.
25. Work to be published in *Acta Chem. Scand.*

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