

SEPARATION OF NONGEMINAL DIVINYLHEXAMETHYLCYCLOTETRASILOXANES

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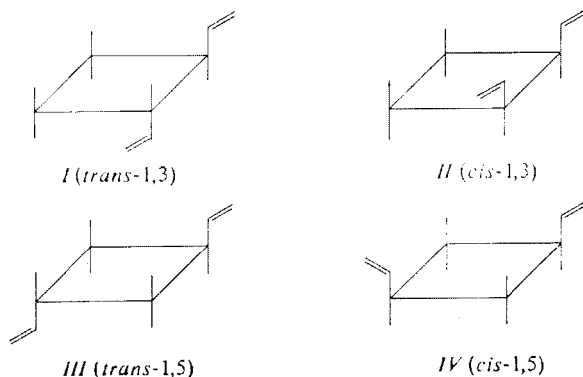
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A nongeminal divinylhexamethylcyclotetrasiloxane obtained by cohydrolysis of dichlorodimethylsilane and dichloromethylvinylsilane is a mixture of the positional (1,3 and 1,5) and configurational (*cis*, *trans*) isomers. Chromatographic separation of this mixture on an AgNO₃—SiO₂ system is described. Four isolated compounds were studied by mass and IR spectra.

Nongeminal divinylhexamethylcyclotetrasiloxane (*A*), used as an unsaturated component in various hydrosilylation reactions and for preparations of polyvinylorganosiloxanes, is usually obtained by cohydrolysis¹ of dichlorodimethylsilane and dichloromethylvinylsilane. In some studies, substance *A* is assumed to be 1,3- (ref.²) or 1,5-divinyl isomer^{3,4} without any evidence or more detailed determination of its configuration⁵⁻¹⁰. In a recent work¹ it was reported that substance *A* is in fact a mixture of 1,3- and 1,5-divinyl isomers (1 : 1). This conclusion has been reached on the basis of ¹H - NMR spectra of the cohydrolysis product, since attempts at isolating individual isomers have failed.

Substance *A* can occur, however, in four isomers (*I-IV*), since the cyclotetrasiloxane skeleton is essentially planar, as shown by electron diffraction¹¹. The aim of this



work was to find the separation method and to identify partially the structure of isolated isomers. As found by preliminary gas chromatographic analysis with the use of common stationary phases, the product of the above cohydrolysis (substance *A*) shows three peaks. First of them (0.5%) belongs to substance *C* (vinylheptamethylcyclotetrasiloxane), the second (approx. 90%) represents a mixture of the substances *D*, *E*, and *F* (divinylhexamethylcyclotetrasiloxanes), and the third (approx. 10%) belongs to substance *B* (decamethylcyclopentasiloxane, the undesired side product formed by hydrolysis of dichlorodimethylsilane).

The well-known interaction of multiple CC bonds with Ag^+ ion¹² indicated the possibility of separating isomers of substance *A* by this way. Positive results were achieved by means of thin layer chromatography on a silica gel impregnated with silver nitrate. Of the eluents tested, a pentane–benzene (1 : 1) system proved most suitable and made it possible to separate five substances *B–F* (Table I). These were isolated by column chromatography, using similar elution system. The compounds obtained were studied by mass and IR spectra, with the exception of substance *C* which was not obtained in the amount sufficient for IR analysis (Table I).

Substance *B* has the simplest mass spectrum and shows a very weak molecular ion which is followed by more intense $(M-15)^+$ fragment ions. The other fragments of the mass spectrum unambiguously prove the presence of the $(\text{CH}_3)_2\text{SiO}$ -groups. From these facts the molecular weight of 370 m.u. can be deduced. It is in consent to the proposed structure of decamethylcyclopentasiloxane for the compound *B*.

The mass spectra of substances *D–F* are different from the spectrum of sample *B*, but are similar to each other, with only small differences in intensities of characteristic ions. From the spectra it can be concluded that all these compounds have molecular weight of 320 m.u. and are thus of general formula $\text{C}_{10}\text{H}_{24}\text{O}_4\text{Si}_4$. They can be regarded as either positional or configurational isomers of divinylhexamethylcyclotetrasiloxane.

TABLE I

Relative Amounts and R_F Values of Substances *B–F* in Thin Layer Chromatography on an AgNO_3 – SiO_2 System

Characteristics	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>
Relative amount	1	traces	1	4	3
R_F (benzene)	0.96	0.93	0.74	0.60	0.28
R_F (n-pentane–benzene)	0.95	0.90	0.71	0.55	0.24
Obtained, mg ^a	195	traces	165	334	142
Fraction ^a	1–4	5, 6	10–14	16–19	32–36

^a Column chromatography.

IR spectra of liquid isomers *D*–*F* showed most distinct differences in the 800 to 600 cm^{-1} region (Fig. 1). It is seen that the band at 750 cm^{-1} has the simplest shape for substance *D*. This leads us to conclude that it should belong to the isomer with the highest symmetry (structure *III*). Substance *D* can be thus assigned the structure of *trans*-1,5-divinyl-1,3,3,5,7,7-hexamethylcyclotetrasiloxane. In the case of compounds *E* and *F*, absorption at 750 cm^{-1} is formed by several overlapping bands which all belong to the stretching vibrations of Si—C= bonds¹³. From this it follows that configuration of both vinyl groups is not symmetrical and is therefore *cis* or 1, 3. This band is not present in the spectrum of the pentamer *B*. Several weak bands in the 600–500 cm^{-1} region of compounds *D*, *E*, and *F* which are due to the symmetrical stretching vibration of the Si—O—Si arrangement with different environment, can be explained similarly. Symmetrical pentamer *B* shows only one band in this region of the spectrum which is located at 530 cm^{-1} . These results can be qualitatively correlated with R_F values given in Table I. Although pentamer *B* has the largest molecular weight, it is eluted most readily, since it does not contain a group able to interact with Ag^+ ions. On the basis of the results discussed above and considerations about the abilities of vinyl groups of individual isomers to interact with Ag^+ ions we believe that substances *E* and *F* possess structures *I* and *II*. This assumption is supported by our finding that the sample of 1,3-divinyl-1,3,5,5,7,7-hexamethylcyclotetrasiloxane yields under the conditions of thin layer chromatographic analysis described in the experimental part only two spots (R_F (benzene) 0.60 and 0.28) whose position is identical with that of the fractions *E* and *F* (Table I).

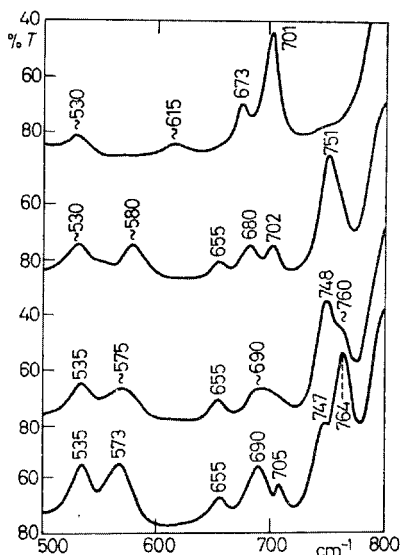


FIG. 1
Infrared Absorption Spectra of Liquid Films
of Compounds *B*, *D*, *E*, and *F* in the descending
order

The presence of the remaining isomer *IV*, although quite probable, was not evidenced. As found by comparison of mass spectra and gas chromatographic retention times of substance *C* with authentic samples of several vinylmethylcyclotetrasiloxanes, the minor fraction *C* is 1-vinyl-1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane and not the divinyl derivative.

EXPERIMENTAL

Preparation of substance A. A mixture of 204 g (1.4 mol) of dichloromethylvinylsilane and 180 g (1.5 mol) of dichlorodimethylsilane was introduced into 800 ml of stirred and cooled aqueous methanol (1 : 1) below its level such that the temperature of the reaction mixture did not exceed 20°C. After completion of the addition, the reaction mixture was allowed to stir for another 0.5 h and then the aqueous-methanolic layer was separated. The cohydrolysate was washed with water, 1% aqueous NaHCO₃ solution and then made neutral (methyl orange) by washing with water. Of the total amount of 222 g of the cohydrolysate, 198 g of volatile siloxanes were obtained by distillation under reduced pressure (20 Torr). These were distilled through a 28 TP column to yield 48 g of substance *A*, b.p. 202–203°C/758 Torr, n^{20}_D 1.4150, d^{20}_4 0.967.

Gas chromatographic analysis of substances A–F was performed on a Perkin-Elmer F 11 chromatograph, equipped with flame ionization detector and a dual system of glass columns (0.3 × 180 cm) packed with 3% SE-30 on silanized Chromosorb G (100–120 mesh). Column temperature was 80°C. Similar results were obtained also with 20% Carbowax 20 M on Chromosorb W and with a 50 m capillary column with tricresyl phosphate as stationary phase.

Column chromatography of substance A. Substance *A* (2.6 g) was chromatographed on a column (3 × 75 cm) which contained 300 g of silica gel PHH (0.10–0.25 mm particle size, Spolana, Velvary, Czechoslovakia) with 15% wt. silver nitrate. The silica gel was first activated at 120°C for 24 h and its activity was modified by 10% wt. water. The elution system was benzene-pentane (1 : 1); starting from fraction 24 polarity of the elution mixture was increased by adding 5% v. diethyl ether and from fraction 34 its amount was further increased to 15% v. Fractions 1–6 had a volume of 25 ml, fractions 7–25 50 ml, and fractions 26–36 100 ml. Composition of individual fractions was checked by thin layer chromatography (2.5 × 7.5 cm) on silica gel impregnated with 15% wt. silver nitrate. Spots were detected by spraying with 0.1% ethanolic solution of 2,7-dichlorofluorescein followed by exposure to UV light. Due to relatively high boiling point of benzene, compounds *B–F* were isolated by vacuum distillation which increased loss of the compounds. Their relative amounts were determined from the size and intensity of individual spots (thin layer chromatography) or by gas-liquid chromatography (substance *B*, Table I).

Mass spectra of pure compounds B–F were recorded on a Gas Chromatograph – Mass Spectrometer, type LKB 9000. The samples were injected into a heated inlet system, the ion source was operated at 270°C and 70 eV ionizing energy of electrons. *IR absorption spectra* (4000–400 cm⁻¹) of liquids were recorded on a prism spectrometer Zeiss (Jena), model UR-20. Samples were studied as capillary films between KBr plates or in 0.0022 cm KBr cells.

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