an increase in electrode area causing a directly proportional increase in the amount of trifluoroacetic acid produced per pass over the variable limits studied. The residence time of the reactants mixture in the operating reactor directly influences the yield of trifluoroacetic acid produced.

Because no undesirable decomposition of either trifluoroacetic acid or of trifluoroethane was noted when the gas mixtures were saturated with water vapor at 30°, independent of the residence times of the reactants in the operating reactor, the chemical reaction shown by Equation 3 is concluded to be highly specific.

ORLANDO, FLA.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Preparation and Thermal Rearrangement of Poly(trimethylsilyl)phenols

GLENN D. COOPER

Received June 15, 1960

Phenols having a single trimethylsilyl group on the ring are conveniently prepared by the hydrolysis of the corresponding aryloxytrimethylsilane:

$$(CH_3)_3SiC_6H_4OSi(CH_3)_3 \xrightarrow[H^+ \text{ or } OH^-]{H_2O} (CH_3)_3SiC_6H_4OH + (CH_3)_3SiOSi(CH_3)_3.$$

Previous attempts to prepare phenols having more than one *ortho-* or *para-*trimethylsilyl substituent have failed because of aryl-silicon cleavage during hydrolysis.[4] It has been found that the aryloxytrimethylsilanes can be converted to the phenols without appreciable silicon-carbon cleavage by treating them with a concentrated solution of sodium methoxide in anhydrous methanol, diluting with water, and extracting the phenol with pentane. Phenols having trimethylsilyl substituents in the 2,4-, 2,6-, and 2,4,6-positions have been prepared in this manner.

Both *o-* and *p-*(trimethylsilyl)phenol are known to rearrange to phenoxytrimethylsilane at 200–250°:[4]

$$(CH_3)_3SiC_6H_4OH \longrightarrow C_6H_5OSi(CH_3)_3.$$

The poly(trimethylsilyl)phenols undergo the same rearrangement. When both *ortho-* and *para-*trimethylsilyl groups are present the rearrangement is exclusively *ortho*. The strong tendency for *ortho* rearrangement is confirmed by a study of the rearrangement of the monosubstituted phenols; the rates are in the order $o \gg p \gg m$. It is suggested that *ortho* rearrangement occurs predominantly by an intramolecular process while *meta* and *para* rearrangements involve a series of intermolecular desilylation reactions.

During the course of another investigation it became desirable to prepare phenols having one or more positions blocked by groups which could be replaced by hydrogen under mild conditions. The trimethylsilyl group attached to an aromatic ring is readily cleaved by acid,[1–3] particularly when electron-releasing groups such as hydroxyl or alkoxyl are present.

$$ArSi(CH_3)_3 \xrightarrow[H_2O]{H^+} ArH + (CH_3)_3SiOSi(CH_3)_3 \qquad (1)$$

The trimethylsilyl group was therefore selected as the blocking group. The three mono(trimethylsilyl)phenols have been prepared previously,[4,5] but phenols having more than one trimethylsilyl substituent in the ring have not been reported. Attempts to prepare compounds of this type by hydrolysis of the corresponding aryloxytrimethylsilane led to cleavage of aryl-silicon bonds. The purpose of this communication is to describe a method by which trimethylsilyl-substituted aryloxytrimethylsilanes can be converted to the corresponding phenols without appreciable carbon-silicon cleavage and to report the synthesis and thermal rearrangement of a number of poly(trimethylsilyl)phenols.

PREPARATION OF PHENOLS

(Trimethylsilyl)phenoxytrimethylsilanes. Mono(trimethylsilyl)phenols are conveniently prepared by the reaction of the corresponding chlorophenoxytrimethylsilane with sodium and trimethylchlorosilane in refluxing toluene, followed by hydrolysis of the (trimethylsilyl)phenoxytrimethylsilane to the phenol:

$$ClC_6H_4OH + (CH_3)_3SiCl \longrightarrow ClC_6H_4OSi(CH_3)_3$$
$$\xrightarrow[(CH_3)_3SiCl]{Na} (CH_3)_3SiC_6H_4OSi(CH_3)_3$$
$$\xrightarrow[H^+ \text{ or } OH^-]{H_2O} (CH_3)_3SiC_6H_4OH \qquad (2)$$

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[1] H. Gilman and F. J. Marshall, *J. Am. Chem. Soc.*, **71**, 2066 (1949).

[2] R. A. Benkeser and H. R. Krysiak, *J. Am. Chem. Soc.*, **76**, 6353 (1954).

[3] C. Eaborn, *J. Chem. Soc.*, 4858 (1956).

[4] J. L. Speier, *J. Am. Chem. Soc.*, **74**, 1003 (1952).

[5] R. A. Benkeser and H. R. Krysiak, *J. Am. Chem. Soc.*, **75**, 2421 (1953).

TABLE I

PROPERTIES OF ARYLOXYTRIMETHYLSILANES, ArOSi(CH$_3$)$_3$

Ar	Yield, %	B.P. °C.	B.P. Mm.	M.P., °C.	n_D^{20}	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	Si, % Calcd.	Si, % Found
2,6-Dichlorophenyl	85	115	15	—	1.5116	46.0	45.9	5.1	5.4	11.9	11.8
2,4,6-Trichlorophenyl	84	110	2	—	1.5252	40.1	40.7	4.1	4.2	10.4	10.3
2,6-Bis(trimethylsilyl)phenyl	28	139	8	57.5–58	—	58.1	57.8	9.8	9.9	27.1	26.7
2,4,6-Tris(trimethylsilyl)phenyl	7	112	0.7	63.5–64	—	56.5	56.7	10.0	10.1	29.3	29.2

This general procedure was followed in this work for the synthesis of phenols having trimethylsilyl groups in the 2-, 3-, 4-, 2,4-, 2,6-, and 2,4,6-positions. Preparation of the chlorophenoxytrimethylsilanes presented no problem and the replacement of ring chlorine by trimethylsilyl groups in the Wurtz coupling gave good yields (70–90%) of the 2-, 3-, 4-, and 2,4-substituted compounds. The yield of 2,6 - bis(trimethylsilyl)phenoxytrimethylsilane was much lower (28%), while the yield of 2,4,6-tris(trimethylsilyl)phenoxytrimethylsilane was only 7%. Both these compounds have two bulky trimethylsilyl groups adjacent to the equally bulky trimethylsiloxy group and would be expected to be formed with difficulty.[6] The lowered yields are also a consequence (particularly in the case of the trisubstituted compound) of the difficulty in separating the desired compounds from partially reacted chlorophenoxytrimethylsilanes, which required a careful fractional distillation, resulting in loss due to thermal rearrangement, followed by repeated recrystallizations from methanol. The properties of the poly(trimethylsilyl)phenoxytrimethylsilanes and some previously unreported chlorophenoxytrimethylsilanes are listed in Table I.

All of the aryloxytrimethylsilanes showed a strong infrared absorption band at 10.5–11.0 μ. This band is believed to be characteristic of the Si–O–Ar linkage, as recently suggested by Wilson, Smith, and Ferris,[6] who observed such a band between 10 and 11μ in a series of 2,6-disubstituted phenoxysilicon compounds. It disappears on hydrolysis to the phenol and its absence provides a sensitive test for completion of the hydrolysis.

Hydrolysis of aryloxytrimethylsilanes. Speier[4] prepared 2,4 - bis(trimethylsilyl)phenoxytrimethylsilane, but on hydrolysis both in aqueous acetone with dilute hydrochloric acid as the catalyst and in aqueous ethanol using ammonia, cleavage of the *para*-trimethylsilyl group occurred, yielding *o*-(trimethylsilyl)phenol as the only phenolic product isolated. We found that all of the poly(trimethylsilyl)phenoxytrimethylsilanes could be converted to the phenols with very little cleavage by dissolving them in a solution of sodium methoxide in absolute methanol, allowing the solution to stand overnight in a refrigerator,[7] diluting with a large volume of water, and extracting the phenol with pentane. In this way it was possible to obtain 80–95% yields of crude phenols which were more than 98 mole % pure. The 2,4-bis(trimethylsilyl)phenol and 2,4,6-tris(trimethylsilyl)phenol, both low melting solids, could then be further purified by recrystallization from hexane.

Aryl-silicon cleavage during hydrolysis. The impurities in the crude phenols were those produced by loss of trimethylsilyl groups from the ring. The extent of this aryl-silicon cleavage was greatly affected by the concentration of the base; the higher the concentration of sodium methoxide, the less cleavage was observed. Desilylation was most serious in the hydrolysis of 2,4,6-tris(trimethylsilyl)phenoxytrimethylsilane. The crude phenol obtained from reaction with 1*M* sodium methoxide contained 25% of mixed 2,4- and 2,6-bis(trimethylsilyl)phenol. When a 2*M* solution was used 9.1% of desilylated phenols were formed and with 4.5*M* sodium methoxide only 1.2% desilylation occurred. The reason for the inverse dependence of desilylation on methoxide ion concentration is not apparent.

Hydrolysis of 2,4,6-tris(trimethylsilyl)phenoxytrimethylsilane in sodium methoxide solution produced approximately ten times as much 2,6- as 2,4-bis(trimethylsilyl)phenol, showing that the trimethylsilyl group *para* to oxygen was selectively cleaved. The ratio of *para* to *ortho* cleavage was even greater with 2,4-bis(trimethylsilyl)phenol. When 0.005 mole of this phenol was heated for one hour at 50° with 20 ml. of 0.4*M* sodium methoxide (0.008 mole) 8.3% of desilylated phenols were formed; it was estimated that the ratio of *para* to *ortho* attack was at least 25 to 1. Desilylation of this

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[6] Wilson and co-workers [G. R. Wilson, A. G. Smith and F. C. Ferris, [*J. Org. Chem.*, 24, 1717 (1959)] were unable to prepare a carbon analog, 2,6-di-*tert*-butylphenoxytrimethylsilane, by the reaction of the bromomagnesium salt with trimethylchlorosilane. In spite of the greater bulk of the trimethylsilyl group compared to the *tert*-butyl group, the fact that the silicon-carbon bond is longer than the carbon-carbon bond appears to make the silicon compound somewhat less strained than the *tert*-butyl compound.

[7] Such a long reaction time is not necessary, and may actually be undesirable. The aryloxytrimethylsilane reacts very rapidly with methoxide ion. An 81% yield of pure 2,4-bis(trimethylsilyl)phenol was obtained when the phenoxytrimethylsilane was allowed to react for only three minutes with 2*M* sodium methoxide solution.

TABLE II

THERMAL REARRANGEMENT OF (TRIMETHYLSILYL)PHENOLS[a]

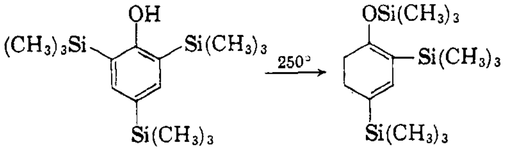
	Product (mole %)			
Compound	$(CH_3)_3SiC_6H_4OH$	$(CH_3)_3SiC_6H_4$-$OSi(CH_3)_3$	$C_6H_5OSi(CH_3)_3$	C_6H_5OH
o-$(CH_3)_3SiC_6H_4OH$	< 0.1	9.1	80.0	10.9
p-$(CH_3)_3SiC_6H_4OH$	42.2	12.7	29.4	15.7
m-$(CH_3)_3SiC_6H_4OH$	>99		tr	tr
m-$(CH_3)_3SiC_6H_4OH$[b]	77.4	6.0	7.6	9.0

[a] Six hours at 200°. [b] Twenty-four hours at 250°.

phenol under the conditions employed by Eaborn[3] (20 minutes at 50° in five volumes of methanol plus two volumes of 0.1055*N* perchloric acid) produced 25.7% of mono(trimethylsilyl)phenols. The ratio of *para* to *ortho* desilylation was 7 to 1. From this the rate constant for *para* desilylation is calculated to be 12.4 × 10^{-3} min.$^{-1}$, compared with 4.91 × 10^{-3} min.$^{-1}$ for the desilylation of *p*-(trimethylsilyl)phenol.[3] The factor of 2.5 between the two rates presumably reflects the added activating influence of a trimethylsilyl group in the *meta* position.

THERMAL REARRANGEMENT OF (TRIMETHYLSILYL)-PHENOLS

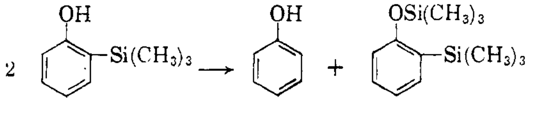
Speier[4] found that both *o*- and *p*-trimethylsilyl)-phenol rearranged to phenoxytrimethylsilane at 250°. The poly(trimethylsilyl)phenols described in the present work also rearranged quantitatively to aryloxytrimethylsilanes when heated for 24 hours at 250°. When both *ortho*- and *para*- trimethylsilyl groups were present the rearrangement was exclusively *ortho*. Thus, 2,4-bis(trimethylsilyl)-phenol yielded only *p*-(trimethylsilyl)phenoxytrimethylsilane, while the 2,4,6-trisubstituted phenol yielded 2,4-bis(trimethylsilyl)-phenol.



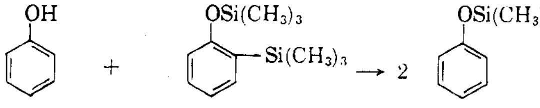
(3)

The relative facility of *ortho* rearrangement was confirmed by the results obtained when the mono-(trimethylsilyl)phenols were heated for six hours at 200° and the products were then analyzed by gas chromatography (Table II). The product in each case was a mixture of phenol, phenoxytrimethylsilane, (trimethylsilyl)phenoxytrimethylsilane, and unchanged trimethylsilylphenol.[8] The rearrangement is obviously complex, but a comparison either of phenoxytrimethylsilane produced or trimethylsilylphenol recovered shows that the rate is in the order *o*>>*p*>>*m*.

Mechanism of rearrangement. This type of rearrangement, in which a group attached to the aromatic ring exchanges with hydrogen attached to another atom which is attached to the ring, has few parallels in strictly carbon chemistry: the best-known example is probably the acid catalyzed "reverse Fries" rearrangement of keto-phenols. The mechanism is therefore of some interest. The ease with which (trimethylsilyl)phenols undergo disilylation suggests that the reaction may proceed by way of a series of such desilylations involving electrophilic attack on the aromatic ring, either by a proton or an unionized phenol molecule. One such possibility, illustrated below for *o*-(trimethylsilyl)-phenol, was considered by Speier:



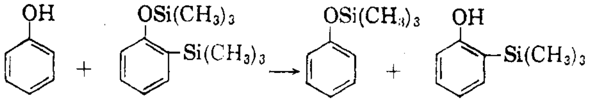
(4)



(5)

The rearrangement of the phenol, followed by a dilatometric technique, appeared to be complete within two hours at 195°. Under the same conditions he was unable to detect any reaction between phenol and *o*-(trimethylsilyl)phenoxytrimethylsilane.

The observation of phenol and *o*-trimethylsilylphenoxytrimethylsilane among the products of the reaction of *o*-(trimethylsilyl)phenol at 200° (Table II) indicates that reaction (4) does indeed occur. It was found in a separate experiment that reaction (5) also occurs,[9] but that the rate is far too slow at 200° to account for the amount of phenoxytrimethylsilane formed.[10] It appears that reaction



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[8] The discrepancy between the values for phenol and trimethylsilylphenoxytrimethylsilane, which must be equal to provide a silicon balance, is probably representative of the error involved in the analysis.

[9] Reaction (5) as written implies attack by the phenol on the trimethylsilyl group attached to the ring; attack on the trimethylsilyl group attached to oxygen leads to the same overall result.

[10] Although reaction (5) proceeds only to a negligible extent in six hours at 200°, it is virtually complete in 24 hours at 250°.

(4) is a side reaction and that the major portion of the reaction proceeds by some other path.

The conclusion that *ortho* rearrangement does not proceed *via* a series of desilylation reactions is supported by the fact that the polysubstituted phenols underwent exclusively *ortho* rearrangement, although desilylation of these phenols, both in acidic and basic solution, occurred predominantly at the *para* position. It appears likely that the *ortho* rearrangement is an intramolecular reaction, while the *para* and *meta* rearrangements are intermolecular reactions proceeding through a series of desilylation reactions similar to (4) and (5).

EXPERIMENTAL

Preparation of chloro-substituted phenoxytrimethylsilanes. These compounds were all prepared by heating the phenol under reflux with a 50% excess of trimethylchlorosilane until evolution of hydrogen chloride ceased. In the case of the least reactive phenols (the 2-chloro- and 2,6-dichloro) refluxing was continued for approximately 10 days. The phenoxytrimethylsilanes were purified by fractional distillation. Yields ranged from 85–95%.

(Trimethylsilyl)phenoxytrimethylsilanes. The *o*-, *m*-, and *p*-(trimethylsilyl)phenoxytrimethylsilanes and 2,4-bis(trimethylsilylphenoxytrimethylsilane) were prepared by reaction of the chloro compound, sodium, and trimethylchlorosilane according to the procedure used by Speier.[4] A high-speed stirrer in a creased reaction flask was employed. Preparation of 2,6-bis(trimethylsilyl)phenoxytrimethylsilane and 2,4,6-tris(trimethylsilyl)phenoxytrimethylsilane required somewhat more vigorous reaction conditions than those described by Speier. The products were purified by fractional distillation followed by recrystallization from methanol in the case of solid compounds.

2,4,6-Tris-(trimethylsilyl)phenoxytrimethylsilane. A suspension of 113 g. (4.9 g.-atoms) of sodium in 325 ml. of toluene was heated under reflux, with vigorous stirring, while a mixture of 201 g. (0.75 mole) of 2,4,6-trichlorophenoxytrimethylsilane and 265 g. (2.45 moles) of trimethylchlorosilane was added slowly from a dropping funnel. After about one-half of the mixture had been added, 100 ml. of toluene was added to the thick slurry and the addition was continued. When addition had been completed (approximately 2 hr.) 200 ml. of toluene was added and heating was continued for 45 min. more. The mixture was cooled and filtered and the filtrate was distilled under reduced pressure. A fraction boiling at 111–119°/0.8 mm. (n_{D}^{20} 1.4921) solidified upon standing. Recrystallization from methanol yielded 19.3 g. (7%) of pure 2,4,6-tris(trimethylsilyl)phenoxytrimethylsilane, m.p. 63.5–64.0°.

2,4-Bis(trimethylsilyl)phenol. A solution of 3.87 g. (0.0125 mole) of 2,4-bis(trimethylsilyl)phenoxytrimethylsilane (b.p. 142°/12 mm., n_{D}^{20} 1.4865; (lit.[4] b.p. 162°/24 mm., n_{D}^{20} 1.4843) in 30 ml. of 2*M* sodium methoxide in methanol (freshly prepared from sodium and anhydrous methanol) was allowed to stand for 18 hr. in a refrigerator at 5°. It was then diluted with 150 ml. of water and extracted with pentane. The pentane solution was dried over sodium sulfate and then evaporated, yielding 2.39 g. (80%) of 2,4-bis-(trimethylsilyl)phenol, a colorless liquid having n_{D}^{20} 1.5071. Analysis by gas chromatography[11] indicated that the phenol was 98.8% pure, the major impurity being *o*-(trimethylsilyl)phenol. The liquid crystallized on standing for a short while, m.p. 33.5–35.5°. After recrystallization from *n*-hexane the phenol melted at 36.5–37°.

Anal. Calcd. for $C_{12}H_{22}OSi_2$: C, 60.4; H, 9.3; Si, 23.6. Found: C, 60.5; H, 9.5; Si. 23.1.

In another experiment carried out in the same manner, except that the reaction time was only 3 min., there was obtained an 89% yield of the 2,4-phenol, m.p. (crude) 33.5–36°, n_{D}^{20} 1.5073. The infrared spectrum showed that the Si-O-Ar band at 10.7 μ had disappeared completely.

2,6-Bis(trimethylsilyl)phenol. A solution of 7.74 g. (0.0249 mole) of 2,6-bis(trimethylsilyl)phenoxytrimethylsilane in 60 ml. of 2*M* sodium methoxide in methanol was allowed to stand for 18 hr. in a refrigerator at 5°. The solution was then diluted with 300 ml. of water and extracted with pentane as in the previous example. Evaporation of the pentane yielded 4.83 g. (81%) of the desired phenol, a colorless oil having n_{D}^{20} 1.5066. Analysis by gas chromatography showed that the product contained 98.7 mole % 2,6-bis(trimethylsilyl)phenol, the remainder being *o*-(trimethylsilyl)phenol and a trace (~0.05%) of phenol. The infrared spectrum showed a very sharp band due to unbonded OH at 2.7 μ. This band, which is characteristic of highly hindered phenols, was also observed in the 2,4,6-trisubstituted compound.

Anal. Calcd. for $C_{12}H_{22}OSi_2$: C, 60.4; H, 9.3; Si, 23.6. Found: C, 60.4; H, 9.3; Si, 23.9.

Two other reactions were carried out using 0.0125 mole of the phenoxytrimethylsilane in 30 ml. of 1*M* sodium methoxide solution. One solution was allowed to stand for 1 hr. at room temperature and the other for 18 hr. at 5°. Both gave identical results: 82% yield, product 97.5% 2,6-bis(trimethylsilyl)phenol, and 2.5% *o*-(trimethylsilyl)phenol.

2,4,6-Tris(trimethylsilyl)phenol. A solution of 7.5 g. (0.0196 mole) of 2,4,6-tris(trimethylsilyl)phenol in 50 ml. of 2*M* sodium methoxide in methanol was allowed to stand for 18 hr. at 5°, diluted with 250 ml. of water, and extracted with pentane. Evaporation of the pentane yielded 5.64 g. (93%) of the crude phenol, a colorless oil which partially crystallized on standing. Analysis by gas chromatography showed that the crude product contained 90.9 mole % 2,4,6-tris-(trimethylsilyl)phenol, 8.1 mole % 2,6-bis(trimethylsilyl)-phenol, 0.9 mole % 2,4-bis(trimethylsilyl)phenol, and a trace (0.1%) of *o*-(trimethylsilyl)phenol. Recrystallization from *n*-hexane yielded pure 2,4,6-tris(trimethylsilyl)phenol, m.p. 41–42°.

Anal. Calcd. for $C_{15}H_{30}OSi_3$: C, 58.0; H, 9.7; Si, 27.1. Found: C, 58.0; H, 9.7; Si, 26.8.

In another experiment carried out under the same conditions, but using a 1*M* sodium methoxide solution, the crude product contained 74.8% of the 2,4,6-compound, 22.6% of the 2,6-compound, and 2.6% of the 2,4-isomer. When 0.01 mole of the phenoxysilane in 25 ml. of 4.5*M* sodium methoxide solution was used, an 81% yield of material melting at 38–40° was obtained. Analysis showed this to be 98.6 mole % 2,4,6-tris(trimethylsilyl)phenol.

Desilylation of 2,4-bis(trimethylsilyl)phenol in sodium methoxide solution A 0.4*M* solution of sodium methoxide in methanol was brought to 50° in a constant-temperature bath and 20 ml. was added to each of two flasks containing 1.18 g. (0.005 mole) of 2,4-bis(trimethylsilyl)phenol. One solution was maintained at 50° for 10 min., poured into 100 ml. of ice water, and extracted with pentane. The other was allowed to stand for 1 hr. at 50° before dilution and extraction. Gas chromatography showed that the 10-min. sample contained 1.4% mono(trimethylsilyl)phenol and the sample which was allowed to react for 1 hr. contained 8.3%, along with a trace of phenol. The *ortho* and *para* isomers were not completely separated, but it was estimated that there was approximately 50 times as much *ortho* as *para*.

Acid cleavage of 2,4-bis(trimethylsilyl)phenol. Ten ml. of 0.1045*N* aqueous perchloric acid, previously brought to 50° in a constant-temperature bath, was added to a solution of 1.19 g. (0.005 mole) of 2,4-bis(trimethylsilyl)phenol in 25 ml. of methanol, also at 50°. After 20 min. at 50° the solution was poured into 100 ml. of ice water and extracted with

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[11] All gas chromatographic analyses of the (trimethylsilyl)phenols were made on a 1-meter Apiezon "L" column on Celite at 150°.

n-pentane. After drying over sodium sulfate, the pentane solution was analyzed by gas chromatography. The product contained 25.7% mono(trimethylsilyl)phenol along with a small amount (<0.5%) of phenol. Fourteen per cent of the (trimethylsilyl)phenol was the *para* isomer.

Thermal rearrangement of poly(trimethylsilyl)phenols at 250°. One-gram samples of 2,4-, 2,6-, and 2,4,6-(trimethylsilyl)phenols were sealed under vacuum in Pyrex tubes and heated for 24 hr. in a circulating air oven at 250°. The product from 2,6-bis(trimethylsilyl)phenol had an infrared spectrum and refractive index identical with that of *o*-(trimethylsilyl)phenoxytrimethylsilane. 2,4-Bis(trimethylsilyl)phenol yielded pure *p*-(trimethylsilyl)phenoxytrimethylsilane, while 2,4,6-tris(trimethylsilyl)phenol yielded 2,4-bis(trimethylsilyl)phenoxytrimethylsilane. The products were also examined in each case by gas chromatography; the only compound observed, other than those described above, were a trace of phenoxytrimethylsilane in the reaction of the 2,6-disubstituted phenol, and a trace of *o*-(trimethylsilyl)phenoxytrimethylsilane from the 2,4-phenol.

Rearrangement at 200°. Samples of the pure mono(trimethylsilyl)phenols were similarly sealed under vacuum and heated for 6 hr. in an oil bath at 200°. The products were then analyzed by gas chromatography. For each of the phenols a single standard mixture containing approximately equal amounts of (trimethylsilyl)phenol, phenoxytrimethylsilane, (trimethylsilyl)phenoxytrimethylsilane, and phenol was prepared and analyzed. It was found that the weight fraction of each component was approximately equal to the ratio of the area under its gas chromatographic peak to the total area, and the analyses of the unknown mixtures were based in this assumption. This yields slightly high values for phenol and low values for (trimethylsilyl)phenoxytrimethylsilane, but is satisfactory for the purposes of the experiment.

An equimolar mixture of phenol and *o*-(trimethylsilyl)phenoxytrimethylsilane yielded 11% phenoxytrimethylsilane when heated for 6 hr. at 200°. A trace (<0.5%) of *o*-(trimethylsilyl)phenol was also produced.

Acknowledgment. The author is indebted to Mr. B. Williams for assistance in the preparation of the phenols and to Mr. E. M. Hadsell for the gas chromatographic analyses.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE MATERIALS DEPARTMENT, ELECTRONICS LABORATORY, HUGHES AIRCRAFT COMPANY]

Preparation and Characterization of Disilylbenzene and Bis(trimethoxysilyl)benzene[1]

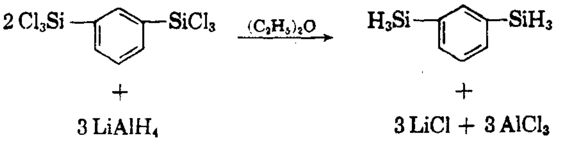
N. BILOW,[2] J. L. BRADY, AND C. L. SEGAL

Received June 24, 1960

1,3-Disilylbenzene has been prepared in good yield by the reduction of bis(trichlorosilyl)benzene[3] with lithium aluminum hydride. The base catalyzed methanolysis of disilylbenzene yields bis(trimethoxysilyl)benzene.

The present paper describes the preparation and characterization of disilylbenzene and bis(trimethoxysilyl)benzene. Although the synthesis of these compounds has not been reported previously, the general methods of preparation are known. Reductions of chlorosilanes with lithium aluminum hydride have been reported by Finholt;[4] and alcoholysis of silanes has been discussed by Price.[5] Structure determinations on the alcoholysis products were, however, not carried out in the work of Price nor do they seem to be reported in other chemical literature.

Products of the reduction of bis(trichlorosilyl)benzene (Eq. 1) and the base catalyzed methanolysis of disilylbenzene (Eq. 2) were identified by elemental analysis, molar refractions, and infrared spectra. An infrared spectrum of the product obtained from the methanolysis of disilylbenzene was identical with that of the product obtained from the methanolysis of bis(trichlorosilyl)benzene.



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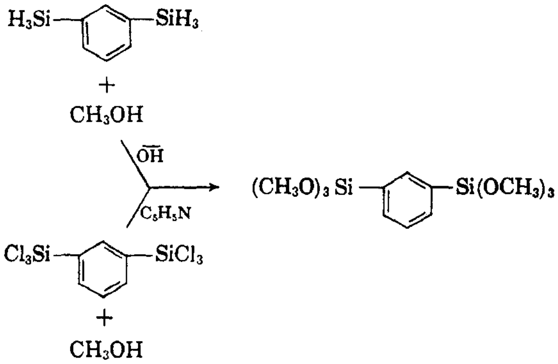

(2)

Several attempts to synthesize bis(trimethoxysilyl)benzene by the reaction of bis(trichlorosilyl)benzene with sodium methylate, or methanol alone, accompanied by a continuous nitrogen purge yielded only polymeric siloxanes. The use of pyridine as a hydrogen chloride acceptor was required to prevent acid catalyzed polymerization.

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[1] Supported in part by the Department of the Navy, Bureau of Ships, Contract NObs-77054.

[2] Hughes Research Laboratories, A Division of Hughes Aircraft Company, Malibu, Calif.

[3] Bis(trichlorosilyl)benzene was 85% *meta* and 15% *para*.

[4] A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Am. Chem. Soc.*, 69, 1199 (1947).

[5] F. P. Price, *J. Am. Chem. Soc.*, 69, 2600 (1947).