[CONTRIBUTION FROM MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER]

SOME NEW PHENYLTRIALKOXYSILANES[1]

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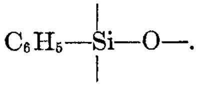
A number of phenyltrialkoxysilanes have been described in the literature (1–6). The preparation and properties of five new members and new data for two previously reported compounds of this series are presented in this paper. These silyl ethers and their physical properties are listed in Table I.

Phenyltri-*n*-propoxysilane, described earlier by Post and Hofrichter (3), was prepared again since the reported properties appeared questionable in the light of data for other members of the series and an erroneous analysis cast further doubt on the validity of the results (see Experimental). The properties found for this compound in the present study differ markedly from those given earlier. The new refractive index and density values, however, are well substantiated by the measurements of Smith (7) in his study of bond refractions of organosilicon compounds.

Phenyltri-*n*-butoxysilane has until now not been fully characterized since only the refractive index and density were reported (7). This compound was also prepared and the known physical constants confirmed.

Phenyl-tri-*sec*-butoxysilane, -tri-*tert*-butoxysilane, -tri-*n*-hexyloxysilane, -tricyclohexyloxysilane, and -tris(2-ethylhexyloxy)silane, as well as the two compounds described above, were prepared in 36–63% yield by the reaction of phenyltrichlorosilane with an excess of the appropriate anhydrous alcohol in the presence of pyridine as the acid acceptor. While the mode of addition generally had no appreciable effect on the yields obtained, somewhat better results were afforded in two cases by adding the alcohol to the chlorosilane-pyridine mixture. This was true for cyclohexanol and *tert*-butyl alcohol. The preparation of the tri-*tert*-butoxy derivative, though only in 37% yield, was in contrast to the unsuccessful attempt to obtain vinyltri-*tert*-butoxysilane (8). Methyltri-*tert*-butoxysilane has been isolated, however (9).

Repeated efforts to prepare phenyltrialloxysilane failed to give the desired product; instead, the reaction mixture polymerized on distillation, similar to the findings of Joffe and Post (10) in the preparation of trialloxysilane. Infrared analysis of the polymer indicated the presence of the phenylsiloxy group,



$$C_6H_5\text{—}\overset{|}{\underset{|}{Si}}\text{—}O\text{—}.$$

The preparation of each of these phenyltrialkoxysilanes was accompanied by the formation of small amounts of a higher-boiling product. Infrared and

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[1] The opinions expressed are those of the author and do not necessarily express the official opinions of the U. S. Air Force or the Wright Air Development Center.

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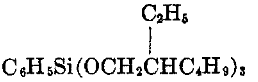
TABLE I

PROPERTIES OF PHENYLTRIALKOXYSILANES

COMPOUND	B.P., °C.	MM.	n^2_D	d^{25}_4	MR_D		ANALYSIS			
							Calc'd		Found	
					Calc'd	Found	C	H	C	H
$C_6H_5Si(OC_3H_7\text{-}n)_3$	96–98	0.5	1.4582[a]	0.960[a]	80.27	80.30	63.79	9.28	63.94	9.45
$C_6H_5Si(OC_4H_9\text{-}n)_3$	115–116	.2	1.4593[b]	.941[b]	94.22	94.31	66.62	9.94	66.66	9.87
$C_6H_5Si(OC_4H_9\text{-}sec)_3$	93	.1	1.4571	.936	94.22	94.41	66.62	9.94	66.71	10.27
$C_6H_5Si(OC_4H_9\text{-}tert)_3$	83–85	.2	1.4540	.929	94.22	94.59	66.62	9.94	66.81	10.41
$C_6H_5Si(OC_6H_{13}\text{-}n)_3$	150	.1	1.4600	.915	122.11	122.33	70.53	10.85	70.55	11.24
$C_6H_5Si(OC_6H_{11})_3$	170	.18	1.5052	1.039	115.47	114.99	71.59	9.49	71.67	9.48
 $C_6H_5Si(OCH_2\overset{\overset{C_2H_5}{\vert}}{C}HC_4H_9)_3$	161–164	.1	1.4638	0.908	149.99	149.76	73.11	11.45	73.09	11.29
$[C_6H_5Si(OC_4H_9)_2]_2O$	163–165	.15	1.4768				64.82	8.94	64.58	8.85

[a] Reported data (7): n^{20}_D 1.46057 and d^{20}_4 0.9627.

[b] Also found n^{20}_D 1.4608. Reported data (7): n^{20}_D 1.46107 and d^{20}_4 0.9447.

elemental analyses indicated that these materials were very probably the corresponding disiloxanes, $[C_6H_5Si(OR)_2]_2O$. Tamborski and Post (9) reported comparable results in the preparation of methyltrialkoxysilanes. While precautions were taken to protect the reaction mixtures from moisture, it is possible that some hydrolysis may have occurred. No other simple explanation for the formation of the disiloxanes is immediately apparent. Physical properties of 1,3-diphenyl-1,1,3,3-tetra-*n*-butoxydisiloxane are included in Table I.

The reaction of chlorosilanes with 2-alkoxyethanols (Cellosolves) has been studied by several workers (4, 11, 12). However, only one compound derived from phenyltrichlorosilane, phenyltris(2-methoxyethoxy)silane, has been reported (4). This compound was obtained by direct reaction of the chlorosilane with 2-methoxyethanol. Attempts during the present study to prepare phenyltris(2-butoxyethoxy)silane and phenyltris[2-(2-ethylbutoxy)ethoxy]silane in pure form by this method were unsuccessful, even when pyridine was employed. Isolation was complicated by the formation of by-products including polymeric materials. Radical interchange has been used successfully for the preparation of tetrakis(2-alkoxyethoxy)silanes (11). When this method was tried using phenyltriethoxysilane and excess 2-butoxyethanol, a mixture was obtained, which did not yield any well-defined products.

The calculated molar refractions of the new compounds were obtained from the bond refraction data of Sauer (13) and of Vogel (14). Warrick's (15) values give approximately the same results. Closer agreement between the experimental and calculated values is often attained, however, when some of the more recent refinements are applied (7). As has also been observed by Smith (7), there appears to be a deviation in the molar refraction, when hydrogen atoms at the α- and β-carbon atoms of the alkoxy groups bonded to silicon are substituted by methyl groups. This may be seen for the *n*-butoxy (94.31), *sec*-butoxy (94.41), and *tert*-butoxy (94.59) derivatives. Smith's experimental values include *n*-butoxy (94.27) and isobutoxy (94.48). A formula has been proposed to account for this deviation.

EXPERIMENTAL

Phenyltri-n-propoxysilane. In a 200-ml. r.b. flask equipped with a Y-type addition tube to which a reflux condenser and a dropping-funnel fitted with drying tubes, were attached, was placed 21.2 g. (0.1 mole) of phenyltrichlorosilane and about half of the 23.7 g. (0.3 mole) of pyridine. Then there was added dropwise, over a period of 15 minutes, 24.0 g. (0.4 mole) of *n*-propyl alcohol, mixed with the remainder of the pyridine. Pyridine hydrochloride precipitated immediately. The reaction mixture was heated under reflux for two hours after which the mixture was allowed to cool and the organic layer was decanted. The pyridine hydrochloride was dissolved in water and the aqueous solution was extracted with ether. The ether was combined with the organic fraction. After drying over sodium sulfate, fractionation of the mixture gave 12 g. (42.6%) of phenyltri-*n*-propoxysilane, b.p. 96–98° (0.5 mm.), n_D^{25} 1.4582, and d_4^{25} 0.960, as well as 6 g. of a higher-boiling fraction, which was probably the disiloxane, b.p. 184–190° (1.6 mm.), 13% yield.

Post and Hofrichter (3) had previously reported the following data for this compound: b.p. 192° (7 mm.), n_D^{20} 1.5025, d_4^{20} 1.036, M.W. (cryoscopic from benzene) 298, (theoretical) 302. Actually M.W. (theoretical) should be 282.4.

The other phenyltrialkoxysilanes were prepared in a similar manner, except for phenyltris(2-ethylhexyloxy)silane which was prepared by addition of the chlorosilane to the alcohol.

Phenyltri-n-butoxysilane. Yield, 41.7%; b.p. 115–116° (0.2 mm.), n_D^{25} 1.4593 and 3% of 1,3-diphenyl-1,1,3,3-tetra-*n*-butoxydisiloxane, b.p. 163–165° (0.15 mm.), n_D^{25} 1.4768.

Phenyltri-sec-butoxysilane. Yield, 49.4%; b.p. 93° (0.1 mm.), n_D^{25} 1.4571 and 5% of a higher-boiling product (probably disiloxane), b.r. 153–161° (0.1 mm.), n_D^{25} 1.4749.

Phenyltri-tert-butoxysilane. Yield, 37%; b.p. 83–85° (0.2 mm.), n_D^{25} 1.4540 and a small amount (about one gram) of a higher-boiling fraction which was not distilled.

Phenyltri-n-hexyloxysilane. Yield, 35.7%; b.p. 150° (0.1 mm.), n_D^{25} 1.4600 and 13% of slightly impure 1,3-diphenyl-1,1,3,3-tetra-*n*-hexyloxydisiloxane, b.p. 190–196° (0.15 mm.).

Anal. Calc'd for $C_{36}H_{62}O_5Si_2$: C, 68.5; H, 9.9.

Found: C, 67.5; H, 9.6.

Phenyltricyclohexyloxysilane. Yield, 50.2%; b.p. 170° (0.18 mm.), n_D^{25} 1.5052 and very small amount of a higher-boiling fraction.

Phenyltrialloxysilane. Upon attempted distillation, the reaction mixture polymerized. Infrared examination of the gummy polymer revealed strong absorption bands at 6.3, 6.7, and 6.98 μ (due to C_6H_5—Si) and a broad band at 8.7–10.0 μ (due primarily to $-\overset{|}{\underset{|}{Si}}-O-$).

Reaction of phenyltrichlorosilane with 2-alkoxyethanols. One mole (118 g.) of 2-butoxyethanol (Butyl Cellosolve) was added to 0.3 mole (63.5 g.) of phenyltrichlorosilane in 1.0 mole (79 g.) of pyridine. Rectification of the reaction mixture gave four fractions, plus some polymeric material, the main fraction having a boiling range of 215–227° (0.5 mm.).

Anal. Calc'd for $C_{24}H_{44}O_6Si$: C, 63.1; H, 9.7.

Found: C, 60.7; H, 8.9.

When the reaction was conducted without pyridine, low-boiling materials and an undistillable fraction were obtained. The latter solidified on cooling.

2-Ethylbutoxyethanol (2-Ethylbutyl Cellosolve) gave similar results. In the presence of pyridine, several fractions were isolated. Main fraction, b.p. 234–237° (0.1 mm.).

Anal. Calc'd for $C_{30}H_{56}O_6Si$: C, 66.6; H, 10.4.

Found: C, 64.3; H, 9.2.

Without pyridine, comparable results were obtained. Main fraction, b.p. 230–236° (0.1 mm.); Found: C, 64.4; H, 9.6.

Reaction of phenyltriethoxysilane with 2-butoxyethanol. A mixture of 11.7 g. (0.049 mole) of phenyltriethoxysilane and 23.6 g. (0.2 mole) of 2-butoxyethanol was heated under reflux for 24 hours. Rectification of the reaction mixture gave a small amount of ethanol and six fractions, ranging from 70–78° (2.5 mm.) to 254–256° (0.55 mm.). None of the possible fractions gave a satisfactory analysis for phenyltris(2-butoxyethoxy)silane. Ten g. of 2-butoxyethanol was recovered.

Phenyltris(2-ethylhexyloxy)silane. In the usual apparatus, was placed 91 g. (0.7 mole) of 2-ethyl-1-hexanol and 47.4 g. (0.6 mole) of pyridine. Then there was slowly added dropwise 42.3 g. (0.2 mole) of phenyltrichlorosilane over a period of 20 minutes. Pyridine hydrochloride precipitated immediately. The reaction mixture was heated under reflux for two hours. The mixture was allowed to cool and the organic layer was decanted. The pyridine hydrochloride was dissolved in water and the aqueous solution was extracted with ether. The ether was added to the organic layer. After drying over sodium sulfate, rectification of the mixture gave 62 g. (63% yield) of phenyltris(2-ethylhexyloxy)silane, b.p. 161–164° (0.1 mm.), n_D^{25} 1.4638 and 8 g. of what was probably the disiloxane, b.p. 205–210° (0.16 mm.), n_D^{25} 1.4749 (5.4% yield).

Phenyltrichlorosilane was obtained from Linde Air Products Company, Tonawanda, New York. The alcohols were all dried and distilled prior to use.

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SUMMARY

1. The preparation and properties of five new phenyltrialkoxysilanes and new data for two previously reported homologs, have been presented.

2. Disiloxanes appear to be by-products in the preparation of these phenyltrialkoxysilanes. Data for two of these disiloxanes have been given.

3. The reaction of phenyltrichlorosilane with 2-alkoxyethanols failed to give the phenyltris(2-alkoxyethoxy)silanes in pure form. Radical interchange was also unsuccessful.

4. Molar refraction data for these compounds have been presented and the effect of structure has been commented on.

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