

GAS CHROMATOGRAPHIC SEPARATION OF NONGEMINAL DIVINYLHEXAMETHYLCYCLOTETRASILOXANES ON SILVER NITRATE-TRIETHYLENE GLYCOL

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A mixture of nongeminal divinylhexamethylcyclotetrasiloxanes was separated by means of gas chromatography on silver nitrate-triethylene glycol.

A mixture of nongeminal divinylhexamethylcyclotetrasiloxanes obtained by rectification from the product of cohydrolysis of dichlorodimethylsilane and dichloromethylvinylsilane (mixture A) was separated into fractions B, C, D, E, and F by means of thin-layer chromatography on silica gel impregnated with silver nitrate. With the use of column chromatography on the same adsorbent, the particular fractions were isolated and subjected to measurements (IR, MS, and NMR) (cf.^{1,2}). As inferred from the recorded data, fraction B is 1,1,3,3,5,5,7,7,9,9-decamethylcyclopentasiloxane, fraction C is 1-vinyl-1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane, fraction D is *trans*-1,5-divinyl-1,3,3,5,7,7-hexamethylcyclotetrasiloxane (structure III), fraction E is a mixture² of *trans*-1,3-divinyl-1,3,3,5,5,7,7-hexamethylcyclotetrasiloxane (structure I) and *cis*-1,5-divinyl-1,3,3,5,7,7-hexamethylcyclotetrasiloxane (structure IV), and fraction F is *cis*-1,3-divinyl-1,3,3,5,5,7,7-hexamethylcyclotetrasiloxane (structure II).

The object of the present paper is the separation of the above substances by means of gas chromatography. A very efficient group separation of mixture A was achieved on Silicone Gum Rubber SE-30 (Fig. 1a). On this nonpolar phase, substances are separated according to their boiling points that are in the present case approximately proportional to molecular weights. The shortest retention time is shown by compound C (M.w. 308.6). Compounds D, E, and F (M.w. 320.6) exhibit somewhat longer retention times. Boiling points and interactions of these particular isomers with the gas-chromatographic phase are as similar that no separation takes place on the packed column and the isomers are eluted as a single chromatographic wave. Compound B exhibits the longest retention time and the highest molecular weight (370.8).

On the highly polar phase Carbowax 400, the separation order is C, then B, and finally D + E + F, almost in accord with the increasing polarity of these substances. Only a partial group separation or no separation at all may be observed on phases SE-52, DEGS (diethylene glycol succinate), and QF-1.

The separation on triethylene glycol saturated with silver nitrate is qualitatively different. Phases of this type have been used in separations³⁻¹⁵ of various low-boiling olefins or in separations of olefins from paraffins. The separation is based on the formation of more or less stable complexes of unsaturated compounds with silver ions¹⁶. Fig. 1*b* shows the chromatographic separation of components of mixture A. In the elution pattern, compounds C containing one vinyl group is followed by compound B lacking the vinyl group but exhibiting a considerably higher molecular weight. As the last members of the mixture, substances D, E, and F are eluted and satisfactorily separated in the same order as on silica gel impregnated with silver nitrate. The fraction E containing a mixture of *trans*-1,3-divinyl and *cis*-1,5-divinyl isomers was not separated even by gas chromatography probably because of similar interactions between silver ions and structures I or IV. However, the non-homogeneity of the elution wave E may be inferred from the width at half-height measurements¹⁷.

The quantitative ratios determined from gas chromatograms were compared (Table I) with those obtained by weighing of fractions from column chromatography

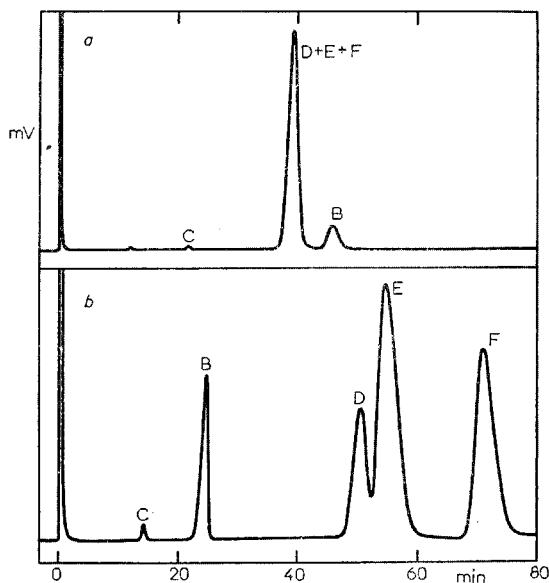


FIG. 1

Gas Chromatogram of Mixture A

a 3% SE-30 on silanized Chromosorb G (100–120 mesh), 0.3 × 180 cm glass column, 50 ml of nitrogen per min, column temperature 65°C, injection port temperature 110°C. *b* 33% triethylene glycol (saturated with silver nitrate) on Chromosorb P (100–120 mesh), 0.4 × 150 cm glass column, 40 ml of helium per min, column temperature 65°C, injection port temperature 110°C.

TABLE I
Content (%) of Components in Mixture A

Compound	B	C	D	E	F
GLC on SE-30	10.3	0.63	89.1		
GLC on AgNO ₃ -triethylene glycol	10.2	0.62	15.4	42.5	31.3
Column chromatography	11.6	0.46	17.2	51.5	19.3

on impregnated silica gel². Taking into consideration that fraction E is a mixture of *trans*-1,3- and *cis*-1,5-divinylhexamethylcyclotetrasiloxane in the ratio 2.5 : 1 (as determined by NMR spectra²), the following conclusions can be drawn: the cohydrolysis of dichlorodimethylsilane and dichloromethylvinylsilane affords mainly a mixture of four nongeminal divinylhexamethylcyclotetrasiloxanes, the content (by weight) of the 1,3 positional isomers being approximately twice as great as that of the 1,5 positional isomers.

EXPERIMENTAL

Finely powdered silver nitrate (6 g) was dissolved with stirring in a centrifugation test tube (50°C, 1 h) containing 4 ml of freshly distilled triethylene glycol (b.p. 115°C/0.01 Torr). The undissolved material was removed by centrifugation. A portion (4.5 g) of the clear supernatant was diluted with methanol (22 ml) and applied to 9 g of Chromosorb P (100–120 mesh). The solvent was removed under diminished pressure of a water pump at 50°C and constant shaking. The glass columns were packed by means of a vibrator and conditioned under helium from 25°C to 65°C (1°C per min) and then for 6 h at 65°C. Compounds A–F were injected as 4% tetrachloromethane solutions. The quantitative evaluation was effected by the method of cutting out and weighing the chromatographic peak. The F 11 Perkin-Elmer gas chromatograph was used with a dual system of flame ionisation detectors.

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