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.

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SCHENECTADY, N. Y.

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

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

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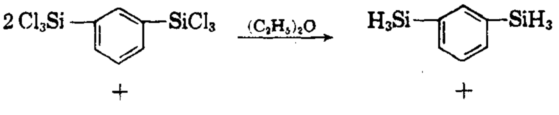
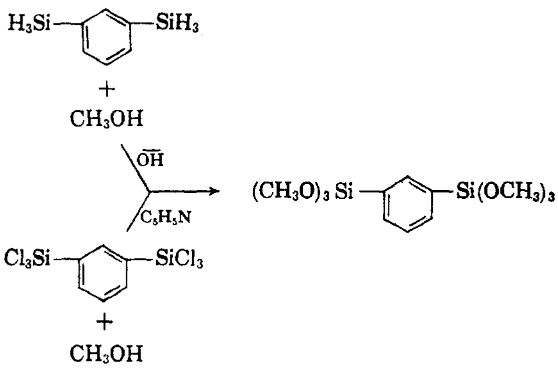
1,3-Disilylbenzene has been prepared in good yield by the reduction of bis(trichlorosilyl)benzene[3] with lithium aluminum hydride. The base catalyzed methanolysis of disilylbenzene yields bis(trimethoxysilyl)benzene.

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.



(1)



(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).

TABLE I

INFRARED SPECTRAL DATA[a]

Compound	Assignments C—H	Si—H	C═C	Probable Si—C_6H_5	Si—O	Unassigned
1,3-bis(trimethoxysilyl)benzene	3.42[b] (63)	—	6.35 (18)	8.40 (66)		12.20 (100)
					9.20 (100)	
	3.56 (56)		6.86 (25)	8.56 (55)		12.70 (65)
					very broad	
	3.64 (13)		7.34 (25)	8.71 (59)		
1,3-disilylbenzene	3.35 (50)		6.40 (28)	8.50 (20)		10.90 (100)
	3.38 (45)	4.69 (100)	6.87 (13)	8.80 (50)		11.70 (50)
			7.30 (70)	8.85 (70)	...	12.35 (35)
				9.07 (75)		12.78 (67)
						13.16 (60)

[a] Beckman I.R. 5 infrared spectrophotometer. [b] Wave lengths in microns: ( ) indicates % absorption.

Disilylbenzene also decomposes slowly in moist alcoholic hydrogen chloride yielding a polymeric product. The decomposition did not appear to evolve hydrogen, but this may be a result of the very slow hydrolysis rate; nevertheless, the reaction is believed to take the following course involving cleavage of the phenyl silicon bonds[6]:

$$H_3SiC_6H_4SiH_3 + H_2O \longrightarrow C_6H_6 + H_2 + (SiH_2O)_n \quad (3)$$

In contrast with the acid catalyzed decomposition, a base catalyzed decomposition of disilylbenzene in absolute methanol was so rapid that it was necessary to cool the reaction mixture to −78° in order to follow the rate of hydrogen evolution. Six moles of hydrogen were liberated per mole of disilylbenzene in the base catalyzed alcoholysis.

A study of the infrared spectra of disilylbenzene, bis(trimethoxysilyl)benzene, and bis(dimethylethoxysilyl)benzene has shown two absorption bands appearing in each of these compounds which are attributed to the phenyl silicon bond; absorptions were observed at 1360–1390 cm.$^{-1}$ and 1165–1190 cm.$^{-1}$ These values may be compared with the phenyl silicon absorptions, which have been reported at 1429 cm.$^{-1}$ and 1110–1124 cm.$^{-1}$ for aryl silanes bearing only monosubstituted aryl groups.[7–9] Strong silicon oxygen absorption was observed at 1080–1100 cm.$^{-1}$, and silicon hydrogen absorption in disilylbenzene was observed at 2260 cm.$^{-1}$ Reported values[10] for the silicon hydrogen stretch have varied between 2100–2274 cm.$^{-1}$, depending upon the specific compound. A previously unreported intense absorption at 908 cm.$^{-1}$ has been observed in disilylbenzene, which we have attributed to the silicon hydrogen bending vibration. This absorption disappears completely with alcoholysis, together with the disappearance of the 2260 cm.$^{-1}$ absorption. Additional infrared data are presented in Table I. In calculating the theoretical molar refractions of disilylbenzene and bis(trimethoxysilyl) benzene, it was necessary to determine the molar refraction of the *meta*-silicon phenyl silicon group. Literature values for the phenyl silicon bond refraction are based on monosubstituted aryl silanes and are significantly different from the phenyl silicon refraction in arylene disilanes. Based on the observed molar refractions of bis(trichlorosilyl)benzene, bis(trimethoxysilyl)benzene, and disilylbenzene, the molar refractions of the *meta*-silicon phenyl silicon groups were found to be respectively 29.48, 28.87, and 28.38. The average of these values (MR_D 28.91) has therefore been accepted as the correct value for calculation of subsequent molar refractions; the pure *para* isomer has been found to have a molar refraction of MR_D 31.8. This value has been calculated from a known sample of *p*-bis(ethoxydimethylsilyl) benzene.

EXPERIMENTAL

Reduction of bis(trichlorosilyl)benzene. Redistilled bis(trichlorosilyl)benzene (121 g., 0.348 mole) was added dropwise to a solution of lithium aluminum hydride (22 g., 0.58 mole)[11] in absolute ethyl ether (450 ml.) maintained between 10–20° by the use of an ice bath. The addition was completed in 30 min. after which time the mixture was heated to reflux for a period of 2 hr. Petroleum ether (150 ml., b.p. 30–60°) was added and the mixture stirred for 15 min.

The reaction mixture then separated into two phases; the upper ether phase was decanted and the lower phase extracted with a mixture of ether (150 ml.) and petroleum ether (150 ml., b.p. 30–60°). Again the upper layer was decanted and combined with the first ether extract. Careful treatment of the remaining lower phase (at 10°) with aqueous hydrochloric acid (55 ml., 1*N*) destroyed most of the excess of lithium aluminum hydride. This again resulted in a separation into two phases, the upper phase being combined with previously obtained ether layers. The combined ether layers were thoroughly washed with ice, the solution was filtered, and the solvents removed by fractional distillation. Thorough washing and drying of the ether layer

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(6) J. F. Hyde and R. C. DeLong, *J. Am. Chem. Soc.*, **63**, 1194 (1941).

(7) R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, **1949**, 124.

(8) C. W. Young, *et al.*, *J. Am. Chem. Soc.*, **70**, 3758 (1948).

(9) M. C. Harvey, W. H. Nebergall, and J. S. Peake, *J. Am. Chem. Soc.*, **76**, 4555 (1954).

(10) L. Bellamy, *The Infrared Spectra of Complex Molecules*, 2d ed., J. Wiley and Sons, Inc., New York, 1958, pp. 340–341.

(11) Higher yields may be obtained by the use of an even larger excess of lithium aluminum hydride.

before distilling is very important. Storage of the unwashed solution will lead to decomposition of the disilylbenzene into products which decompose further during distillation. This latter decomposition results in the formation of a gas which is highly explosive in air (probably silane). Gilman[12] has reported that arylsilanes may disproportionate at elevated temperatures. Evidence that the liberated gas does not actually come from disilylbenzene itself was obtained when a sample of purified disilybenzene was heated at reflux (155°) for 3 hr.: no sign of gas evolution occurred after the first 20 min., and the amount of gas liberated during the initial phase accounted for no more than 2% of the theoretical amount. This small amount of gas, therefore, is probably due to a trace impurity. After removal of the major portion of the solvents the pressure was gradually reduced to prevent the distillate on pot temperature from exceeding 75°, and disilylbenzene was fractionally distilled (b.p. 59° (25 mm.), 39 g., 81% yield, n_D^{25} 1.5256, sp. gr.$_{25}^{25}$ 0.8914, b.p. 155° (760 mm.). A liquid residue (3 g.) remained in the pot.

Elemental analysis, molecular refraction, and infrared spectrometry were used to substantiate the disilylbenzene structure.

Anal. Calcd. for $C_6H_{10}Si_2$: C, 52.09; H, 7.29; MR_D 48.23. Found: C, 52.09; H, 7.34; MR_D 47.7.

Bis(trimethoxysilyl)benzene from disilylbenzene. Disilylbenzene (4.4 g., 0.032 mole) was added with extreme caution to a solution of sodium (approximately 50 mg.) in absolute methanol (50 ml.). The reaction was extremely vigorous. After removal of the major portion of the methanol by normal distillation, the high boiling product was distilled by molecular distillation (at 2 mm.) yielding *m*-bis(trimethoxysilyl)benzene (8.0 g., 0.025 mole, 78% yield, sp. gr. 1.1188$_{23}^{23}$, n_D^{24} 1.4650).

Anal. Calcd. for $C_{12}H_{22}O_6Si_2$: C, 45.26; H, 6.96; MR_D 78.86. Found: C, 45.02; H, 7.13; MR_D 78.82.

Bis(trimethoxysilyl)benzene from bis(trichlorosilyl)benzene. Bis(trichlorosilyl)benzene (10 g., 0.029 mole) was slowly added to a stirred solution of pyridine (13.8 g., 0.174 mole) in methanol (50 ml.). An exothermic reaction was observed, and after cooling the reactants were stirred for 24 hr. at room temperature. The excess of methanol was then removed from the clear reaction mixture by distillation and the residual material extracted with a 50–50 mixture of ether in hexane. The ether solution was then concentrated by normal distillation and the high boiling product (5 g.) was distilled by molecular distillation (at 2 mm.) to give four fractions. The last fraction (n_D^{24} 1.4646) was found to have an infrared spectrum identical to that of the product obtained from the methanolysis of disilylbenzene described above. Based on the total weight of crude product the yield was 50%.

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(12) H. Gilman and D. H. Miles, *J. Org. Chem.*, **23**, 326 (1958).