trolled Glas-Col mantle. Commercial "98% plus" cresols were used and showed the following impurities by infrared analysis: *ortho*, 0.3% each of *para* and *meta; meta*, no ortho but 0.6% *para;* para, no *meta* but 2.3% *ortho*. The aluminum chloride used was commercial fine grind, 98% pure.

In all runs, 1440 g. of cresol was charged to the flask, and aluminum chloride added slowly after heating to 175°, which is the lowest temperature at which the reaction mass does not solidify when the molal ratio of aluminum chloride to cresol reaches 0.5. Aluminum chloride additions were stopped just short of a ratio of 1:1 at which point solidification temperature had dropped below 125°. The flask temperature was now adjusted so that addition of the remaining catalyst caused a drop to the desired operating temperature, which was then maintained to within $\pm {}^3/_4$°.

Substantially no tar formation (below 3%) or isomerization occurred until this final catalyst addition, which was taken as zero time. The reaction mixture was in all cases a homogeneous solution throughout the run, although it became more viscous and deeper black in color with time.

Samples of about 200 ml. were taken at intervals and poured directly onto about 2 kg. of cracked ice, to which enough hydrochloric acid had been added to keep the aluminum chloride in solution (about 400 ml. for a catalyst-cresol ratio of 2). The cresol layer was decanted, washed successively with two 100-ml. portions of water, and the washings added to the aqueous layer, which was then extracted with two 250-ml. portions of ethyl ether. The ether was next distilled off and the recovered cresol combined with the original cresol layer.

The water remaining in the cresol was separated in a simple distillation and the tar determined by continuing the distillation until the residue boiled over 230°. The principal part of the residual tar had a b.p. over 275° at normal pressure. Although the nature of this tar was not investigated, it appeared smooth and homogeneous and was almost completely soluble in acetone.

After drying over "Drierite" the cresol fraction was separated from phenol and xylenols by fractional distillation in a 90-cm. by 5-mm. i.d. Widmer spiral column using 50:1 reflux ratio.

Infrared Analysis of Cresols.—Since the cresols have strong, well-separated absorption bands in the infrared region, infrared spectroscopy can be used for analysis if care is taken to remove phenol and the xylenols which have interfering bands.[6] Three grams of the cresol fraction were dissolved in 100 ml. of cyclohexane and part of this solution used to fill a sodium chloride cell with 0.1-mm. absorption path. The Beckman IR-2 spectroscope gave good results at this concentration when a slit width of 1.6 mm. was used. Since completion of this work two articles describing the infrared analytical procedure have appeared in the literature.[7,8]

To obtain standard samples the cresols were purified—*ortho* by careful fractional distillation, in the column previously described, to a b.p. of 190.8; and *m*- and *p*-cresols by fractional crystallization from a melt until their melting points were 11.6 and 35.2°, respectively. Using these samples a calibration chart of net optical density as a function of concentration was prepared at each of three absorption maxima: ortho, 750 cm.$^{-1}$; meta, 774 cm.$^{-1}$; and para, 815 cm.$^{-1}$. The optical densities obtained for the pure cresols at these frequencies and at 3 g. per 100 ml. were: ortho, 0.641; meta, 0.334; and para, 0.367. Using these calibration curves as standards the accuracy obtained on known samples of the cresols was about 0.5%. Samples from the experimental runs contained small amounts of homologous impurities which reduced the accuracy to 1%.

Acknowledgment.—We wish to express our appreciation to the Standard Oil Company of California and the California Research Corporation for the fellowship grant to the junior author under which this study was carried out. The infrared analyses were carried out in the M.I.T. Spectroscopy Laboratories through the courtesy of Professor Richard C. Lord.

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CAMBRIDGE, MASSACHUSETTS RECEIVED AUGUST 6, 1951

[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP ON TECHNICAL GLASSWARE MAINTAINED AT MELLON INSTITUTE BY THE CORNING GLASS WORKS, CORNING, N. Y., IN COÖPERATION WITH THE DOW CORNING CORPORATION]

The Preparation and Properties of (Hydroxyorgano)-silanes and Related Compounds

BY JOHN L. SPEIER

Certain halophenols were treated with chlorosilanes to form (halophenoxy)-silanes. Silylphenoxysilanes were prepared in good yields from (halophenoxy)-silanes, chlorosilanes and sodium or potassium metal. Hydrolysis of silylphenoxysilanes is described as leading to various silylphenols or, in some cases, complex cleavage products. Chlorohydrins were treated with chlorosilanes to form chloroalkoxysilanes, which reacted with sodium, lithium or magnesium and a chlorosilane to prepare silylalkoxysilanes. In the absence of a chlorosilane, silylalkanols were formed. These were also prepared by hydrolysis of the silylalkoxysilanes. An apparent rearrangement during the reaction of halophenoxysilanes with a chlorosilane and sodium is described and a hypothesis explaining the rearrangement is described. An irreversible thermal rearrangement of silylphenols to form phenoxysilanes is described. The catalytic hydrogenation of *p*-trimethylsilylphenoxytrimethylsilane to form 4-trimethylsilylcyclohexyloxytrimethylsilane is described. The *cis*- and *trans*-isomers of 4-trimethylsilylcyclohexanol were prepared and separated. The oxidation of these with nitric acid to form 3-trimethylsilyladipic acid is described. The formation of 5-trimethylsiloxypentylmagnesium chloride and its reaction with mercuric chloride is described.

The literature of organosilicon compounds contains no examples of a silane with a hydroxyphenyl substituent, and only a few with hydroxyalkyl substituents. Known methods of synthesis for organosilicon compounds do not readily lend themselves to the preparation of products containing reactive functional groups on organic substituents attached to silicon. Usually the formation of a silicon–carbon bond involves coupling an alkoxy or chlorosilane with organo-metallic reagents. The high temperature reaction of halogenated hydrocarbons with silicon is another well known process of forming silicon–carbon bonds. A third process involves the addition of trichlorosilane to an olefin under the influence of a peroxide catalyst or under the influence of light or heat. No example could be found in which any of these methods were employed for the synthesis of functional products containing groups such as hydroxyl, carboxyl, carbonyl, etc., on an organic radical attached to silicon.

The few (hydroxyorgano)-substituted silicon compounds that are described in the literature were in general made from a (haloaryl)- or (haloalkyl)-

silane intermediate. For example, Friedel and Crafts[1] chlorinated tetraethylsilane, and from the chloroethyltriethylsilane which resulted they prepared the corresponding alcohol. By similar procedures, Speier, Daubert and McGregor[2] prepared trimethylsilylmethanol, dimethylsilylenedimethanol and *sym*-bis-hydroxymethyltetramethyldisiloxane (tetramethyldisiloxylene-1,3-dimethanol). Sommer and co-workers[3,4] have made compounds such as 3-trimethylsilylpropionic acid and 1-trimethylsilyl-2-propanol.

There are a few other examples of silicon substituted organo functional compounds containing hydroxyl groups. All were prepared more or less laboriously usually from a chlorinated alkyl or aryl silane.

Gilman and co-workers[5a,b] have reported recently their efforts to synthesize ortho and para trimethylsilylphenol by several methods which proved unsuccessful. They concluded that such phenols were unstable structures. They have succeeded recently in preparing trimethyl- and triphenylsilylnaphthols.[5b]

In this Laboratory it has been found that many hydroxylated compounds, either phenols or alcohols, containing a silicon substituent may be made relatively easily by first forming a silicon ester and then carrying out the reactions outlined by the following equations.

$$\equiv SiCl + HO(R)X \longrightarrow \equiv SiO(R)X + HCl$$

$$\equiv SiO(R)X + 2M + \equiv SiCl \longrightarrow \equiv SiO(R)Si + MX + MCl$$

$$\equiv SiO(R)Si\equiv + H_2O \longrightarrow \equiv SiOH + HO(R)Si\equiv$$

In these equations (R) can be aromatic or aliphatic. If it is aliphatic, (R) must be such that the hydroxyl and X are separated by more than two carbon atoms and M can be sodium, lithium or magnesium and possibly other active metals. If (R) is aromatic, X may be chlorine, bromine or iodine, and M must be sodium. If (R) is aliphatic the second and third equations may be changed to

$$\equiv SiO(R)X + 2M \longrightarrow \equiv Si(R)OM + MX$$

$$\equiv Si(R)OM + HA \longrightarrow \equiv Si(R)OH + MA$$

In practice the reactions are more complex than indicated in these equations. These complexities will be illustrated by examples and discussed further.

The esters used in such syntheses are mostly unreported compounds and are to be found along with other previously unreported phenoxysilanes in Table I. They may be prepared from the alcohol or phenol and a chlorosilane, usually best in the presence of a hydrogen chloride acceptor such as an amine. They also may be made by ester interchange between an ethoxysilane and the alcohol or phenol. In some cases a silazane and the alcohol or the phenol reacted. Ammonia was evolved rapidly and the highest yield of pure product resulted. This last method is apparently a very generally applicable one but involves the trouble of preparing the silazane. All analyses for silicon content were performed by the wet oxidation in sulfuric acid approximately as described by Hyde and DeLong.[6] The specific refractions were calculated from the data of Warrick.[7]

The Synthesis of Halophenoxysilanes and Haloalkoxysilanes.—The common procedures for the synthesis of phenoxy or alkoxysilanes are generally applicable to the synthesis of the halophenoxy or haloalkoxysilanes. Some examples of the processes used are as follows:

(1) ***p*-Chlorophenoxytrimethylsilane.**—Dry *p*-chlorophenol (257 g., 2 moles) was mixed with an excess of trimethylchlorosilane (336 g., 3.1 moles) and heated to reflux. A rapid stream of hydrogen chloride was produced immediately, continuing at a diminishing rate for several hours. When no detectable quantity of hydrogen chloride was being formed, the mixture was distilled. Excess trimethylchlorosilane was recovered. *p*-Chlorophenoxytrimethylsilane was obtained as the only product in quantitative yields.

This method applied to alkylenechlorohydrins produces chloroalkoxysilanes in only 50–80% yield, along with siloxanes and dichloroalkanes.

(2) **4-Chlorobutoxytrimethylsilane.**—One mole of tetramethylenechlorohydrin (108.5 g.) was mixed with one mole of trimethylchlorosilane (108.5 g.) in one liter of dry benzene. The mixture was stirred in an ice-bath as anhydrous ammonia was passed through it at a rapid rate. The ammonia stream was discontinued when the odor of ammonia persisted above the mixture. The mixture was filtered free of ammonium chloride and distilled. 4-Chlorobutoxytrimethylsilane was obtained (145 g., 80%). Pyridine, quinoline or other amines were also used as acceptors for hydrogen chloride, but showed no noticeable advantage.

(3) **5-Chloropentoxytrimethylsilane.**—One mole of pentamethylenechlorohydrin (122.5 g.) was cooled and maintained at less than 20° as one equivalent of hexamethyldisilazane (81 g.) was added. A gentle reaction occurred during the addition and ammonia was evolved. When the addition was complete, the mixture was warmed slowly to boiling at 25 mm. and distilled. The material was essentially pure 5-chloropentoxytrimethylsilane (yield 96%).

(4) **Bis-(*p*-chlorophenoxy)-dimethylsilane.**—*p*-Chlorophenol (900 g., 7 moles) was dissolved in dimethyldiethoxysilane (1580 g., 10.6 moles) and heated to reflux under a small fractionating column. Ethanol was stripped off the mixture periodically during two days as an azeotrope with dimethyldiethoxysilane containing approximately 88% by weight of ethanol, b.p. 77°, wt. 379 g. The remainder was distilled and was found to be dimethyldiethoxysilane (*p*-chlorophenoxy)-ethoxydimethylsilane (530 g., 2.30 moles, 32%) and bis-(*p*-chlorophenoxy)-dimethylsilane (757 g., 2.42 moles, 69%). The yields were based on the amount of chlorophenol used.

The Synthesis of Silylphenoxysilanes.—The general procedure for the preparation of silylphenoxysilanes is illustrated in the following examples. All yields were calculated as based on the halophenoxysilane.

(1) ***p*-Trimethylsilylphenoxytrimethylsilane.**—To molten sodium (100 g., 4.34 g. atoms) in refluxing toluene (400 ml.) sufficient trimethylchlorosilane from a total of 237 g., 2.2 moles, was added to lower the boiling point of the mixture to about 101°. *p*-Chlorophenoxytrimethylsilane (401 g., 2.0 moles) was mixed with the remainder of the trimethylchlorosilane and added cautiously to the molten sodium with vigorous stirring under an efficient reflux condenser. The reaction was very vigorous and the addition was made at a rate sufficient to keep the reaction mixture boiling. If the sodium should solidify in such a mixture, experience has shown that all reaction ceases. When the addition was complete, the mixture was stirred and heated for one-half hour, filtered and distilled. There was obtained 398 g., 84% of *p*-trimethylsilylphenoxytrimethylsilane and 20 g., 6% of phenoxytrimethylsilane. Almost no higher boiling material was found. The remainder could be found firmly adsorbed on the finely divided sodium chloride produced. This

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TABLE I

VARIOUS PHENOXYSILANES

No.	Empirical formula	Structure	B.p. °C.	B.p. Mm.	$n^{25}D$	$d^{25}{}_4$	Si, % Found	Si, % Calcd.	Sp. ref. Found	Sp. ref. Calcd.[d]
1	$C_8H_{10}OCl_2Si$	$ClMe_2Si(p\text{-}OC_6H_4Cl)$	121	20	1.5033	1.173	16.05[b]	16.05[b]	0.2521	0.2501
2	$C_9H_{12}OCl_2Si$	$Me_3Si(2,4\text{-}OC_6H_3Cl_2)$	132	24	1.5070	1.150	29.9[c]	30.1[c]	.2586	.2571
3	$C_9H_{13}OBrSi$	$Me_3Si(p\text{-}OC_6H_4Br)$	126	25	1.5123	1.252	11.7	11.4	.2398	.2385
4	$C_9H_{13}OClSi$	$Me_3Si(o\text{-}OC_6H_4Cl)$	106	23	1.4910	1.042	14.0	14.0	.2779	.2772
			212	742						
5	$C_9H_{13}OClSi$	$Me_3Si(p\text{-}OC_6H_4Cl)$	101	14	1.4923	1.042	14.0	14.0	.2786	.2772
6	$C_9H_{13}OISi$	$Me_3Si(o\text{-}OC_6H_4I)$	134	25	1.5441	1.447	9.57	9.60	.2182	.2179
7	C_9H_4OSi	$Me_3SiOC_6H_5$	81	23	1.4753	0.920	16.8	16.9	.3058	.3055
			182.5	736						
8	$C_{10}H_{14}O_2Si$	$o\text{-}Me_3SiOC_6H_4CHO$	142	25	1.5079	1.013	14.2	14.4	.2942	.2853
9	$C_{10}H_{15}OBrSi$	$Me_2EtSi(p\text{-}OC_6H_4Br)$	142	25	1.5128	1.229	10.6	10.8	.2445	.2435
10	$C_{10}H_{15}OClSi$	$Me_2EtSi(p\text{-}OC_6H_4Cl)$	134	26	1.4941	1.034	13.1	13.1	.2817	.2810
11	$C_{10}H_{15}O_2BrSi$	$EtOMe_2Si(p\text{-}OC_6H_4Br)$	142	25	1.4986	1.254	10.1	10.2	.2339	.2349
12	$C_{10}H_{15}OClSi$	$Me_3Si(3\text{-}Me\text{-}4\text{-}ClC_6H_3O)$	125	23	1.4963	1.034	13.3	13.1	.2827	.2807
13	$C_{10}H_{15}O_2ClSi$	$EtOMe_2Si(o\text{-}OC_6H_4Cl)$	128	22	1.4805	1.069	12.1	12.2	.2660	.2645
14	$C_{10}H_{15}O_2ClSi$	$EtOMe_2Si(p\text{-}OC_6H_4Cl)$	132	24	1.4815	1.069	12.3	12.2	.2664	.2645
15	$C_{10}H_{16}OSi$	$Me_2EtSiOC_6H_5$	101	26	1.4791	0.921	15.6	15.6	.3080	.3074
16	$C_{11}H_{16}O_3Si$	$o\text{-}Me_3SiOC_6H_5COOMe$	142	25	1.4911	1.040	12.3	12.5	.2790	.2757
17	$C_{12}H_{21}O_2ClSi_2$	$2,4\text{-}(Me_2SiO)_2C_6H_3Cl$	153	25	1.4818	1.022	19.5	19.4	.2785	.2767
18	$C_{14}H_{14}O_2Br_2Si$	$Me_2Si(p\text{-}OC_6H_4Br)_2$	219	1	1.5707	1.514	6.9	6.9	.2169	.2155
19	$C_{14}H_{14}O_2Cl_2Si$	$Me_2Si(p\text{-}OC_6H_4Cl)_2$	230	27	1.5451	1.236	9.1	9.0	.2599	.2586
20	$C_{15}H_{17}OCl$	$Me_3Si(2\text{-}C_6H_5\text{-}4\text{-}Cl\text{-}C_6H_4O\text{-})$	151	6	1.5562	1.092	9.9	10.1	.2944	.2941
21	$C_{15}H_{17}OCl$	$Me_3Si(2\text{-}C_6H_5\text{-}6\text{-}Cl\text{-}C_6H_4O\text{-})$	195	25	1.5582	1.101	9.7	10.1	.2926	.2941
22	$C_{15}H_{18}OSi$	$Me_3Si(2\text{-}C_6H_5C_6H_4O\text{-})$	164	21	1.5455	1.003	11.3	11.6	.3158	.3160
23	$C_{19}H_{15}O_3Cl_3Si$	$MeSi(p\text{-}OC_6H_4Cl)_3$	287	10	1.5695	1.308	6.7	6.6	.2506	.2498
24	$C_{24}H_{16}O_4Cl_4Si$	$Si(p\text{-}OC_6H_4Cl)_4$	M.p. 70				5.2	5.2		
CHLOROALKOXYSILANES AND OTHER ALKOXYSILANES										
25	$C_6H_{15}OClSi$	$Me_3SiO(CH_2)_3Cl$	155	733	1.4160	0.930	[a]	16.79	0.2697	0.2708
26	$C_7H_{17}OClSi$	$Me_2EtSiO(CH_2)_3Cl$	80	24	1.4237	.937	[a]	15.53	.2723	.2754
27	$C_7H_{17}OClSi$	$Me_3SiO(CH_2)_4Cl$	81	24	1.4218	.924	16.60[c]	16.63[c]	.2747	.2754
28	$C_8H_{18}O_2Cl_2Si$	$Me_2Si[O(CH_2)_3Cl]_2$	141	25	1.4413	1.084	11.39	11.44	.2438	.2447
29	$C_8H_{19}OClSi$	$Me_2EtSiO(CH_2)_4Cl$	94	24	1.4295	0.927	14.41	14.40	.2783	.2793
30	$C_8H_{19}OClSi$	$Me_3SiO(CH_2)_5Cl$	98	24	1.4268	0.923	[a]	14.40	.2782	.2793
31	$C_{10}H_{22}O_2Cl_2Si$	$Me_2Si[O(CH_2)_4Cl]_2$	See experimental section. Compound decomposed.							
32	$C_{11}H_{17}O_2ClSi$	$Me_3SiOCH_2CH_2O(p\text{-}ClC_6H_4)$	166	29	1.4927	1.061	11.14	11.46	.2738	.2723
33	$C_{11}H_{17}O_2ClSi$	$Me_3SiOCH_2CH_2(o\text{-}ClC_6H_4)$	158	26	1.4948	1.066	11.1	11.46	.2735	.2723
34	$C_{12}H_{19}O_2ClSi$	$Me_3SiOCH_2CHO(p\text{-}ClC_6H_4)$				Not isolated as such				
35	$C_{14}H_{26}O_2Cl_2Si$	$Me_2Si[O(CH_2)_5Cl]_2$	204	26	1.4763	1.026	10.60	9.35	.2601	.2606

[a] These compounds were not analyzed, but their identity is assumed because of their origin and because of the products derived from them described later. [b] Per cent. hydrolyzed Cl. [c] Per cent. total Cl.

was sometimes recovered by dissolving the salts in water, but the presence of unreacted sodium metal in the salts usually made this inadvisable. The properties of the products obtained may be found in Table II.

The use of *p*-bromophenoxysilane led to nearly identical results. Potassium could be substituted successfully for sodium, but lithium and magnesium led to no reaction.

(2) **o-Trimethylsilylphenoxytrimethylsilane.**—By the same procedure, *o*-chlorophenoxytrimethylsilane (200 g., 1.0 mole), trimethylchlorosilane (129 g., 1.2 mole) and sodium (49 g., 2.1 g. atoms) yielded, *o*-trimethylsilylphenoxytrimethylsilane in 94% yield (224 g.). No phenoxytrimethylsilane was found.

(3) **1,3-Bis-(trimethylsiloxy)-4-trimethylsilylbenzene.**—By the same technique, sodium (24.4 g., 1.06 g. atoms) in 150 ml. of toluene reacted with trimethylchlorosilane (57.5 g., 0.53 mole) and 1,3-bis-(trimethylsiloxy)-4-chlorobenzene (138.5 g., 0.48 mole). A yield of 146 g. (98%) of 1,3-bis-(trimethylsiloxy)-4-trimethylsilylbenzene was obtained.

(4) **2,4-Bis-(trimethylsilyl)-phenoxytrimethylsilane.**—In the same manner, 2,4-dichlorophenoxytrimethylsilane (173 g., 0.78 mole), sodium (78 g., 3.34 g. atoms) and trimethylchlorosilane (170 g., 1.58 mole) in boiling toluene yielded 2,4-bis-(trimethylsilyl)-phenoxytrimethylsilane (202 g., 0.65 mole, 83%).

(5) **2-Phenyl-4-trimethylsilylphenoxytrimethylsilane.**—2-Phenyl-4-chlorophenoxytrimethylsilane (149 g., 0.73 mole) reacted with trimethylchlorosilane (79 g.) (0.73 mole) and sodium (37 g., 1.6 g. atoms) yielded 2-phenylphenoxytrimethylsilane (20 g., 11%) and 2-phenyl-4-trimethylsilylphenoxytrimethylsilane (173 g., 75.5%) along with a viscous high boiling material which was not identified.

(6) **Apparent Rearrangements. o-Trimethylsilylphenoxyethyldimethylsilane.**—*o*-Chlorophenoxytrimethylsilane (150 g., 0.75 mole) reacted with ethyldimethylchlorosilane (92 g., 0.8 mole) and sodium (36.8, 1.6 g. atoms). The product was unexpectedly found to be almost exclusively *o*-trimethylsilylphenoxyethyldimethylsilane (160 g., 86%). No indication of the formation of the expected isomer, *o*-ethyldimethylsilylphenoxytrimethylsilane, was found. The identity of the product was established by analysis as given in Table II, and subsequent hydrolysis to *o*-trimethylsilylphenol and diethyltetramethyldisiloxane. The complete absence of the expected product is apparently characteristic of only the ortho-halophenoxysilanes. See the next example.

(7) **p-Trimethylsilylphenoxytrimethylsilane, p-Trimethylsilylphenoxyethyldimethylsilane, p-Ethyldimethylsilylphenoxyethyldimethylsilane, p-Ethyldimethylsilylphenoxytrimethylsilane.**—*p*-Chlorophenoxytrimethylsilane (150 g., 0.75 mole) reacted with ethyldimethylchlorosilane (92 g.,

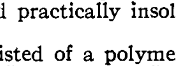
TABLE II

SILYLPHENOXYSILANES

No.	Empirical formula	Structure	B.p. °C.	Mm.	n^{25}_D	d^{25}_4	Si, % Found	Si, % Calcd.	Sp. ref. Found	Sp. ref. Calcd.[6]
1	$C_{12}H_{22}OSi_2$	$Me_3Si(p\text{-}OC_5H_4SiMe_3)$	132	25	1.4794	0.900	23.5	23.5	0.3198	0.3120
2	$C_{12}H_{22}OSi$	$Me_3Si(o\text{-}OC_6H_4SiMe_3)$	128	25	1.4830	.910	23.3	23.5	.3133	.3120
3	$C_{13}H_{24}OSi_2$	$EtMe_2Si(o\text{-}Me_3SiC_6H_4O\text{–})$	144	23	1.4873	.9136	22.2	22.2	.3149	.3130
4	$C_{13}H_{24}OSi_2$	$Me_3Si(3\text{-}Me\text{-}4\text{-}Me_3SiC_6H_3O\text{–})$	148	24	1.4892	.916	22.3	22.2	.3142	.3130
5	$C_{13}H_{24}OSi_2$	$Me_3Si(p\text{-}Me_2EtSiC_6H_4O\text{–})$ $EtMe_2Si(p\text{-}Me_3SiC_6H_4O)$ } Mixed	144	23	1.4806	.902	22.2	22.2	.3153	.3130
6	$C_{13}H_{24}O_2Si_2$	$Me_3Si(o\text{-}EtOMe_2Si)C_6H_4O\text{–})$	142	24	1.4764	.946	20.9	20.9	.2985	.2972
7	$C_{13}H_{24}O_2Si_2$	$Me_3Si(p\text{-}EtOMe_2SiC_6H_4O\text{–})$ $EtOMe_2Si(p\text{-}Me_3SiC_6H_4O\text{–})$ } Mixed	152	25	1.4727	.931	20.7	20.9	.3011	.2972
8	$C_{14}H_{26}O_3Si_2$	$EtOMe_2Si(p\text{-}(EtOMe_2Si)C_6H_4O\text{–})$	168	25	1.4634	.957	18.8	18.8	.2894	.2853
9	$C_{14}H_{26}OSi_2$	$EtMe_2Si(p\text{-}Me_2EtSiC_6H_4O\text{–})$	164	25	1.4841	.906	21.1	21.1	.3159	.3140
10	$C_{15}H_{30}OSi_3$	$Me_3Si(2,4(Me_3Si)_2C_6H_3O\text{–})$	162	24	1.4843	.899	C, 57.0 H, 9.4 27.6	57.9 9.7 27.0	.3184	.3154
11	$C_{15}H_{30}O_2Si_3$	$Me_3Si(2,4\text{-}(Me_3SiO)_2C_6H_3)$	169	19	1.4772	.947	25.2	25.4	.3050	.3022
12	$C_{18}H_{26}OSi_2$	$Me_3Si(2\text{-}C_6H_5\text{-}4\text{-}Me_3SiC_6H_3O)$	195	21	1.5329	.974	17.6	17.8	.3194	.3188
13	$C_{18}H_{26}OSi_2$	$Me_3Si(2\text{-}C_6H_5\text{-}6\text{-}Me_3SiC_6H_3O\text{–})$	200	24	M.p. one form 62.9°; other form 71.6°		17.6	17.8	....	.3188
14	$C_{20}H_{32}O_2Si_3$	$Me_2Si(p\text{-}Me_3SiOC_6H_4\text{–})_2$	*ca.* 226	1.5	1.5139	.973	C, 61.6 H, 8.2	61.8 8.3	.3086	.3058
15	$C_{22}H_{36}O_2Si_3$	$Me_2Si[2\text{-}Me\text{-}4(Me_3SiO)C_6H_3]_2$	Identified by hydrolysis to $Me_2Si(2\text{-}Me\text{-}4\text{-}HOC_6H_3)_2$							

0.80 mole) and sodium (36.8 g., 1.6 g. atoms). Distillation of the products revealed phenoxytrimethylsilane (8.6 g., 7%); *p*-trimethylsilylphenoxytrimethylsilane (50 g., 28%); a very close boiling mixture of isomers, *p*-trimethylsilylphenoxyethyldimethylsilane and *p*-ethyldimethylsilylphenoxytrimethylsilane (59 g., 30%); and *p*-ethyldimethylsilylphenoxyethyldimethylsilane (57 g., 29%). The identity of each product was established by analyses given in Table II and also by hydrolysis. Hydrolysis of the second fraction yielded *p*-trimethylsilylphenol and hexamethyldisiloxane. The third fraction yielded a mixture of phenols. The fourth fraction yielded pure *p*-ethyldimethylsilylphenol and *sym*-diethyltetramethyldisiloxane, b.p. 152° at 742 mm., n^{25}_D 1.3984, d^{25}_4 0.792, sp. ref. 0.3055; calculated sp. ref. 0.3055. *Anal.* Calcd. for $C_8H_{22}OSi_2$: Si, 29.56. Found: Si, 29.59.

(8) **(*p*-Ethoxydimethylsilylphenoxy)-ethoxydimethylsilane.**—*p*-Chlorophenoxyethoxydimethylsilane (106 g., 0.46 mole) was mixed with ethoxydimethylchlorosilane (76 g., 0.55 mole)[8] and reacted with molten sodium (23 g., 1 g. atom) in toluene. About 45 g., 33% of [*p*-ethoxydimethylsilylphenoxy]-ethoxydimethylsilane was obtained. A large amount of very viscous non-volatile material also resulted. This polymeric residue on hydrolysis yielded phenol, polysiloxanes, ethanol, and bis-(*p*-phenylol)-dimethylsilane about 20–30%. The bisphenol could be extracted from the other products with hot water. It crystallized readily from water as the solution cooled. The compound is only sparingly soluble in hot water and practically insoluble in cold water.

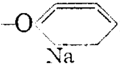
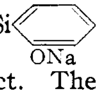
The residue probably consisted of a polymer containing units such as $\text{–O–}C_6H_4SiMe_2C_6H_4\text{–O–}$, $\text{–O–}C_6H_4SiMe_2OC_6H_4\text{–}SiMe_2\text{–}$, $EtOSiMe_2OC_6H_4\text{–}$, etc. Hydrolysis of any of the structures containing an O–Si–O unit led to cleavage of the Si–C bond. Only the structures containing four Si–C bonds, thus, $Me_3SiC_6H_4OH$ or $Me_2Si(C_6H_4OH)_2$, etc., survive mild hydrolytic conditions with all the Si–C bonds intact.

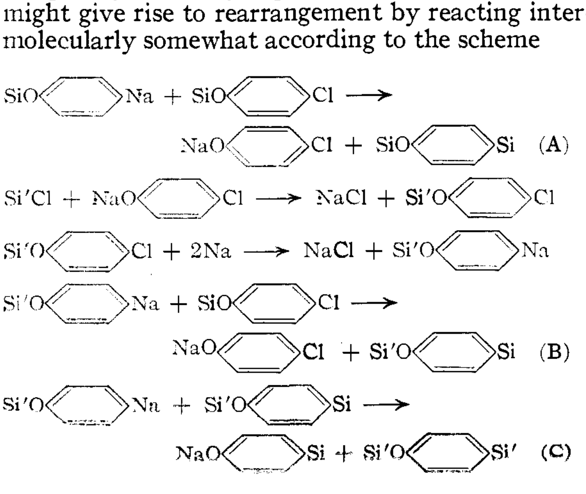
By procedures described in the preceding eight examples the structures listed in Table II were prepared from the appropriate chlorosilanes and the compounds of Table I.

Discussion

The formation of the products obtained in examples 6 and 7 indicates that the Si–O–C bond in the phenoxysilane is subject to attack and rearrangement. It was thought that perhaps a series of consecutive reactions proceeded according to the scheme

$$SiOArCl + 2Na \longrightarrow NaCl + SiOArNa$$
$$SiOArNa \longrightarrow SiArONa$$
$$SiArONa + ClSi' \longrightarrow SiArOSi' + NaCl$$

The organosodium intermediate should by this scheme react first with the ester linkage and then the product of this reaction might react with the chlorosilane to form an ester. If Si and Si′ were distinguishable as in the Me_3Si and Me_2EtSi groups the result of these reactions might well be as found in examples 6 and 7. The ortho-sodium derivative Si–Omight rearrange intramolecularly extremely rapidly to Si and lead to completely rearranged product. The para isomer might give rise to rearrangement by reacting intermolecularly somewhat according to the scheme



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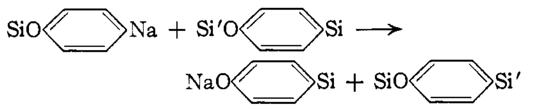
[8] Ethoxydimethylchlorosilane may be prepared by refluxing an equimolar mixture of diethoxydimethylsilane and dichlorodimethylsilane for several hours and distilling the product fairly rapidly, b.p. 95–96° at atmospheric pressure, d^{25}_4 0.94, neut. equiv., 136–144, yield 80%; calcd. neut. equiv., 138.5.



(D)

etc., etc.

By such a scheme of consecutive competitive reactions all the products found would be produced. The scheme is based on the hypothesis that the chief fate of the possible organosodium intermediate was reaction with a Si–O–C linkage in any of the structures present during the experiment. This reaction established an Si–C linkage and produced a sodium phenoxide. The only fate of the sodium phenoxide was reaction with a Si–Cl linkage to establish a new Si–O–C linkage and sodium chloride. The final amounts of each product, of types A, B, C or D in the equations must then be a function of the rates of each reaction. Since the concentrations of any reactant varied during the experiment in an unknown manner, not much can be calculated concerning these rates on the basis of the distribution of end products.

To check the hypothesis outlined in the above equations an experiment was run as follows: A mixture was made up of one mole each of phenoxytrimethylsilane, ethyldimethylchlorosilane and chlorobenzene and added slowly to two moles of molten sodium in refluxing toluene. This mixture seemed to closely approximate the mixtures used to prepare the silylphenoxysilanes, but it precluded the possibility of intramolecular rearrangement of the organosodium intermediate. The mixture reacted smoothly and from the products the following compounds were isolated: phenoxytrimethylsilane, 0.8 mole; phenyltrimethylsilane, 0.15 mole; phenoxyethyldimethylsilane, 0.18 mole; and phenylethyldimethylsilane, 0.74 mole.

The products found are those expected on the basis of the hypothesis advanced, but the quantities produced are not the same as those one would be led to expect from example 7. This difference may be due to the impossibility of intramolecular reaction of the type $SiOC_6H_4Na \rightarrow SiC_6H_4ONa$ in the synthetic mixture, or it might be that the SiOC linkage in $SiOC_6H_5$ is less reactive than the SiOC linkage in $SiOC_6H_4X$ where X may be Na, Cl or Si. Qualitatively, however, the same type of redistribution occurred in all the mixtures.

Phenols and Their Reactions—The silylphenoxysilanes of Table II were very readily hydrolyzed in alcohol, acetone, dioxane or other water-miscible solvents using a trace of either an acid or a base as catalyst. Any of the compounds of Table II having no oxygen on the same silicon atom as the phenylol group, thus $Me_3SiC_6H_4OSiMe_3$, $Me_2Si(C_6H_4OSiMe_3)_2$, etc., yielded the corresponding silicon-substituted phenol in nearly quantitative yields on hydrolysis. Any structure of the type $EtOMe_2SiC_6H_4OSiMe_2OEt$, having an oxygen attached to the same silicon atom as the phenoxy group, yielded in each case only products in which the silicon–phenyl linkage had been broken. Thus, we were unable to isolate any structures having units of the type $O–Si–C_6H_4OH$. Even under the mildest of hydrolytic conditions, cleavage of the Si–C bond occurred. Also where two silyl groups were on the same phenoxy radical, one para to the oxygen was very easily cleaved by hydrolysis.

The phenols of the type $R_3SiC_6H_4OH$ were similarly cleaved by hot dilute acids or alkalies, however, *p*-$Me_3SiC_6H_4ONa$ (0.2 *N*) was found unchanged in a glass-stoppered flask after standing at room temperature for six months. *p*-Trimethylsilylphenol was isolated from this solution on acidification.

Apparently all the phenols were unstable at temperatures above about 150°. They underwent an interesting rearrangement forming the phenoxysilane from the silylphenol according to the equation

$$SiC_6H_4OH \longrightarrow SiOC_6H_5$$

The change was irreversible.

As examples illustrating the preparation of the silylphenols and their reactions the following experiments are described.

***p*-Trimethylsilylphenol.**—Trimethylsilylphenoxytrimethylsilane (24 g., 1 mole) was dissolved in 15 ml. of 95% ethanol, acidified with one drop of concentrated hydrochloric acid and diluted with 3 ml. of water. The mixture grew warm. It was chilled in an ice-bath and diluted to turbidity and permitted to stand for a few minutes. Ice was added to chill and dilute the mixture. An organic liquid separated. This was removed and soon crystallized. The crystals were spread out to permit the solvent and hexamethyldisiloxane to evaporate. Fine white needles of *p*-trimethylsilylphenol were thus obtained (16 g., 96% of theory), m.p. 74–74.2°.

Hydrolysis of 2,4-Bis-(trimethylsilyl)-phenoxytrimethylsilane.—2,4-Bis-(trimethylsilyl)-phenoxytrimethylsilane was hydrolyzed in cold aqueous acetone with a few drops of dilute hydrochloric acid as the catalyst. A phenolic product was obtained, containing only 16.7% silicon. Theory requires 23.5% Si for the bis-(trimethylsilyl)-phenol. The phenol was converted to the 3,5-dinitrobenzoate, m.p. 122–123°. This derivative showed no depression of melting point when mixed with authentic *o*-trimethylsilylphenyl 3,5-dinitrobenzoate, m.p. 123–124°. From these data it is apparent that the trimethylsilyl group para to the oxygen was selectively cleaved during hydrolysis leaving the same group ortho to the oxygen undisturbed.

A similar hydrolysis in alcohol as the solvent using dilute ammonium hydroxide as catalyst led to the same result.

Hydrolysis of 2,4-Bis-(trimethylsiloxy)-trimethylsilylbenzene.—Repeated attempts to hydrolyze 2,4-bis-(trimethylsiloxy)-trimethylsilylbenzene and to isolate 4-trimethylsilylresorcinol led to failure. In each case attempts with no catalyst led to no hydrolysis, and either a weak dilute acid or base led to a very vigorous reaction resulting in the cleavage of the Si–C bond and hydrolysis to produce resorcinol. The presence of two oxygens on the same ring as the trimethylsilyl group very greatly enhances the tendency for hydrolytic cleavage of the trimethylsilyl group.

Some of the phenols isolated by hydrolysis of silylphenoxysilanes are listed in Table III.

Thermal Rearrangement of Trimethylsilylphenols.—Samples of pure trimethylphenoxysilane, and *o*- and *p*-trimethylsilylphenols were each sealed into clean Pyrex glass tubes and heated at 250° for 24 hours. At the end of this time, the contents of all the tubes were nearly identical. The *p*-phenol sample had acquired the properties: b.p. 180.5–181.2°, d^{25}_4 0.924, $n^{25}D$ 1.4778. The *o*-phenol sample had: b.p. 180.3–181.2°, d^{25}_4 0.924, $n^{25}D$ 1.4783. The sample of phenoxytrimethylsilane remained essentially unchanged and had the properties: b.p. 181.5°, $n^{25}D$ 1.4760, d^{25}_4 0.921. The original properties of these samples were: for the *p*-phenol: solid, m.p. 74–74.2°; for the *o*-phenol: b.p. 113° at 26 mm., $n^{25}D$ 1.515, d^{25}_4 0.966; and for the trimethylphenoxysilane, b.p. 182.5° at 736 mm., d^{25}_4 0.920; $n^{25}D$ 1.4753. The hydroxyl content of each sample after heating was practically nil. From these data it was concluded that heating at 250° caused both the *o*- and *p*-trimethylsilylphenols to rearrange to form trimethylphenoxysilane, which is essentially stable at this temperature.

An effort to follow the kinetics of the rearrangement was made by sealing samples of the phenols in small bulbs con-

TABLE III

SILYL-SUBSTITUTED PHENOLS

No.	Empirical formula	Structural formula	Physical properties	Analyses, % Found	Calcd.
1	$C_9H_{14}OSi$	*p*-$Me_3SiC_6H_4OH$	M.p. 74–74.2	C, 64.6	65.0
				H, 8.21	8.42
				Si, 16.7	16.9
				OH, 10.17	10.3
		3,5-Dinitrobenzoate	M.p. 142.5–143	Si, 7.89	7.78
		α-Naphthylurethan	M.p. 153.5–155.0	Si, 8.22	8.36
2	$C_9H_{14}OSi$	*o*-$Me_3SiC_6H_4OH$	M.p. 8.6–9.2	C, 65.2	65.0
	B.p. 113° at 26 mm., d^{25}_4 0.966, n^{25}_D 1.515; sp. ref. calcd. 0.3105, found 0.3106			H, 8.31	8.42
		3,5-Dinitrobenzoate	M.p. 123–124	Si, 7.61	7.78
3	$C_{10}H_{16}OSi$	3-Me-4-$Me_3SiC_6H_3OH$	M.p. 51–51.5	OH, 9.31	9.43
		p-Nitrobenzoate	M.p. 129–129.5	Si, 8.51	8.45
4	$C_{10}H_{16}OSi$	*p*-$EtMe_2SiC_6H_4OH$	M.p. 32.3–33		
			B.p. 148 (24 mm.)	Si, 15.6	15.6
5	$C_{14}H_{16}O_2Si$	$Me_2Si(p\text{-}C_6H_4OH)_2$	M.p. 170–171	Si, 11.5	11.5
6	$C_{16}H_{20}O_2Si$	$Me_2Si(3\text{-}Me\text{-}4\text{-}OHC_6H_3)_2$	M.p. 208–210	Si, 10.4	10.3

nected to a 1-mm. capillary so that the rate of reaction could be followed by measuring the movement of the meniscus of the liquid in the capillary. The results of this were not reproducible and reliable but at 195.5 ± 0.1° the rearrangement of the *o*-trimethylsilylphenol was essentially complete in about two hours. The curve of distance of travel of the meniscus *vs.* time was not that of a first order reaction but seemed to approximate that of a second order reaction.

No meniscus movement was detectable for a sample of trimethylphenoxysilane. No reaction could be detected between phenol and *o*-trimethylsilylphenoxytrimethylsilane. It was thought that perhaps these compounds could react according to the equation

$$o\text{-}Me_3SiC_6H_4OSiMe_3 + C_6H_5OH \longrightarrow 2Me_3SiOC_6H_5$$

This, however, was not the case at 200° even on prolonged heating.

Hydrogenation of *p*-Trimethylsilylphenoxytrimethylsilane.—The hydrogenation of *p*-trimethylsilylphenoxytrimethylsilane was found sometimes to be a simple matter using Raney nickel (10% by weight) in isoöctane solution.

On one occasion hydrogenation started at 1000 p.s.i. of hydrogen at 100° and proceeded to completion in 70 minutes. On some other occasions the hydrogenation could not be readily effected under conditions made as nearly identical as possible. The cause of this is not known. On one occasion when hydrogenation did not take place, the bomb was opened and benzene was added to the mixture already present in the bomb. The benzene was quantitatively hydrogenated in the mixture leaving the phenoxysilane unaffected. On such occasions the use of more catalyst, more pressure and a higher temperature was of little or no avail. When the compound could be hydrogenated it was done easily at 95–105° and 300–1000 p.s.i.

The hydrogenated product was distilled and yielded two isomers, the *cis*- and *trans*-4-trimethylsilylcyclohexyloxytrimethylsilane. These boil at about 115° at 23 mm., n^{25}_D 1.4409, d^{25}_4 0.854, sp. ref. 0.3092; and 120° at 23 mm., n^{25}_D 1.4427, d^{25}_4 0.857, sp. ref. 0.3092. Calculated sp. ref. for $Me_3SiC_6H_{10}OSiMe_3$ is 0.3092. The silicon content was constant at 22.7 to 22.9%; calcd. 22.96%. These isomers probably were not completely separated from one another.

The lower boiling fractions were hydrolyzed in dilute acid and yielded a 4-trimethylsilyl-cyclohexanol which, when crystallized from aqueous acetone, melted at 57–57.5°. *Anal.* Calcd. for $C_9H_{20}OSi$: Si, 16.3. Found: Si, 16.2.

The higher boiling isomer on the same treatment yielded an alcohol, m.p. 75–76.5°. *Anal.* Calcd. for $C_9H_{20}OSi$: Si, 16.3. Found: Si, 16.4.

Both isomers smell very much like menthol. It is impossible at this time to state which isomer is *cis* and which is *trans*.

Either isomer oxidized in nitric acid by the procedure outlined by Gilman and Blatt[9] yielded 3-trimethylsilyladipic acid, m.p. 85–87°.

Anal. Calcd. for $Me_3SiCH(CH_2COOH)CH_2CH_2COOH$: neut. equiv., 109.2. Found: neut. equiv., 109.4.

The Synthesis of Silyl-substituted Alcohols.—(Chloroalkoxy)-silanes were treated with an active metal such as sodium, lithium or magnesium in any of several ways. The following equations outline the reactions

$$SiO(CH_2)_xCl + 2Na + ClSi \longrightarrow SiO(CH_2)_xSi + 2NaCl$$

$$SiO(CH_2)_xCl + 2M \longrightarrow Si(CH_2)_xOM + MCl$$

$$R_3SiO(CH_2)_xCl + Mg \longrightarrow R_3SiO(CH_2)_xMgCl \longrightarrow R_3Si(CH_2)_xOMgCl$$

In these equations *x* must be greater than two. When *x* = 2, a reaction occurred producing ethylene[10]; for example

$$Me_3SiO(CH_2)_2Cl + 2Na + ClSiMe_3 \longrightarrow (Me_3Si)_2O + CH_2CH_2 + 2NaCl$$

When *x* = 3, magnesium could not be caused to react. When *x* = 4 or 5, sodium, lithium or magnesium all reacted smoothly provided only one $Cl(CH_2)_x$–O– group was present on the silicon. When more than one such group was present only sodium and lithium reacted. When *x* = 4 or 5 the intermediate Grignard reagent shown in the third equation was found to be quite stable at room temperature, rearranging only at elevated temperatures. The reagent of the type $R_3SiO(CH_2)_{4-5}MgCl$ might well be useful in organic synthesis for the introduction of an hydroxyl ended chain of four or five carbon atoms into any molecule capable of coupling readily with a Grignard reagent.

The general procedure for carrying out the reaction outlined in the first equation was nearly identical to that described in example 1 for the production of trimethylsilylphenoxytrimethylsilane. Yields in general were considerably lower for preparation of the alcohols than for the phenoles and are given in Table IV.

The process using no chlorosilane as in the second equation above was slightly modified depending upon the metal used. When sodium was used, the chloroalkoxysilane was added slowly to molten sodium in refluxing toluene, *i*-isooctane, or similar inert solvent. The mixture was stirred vigorously until reaction was complete. A small amount of alcohol followed by aqueous acid was then added to dissolve the sodium salts. The aqueous layer then was separated, dried and distilled. Lithium was used in the same way using a lower boiling solvent such as hexane or pentane. Reactions using lithium were less vigorous, but proceeded smoothly to completion after a variable induction period before starting. Magnesium was used in a typical Grignard apparatus using absolute ether as the solvent. When the reaction appeared to be complete, the ether was evaporated and the residue was heated to 100–135° for 3–12 hours to cause coupling. It was then washed up and distilled.

The results of such processes are outlined in Table IV.

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[9] H. Gilman and A. H. Blatt, "Organic Syntheses," Vol. 1, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., p. 18.

[10] L. S. Moody, THIS JOURNAL, **72**, 5754 (1950), found that β-chloroethoxytrimethylsilane and magnesium in diethyl ether also formed ethylene.

TABLE IV

PREPARATION OF SILYL-SUBSTITUTED ALCOHOLS AND INTERMEDIATES

Chloroalkoxysilane	Chlorosilane	M	Products	Yield, %
$Me_3SiO(CH_2)_3Cl$	Me_3SiCl	Na	$Me_3SiO(CH_2)_3SiMe_3$	68
			$Me_3SiO(CH_2)_3H$	20
	None	Na	$Me_3Si(CH_2)_3OH$	61
	None	Li	$Me_3Si(CH_2)_3OH$	60
	None	Mg	No reaction	
$Me_2EtSiO(CH_2)_3Cl$	$Me_2EtSiCl$	Na	$Me_2EtSiO(CH_2)_3SiEtMe_2$	63
$2Me_3SiO(CH_2)_3Cl$	Me_2SiCl_2	Na	$Me_2Si[(CH_2)_3OH]_2$	14
Followed by hydrolysis			$Me_3Si(CH_2)_3OH$	38
$Me_2Si[O(CH_2)_3Cl]_2$	$2Me_3SiCl$	Na	$Me_2Si[(CH_2)_3OH]_2$	47
Followed by hydrolysis			*n*-PrOH	*ca.* 50
			$Me_3Si(CH_2)_3OH$	*ca.* 5
$Me_2Si[O(CH_2)_3Cl]_2$	None	Li	No reaction	
$Me_3SiO(CH_2)_4Cl$	Me_3SiCl	Na	$Me_3SiO(CH_2)_4SiMe_3$	61
$Me_2EtSiO(CH_2)_4Cl$	Me_3SiCl	Na	Inseparable mixture	
$Me_3SiO(CH_2)_4Cl$	None	Na	$Me_3Si(CH_2)_4OH$	Small
	None	Na[a]	*n*-BuOH	75
	None	Li	$Me_3Si(CH_2)_4OH$	56
	None	Mg	$Me_3Si(CH_2)_4OH$	63
$Me_3SiO(CH_2)_5Cl$	Me_3SiCl	Na	$Me_3SiO(CH_2)_5SiMe_3$	40
	None	Na	$Me_3Si(CH_2)_5OH$	14
	None	Mg	$Me_3Si(CH_2)_5OH$	45
	None	Li	$Me_3Si(CH_2)_5OH$	79
$Me_2Si[O(CH_2)_5Cl]_2$	None	Mg	No reaction	
$Me_3SiO{-}CHCH_3CH_2O(p\text{-}ClC_6H_4)$	Me_3SiCl	Na	$Me_3SiOCHCH_3CH_2(p\text{-}C_6H_4SiMe_3)$	84
$Me_3SiOCH_2CH_2O(o\text{-}ClC_6H_4)$	Me_3SiCl	Na	$Me_3SiOCH_2CH_2O(o\text{-}C_6H_4SiMe_3)$	92

[a] A sodium emulsion in tetralin supplied by E. I. du Pont de Nemours & Co., Inc., Electrochemicals Department, was used with pentane as the solvent.

From any of the esters of Table IV, the corresponding alcohols were easily obtainable by hydrolysis usually in acidified aqueous alcohol. The physical properties of the products of these reactions are given in Table V.

TABLE V

SILYL-ALKOXYSILANES AND SILYLALCOHOLS AND DERIVATIVES

Structure	B.p. °C.	B.p. Mm.	$n^{25}D$	d^{25}_4	Sp. ref. Found	Sp. ref. Calcd.	Silicon, % Found	Silicon, % Calcd.
$Me_3Si(CH_2)_3OH$	82	24	1.4250	0.822	0.3109	0.3106	21.2	21.2
Adipic ester	210	3	1.4471	.930	.2873	.2890	14.8	15.0
$EtMe_2Si(CH_2)_3OH$	101	25	1.4370	.839	.3125	.3125	19.5	19.2
$Me_3Si(CH_2)_4OH$	96	25	1.4315	.830	.3122	.3125	19.1	19.2
$Me_3Si(CH_2)_5OH$	110	25	1.4358	.841	.3108	.3141	17.5	17.5
$EtMe_2Si(CH_2)_5OH$	124	24	1.4421	.838	.3157	.3154	16.2	16.1
$p\text{-}Me_3SiC_6H_4OCH_2CHOHCH_3$	283	747	M.p. 62–63°				12.5	12.5
$p\text{-}Me_3SiC_6H_4OCH_2CH_2OH$	128-132	0.7–1.2	1.514	1.01	.301	.2981	13.1	13.3
$o\text{-}Me_3SiC_6H_4OCH_2CH_2OH$	106	0.8	1.5157	1.01	.298	.2981	13.1	13.3
$Me_2Si[(CH_2)_3OH]_2$	176	24	1.4649	0.940	.2942	.2944	15.9	15.9
$Me_3Si(CH_2)_3OSiMe_3$	81	25	1.4120	.796	.3120	.3124	21.4	21.4
$EtMe_2Si(CH_2)_3OSiEtMe_2$	115	25	1.4251	.817	.3139	.3143	24.2	24.6
$Me_3Si(CH_2)_4OSiMe_3$	94	24	1.4166	.802	.3133	.3134	25.4	25.7
$Me_3Si(CH_2)_5OSiMe_3$	112	24	1.4200	.804	.3147	.3143	24.1	24.6
$EtMe_2Si(CH_2)_5OSiMe_2Et$	140	24	1.4328	.826	.3145	.3163	..	..
$p\text{-}Me_3SiC_6H_4OCH_2CHCH_3OSiMe_3$	179	24	1.4770	.922	.3064	.3095	18.7	18.9
$p\text{-}Me_3SiC_6H_4OCH_2CH_2OSiMe_3$	172	24	1.4827	.935	.3053	.3023	19.4	19.9
$o\text{-}Me_3SiC_6H_4OCH_2CH_2OSiMe_3$	166	24	1.4818	.945	.3016	.3023	..	..

The alcohols of Table V appear to be stable structures possessing the reactivities of typical alcohols. They did not rearrange at elevated temperatures as the phenols did, and they were not cleaved by dilute aqueous acids or bases even under prolonged refluxing.

5-Hydroxypentylmercuric Chloride.—As an example of the possible utility of the Grignard reagents of the chloroalkoxysilanes described above, the following experiment will be described.

In a typical Grignard apparatus, 2.5 g. of magnesium (0.1 mole) in absolute ether (100 ml.) was treated with somewhat less than 1 ml. of ethyl bromide. When reaction was complete, 19.5 g., 0.1 mole of 5-chloropentoxytrimethylsilane was added in one portion. A smooth reaction took place which kept the mixture gently refluxing four hours until almost all the magnesium had been dissolved. It was stirred and heated to reflux one additional hour, then cooled to 0°. Mercuric chloride (27 g., 0.1 mole) was added in small portions. This addition caused the evolution of much heat. When the addition was complete, the ether was removed by evaporation on a steam-bath. The solid residue was shaken with dilute hydrochloric acid to dissolve the salts and to hydrolyze the siloxy linkage. The solids present were removed by filtration and shaken with 200 ml. of hot alcohol. About 5–7 g. of insoluble inorganic matter was filtered out of the mixture. The filtrate yielded soft white crystals (21.5 g.), m.p. 138–42°, followed by successive crops (9 g.) of about the same m.p. Recrystallized from methanol these had a m.p. 142–143.5°, 18 g., 54% yield. Less pure product, 10.5 g., 32% of m.p. 136–142°

was also obtained. *Anal.*[11] Calcd. for $C_5H_{11}OClHg$: Hg, 62.07. Found: Hg, 61.3.

This experiment suggests that many unusual hydroxyalkyl compounds might be synthesized with a trialkylsiloxyalkylmagnesium halide as a convenient reagent.

PITTSBURGH, PENNA. RECEIVED APRIL 25, 1951

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[11] Analysis was by the method of F. C. Whitmore and R. J. Sobatski, THIS JOURNAL, **55**, 1128 (1933).

[CONTRIBUTION FROM THE CHEMICAL FOUNDATION LABORATORY AND THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF COLORADO]

Some Reactions of the Sodium Salts of Certain Amides[1]

BY JOSEPH D. PARK, ROBERT D. ENGLERT[1a] AND JOHN S. MEEK

The reactions of the sodium salts of some amides with certain halohydrocarbons were studied. The products formed when alkylene dihalides were used were explained on the basis of inductive effects of the halogen atoms and the relative nucleophilic power of the attacking ion toward hydrogen and carbon. The products were tested for their insecticidal action against the roach, *Periplaneta americana*, and the per cent. knockdown and per cent. kill observed.

In connection with the program in this Laboratory on insecticides, it was of interest to study the reactions of the sodium salts of amides with certain halogen-containing compounds.

Three main methods of synthesis were used: Hepp's[2] procedure using an amide and sodium in an inert solvent such as toluene followed by the addition of a halohydrocarbon; Pictet's[3] method using an amide, potassium hydroxide and a halohydrocarbon in ethyl alcohol; and a method utilizing sodium hydride in much the same manner as has recently been described by Fones.[4]

It was necessary in Hepp's method to use large volumes of solvent and vigorous stirring to complete the reaction of the sodium with the amide reactant. When using sodium hydride, the sodium salt of the amide would coat the granules of the hydride and hinder its complete reaction. It was found that the halohydrocarbon could be included with the initial reactants provided it had no active hydrogen, whereupon the halogen compound would continuously react with the sodium salt of the amide eliminating to a great extent any coating of the sodium hydride granules. By such a procedure the yield of product was considerably increased over that found when using Hepp's method. Both Hepp's procedure and the utilization of sodium hydride to form the sodium salt failed to produce an alkylated product when the amide reactant was a benzenesulfonamide derivative and the insolubility of the sodium salt of the amide in toluene is suggested as a reason for this result. The same benzenesulfonamide derivative was easily alkylated by the method of Pictet in which the sodium salts are soluble in the alcohol solvent.

Titherley[5] found that the reaction between sodamide derivatives of the type RCONHNa reacted normally with various halogen compounds such as alkyl halides, acid chlorides and halogen-substituted esters if R was an aryl group. However, if R was an alkyl group, only small quantities (if any) of product was formed owing to unexpected side reactions.

A much easier way of replacing the sodium atom in the sodium derivatives by alkyl groups, and thus synthesizing various alkyl-substituted amides, is by heating the sodamide with potassium alkyl sulfates (R and R′ = alkyl or aryl)

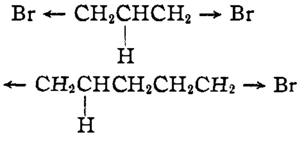
$$RCONHNa + KR'SO_4 \longrightarrow RCONHR' + KNaSO_4$$

This method, however, was not used in the synthesis of the products tested in this program.

Pictet's method has been described as producing good yields of alkylated products from such compounds as acetanilide; however, it was found to fail with a compound such as N-ethylacetamide. Acetanilide has a much greater resonance stabilization than N-ethylacetanilide which would favor the release of the proton.

Sodium N-ethylacetamide was allowed to react with pentamethylene chloride for a week, but only a poor yield of 1,5-bis-(N-ethylacetamide)-pentane was isolated. A good yield of the same product was obtained in 24 hours from pentamethylene bromide. Allylic compounds such as benzyl chloride reacted in a shorter time to produce good yields of alkylated products.

When sodium N-ethylacetamide was treated with pentamethylene bromide the bis-amide was produced; however, with trimethylene bromide N-allyl-N-ethylacetamide was formed. With trimethylene bromide an elimination reaction must have occurred first followed by the usual alkylation reaction. The elimination mechanism (E2) was favored by the inductive (−I) effects of both bromine atoms affecting the same or beta carbon atom favoring the release of a proton. In pentamethylene bromide the inductive effects must pass over a longer carbon chain and consequently a substitution mechanism (S_N2) is favored.



$$Br \leftarrow CH_2\underset{\displaystyle H}{\underset{|}{C}}HCH_2 \rightarrow Br$$

$$Br \leftarrow CH_2\underset{\displaystyle H}{\underset{|}{C}}HCH_2CH_2CH_2 \rightarrow Br$$

When sodium N-ethylbenzenesulfonamide was allowed to react with trimethylene bromide, 1,3-bis-(N-ethylbenzenesulfonamide)-propane was produced. Using the same alkylene dibromide, elimination or substitution can occur as determined by the

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[1] This paper represents part of a thesis submitted by Robert D. Englert to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the degree Doctor of Philosophy, August, 1949.

[1a] Chemical Foundation Fellow in Chemistry.

[2] P. Hepp, *Ber.*, **10**, 327 (1877).

[3] A. Pictet, *ibid.*, **20**, 3422 (1887).

[4] W. W. Fones, Abstracts of Papers of the 115th Meeting of the A.C.S., San Francisco, Calif., March 27-April 1, 1949, p. 60L.

[5] A. W. Titherley, *J. Chem. Soc.*, **79**, 391 (1901).