STRUCTURE OF bis(DICHLOROMETHYLSILYLETHYL)BENZENE
AND ITS DERIVATIVES

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The synthesis and certain properties of bis(trichlorosilylethyl)benzene and its derivatives have been described in a number of studies [1-3], but the structure of the compounds obtained has not been established.

The purpose of the present investigation was to establish the structure of previously synthesized compounds with the general formula

\[
\left[ (\text{C}_{6}\text{H}_{5}\text{Si})_{2} \right] \left[ \left( \text{R} \right) \left( \text{R}' \right) \right] \left( \text{Si} \left( \text{Si} \left( \text{C}_{6}\text{H}_{5} \right) \right)_{2} \right)
\]

where \( \text{R} \) = H, CH\(_{3}\), Cl; \( \text{R}' = \text{CH}_{3}, \text{C}_{6}\text{H}_{5}\text{Si} \).

We were unable to isolate polycarboxylic acids of known structure by the oxidation of bis(trichlorosilylethyl)aryls with potassium permanganate in alkaline medium. Probably polycarboxylic acids liberated in the oxidation of bis(trichlorosilylethyl)aryls are strongly adsorbed by the substantially larger (200% by weight) amount of silicon dioxide which is formed during oxidation. In the silicon dioxide we detected titratable carboxyl groups, the amount of which practically corresponded to the calculated amount.

For the synthesized compounds we took the IR spectra, but it proved impossible to determine the order of substitution in the aromatic ring with their aid, since the frequencies of the nonplanar vibrations of the C-H bonds of the benzene ring, according to which the type of substitution is usually determined, are situated in the same region as the frequencies of the vibrations of the alkyl groups bonded to silicon. An attempt to take the Raman spectra of these compounds proved unsuccessful on account of their strong

![Fig. 1](attachment:fig1.png)

![Fig. 2](attachment:fig2.png)

**Fig. 1.** UV spectra: 1) bis-di(triethylsiloxy)methylsilylethylbenzene; 2) bis-di(triethylsiloxy)methylsilylethyltoluene; 3) di(triethylsiloxy)methylsilylethyltoluene.

**Fig. 2.** UV spectra: 1) bis-di(triethylsiloxy)methylsilylethylchlorobenzene; 2) di(triethylsiloxy)methylsilylethylchlorobenzene.
fluorescence. Therefore we used the UV absorption spectra, based on the fact that alkylbenzenes, depending on the type of substitution, are characterized by definite contours of the absorption band in the region of 2300-2800 Å [4].

The products of monoaddition of the type

\[ \text{RC}_6\text{H}_4\text{CH}_2\text{Si}[\text{OSi}(\text{C}_2\text{H}_5)_3]_2 \quad \text{R}=\text{H}, \text{CH}_3, \text{Cl} \quad \text{R'}=\text{CH}_3 \]

were also synthesized as models.

In the case of the products of monoaddition of vinylmethyldichlorosilane to benzene derivatives, we might expect the formation of ortho-para derivatives, since the substituents already present in the benzene ring (CH₃, Cl) are orienters of the first kind. Actually, as can be seen from Figs. 1 and 2, the C₂H₄SiCl₂(Me) group is inserted in the ortho-position with respect to the substituent present in the ring, and the synthesized products have the structure \( \text{R} = \text{CH}_3 \) (see Fig. 1, curve 3) and \( \text{R} = \text{Cl} \) (see Fig. 2, curve 2). The para-isomer was not detected. In the case of the addition products of two molecules of vinylmethyldichlorosilane to benzene and its homologs, a more complex picture is observed.

In the case of step-wise addition of vinylmethyldichlorosilane to benzene and its derivatives, it should be considered that the nucleus already contains two substituents, and the resultant inductive effect is made up of the inductive influences of these two substituents, namely, the CH₃ or Cl group and the C₂H₄SiCl₂(CH₃) group.

It is known [5, 6] that the CH₂SiCl₃ group in benzyldichlorosilane is a strong ortho-para-orienter. In our case we have the group CH₂-CH₂SiCl₂, and we assume that this group is also an ortho-para-orienter, perhaps not as strong, since the bridge -CH₂- group insulates the reaction center from the electronic influence of the substituent [7]. This has been demonstrated by the studies of Jaffe [8, 9] of the transmission coefficient \( \pi = \rho_1/\rho_0 \) (p is the reaction constant in the Hammett equation, serving as a characteristic of the structural peculiarities of the reacting compound), for the series

\[ \text{ArCOOH} \rightarrow \text{ArCH}_2\text{COOH} \quad \text{ArCOOH} \rightarrow \text{ArCH}_2\text{CH}_2\text{COOH}. \]

From the data of [8, 9] it is evident that the coefficient decreases as we go to the series ArCH₂CH₂

COOH, from a value of 0.49-0.43 to a value of 0.22. This permits us to assert that the CH₂CH₂SiCl₂(Me) group is also an orienter of the first kind.

The UV spectra, obtained for compounds of the type

\[ [(\text{C}_6\text{H}_5)_3\text{Si}]_2\text{Si}-\text{C}_6\text{H}_4\text{CH}_2(R)-\text{C}_6\text{H}_4\text{Si}[\text{OSi}(\text{C}_2\text{H}_5)_3]_2, \]

were: