^{29}Si AND ^{13}C-NMR SPECTRA OF NON-GEMINAL DIVINYLHEXAMETHYLCYCLOTETRASILOXANES

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^{29}Si and ^{13}C-NMR spectra of fractions chromatographically isolated from the product of dichloromethylsilane and dichloromethylvinylsilane cohydrolysis agree with the structures proposed previously on the basis of mass and IR spectra. As one of the non-geminal divinylhexamethylcyclotetrasiloxane fractions is shown by ^{29}Si-NMR to consist of two compounds, it is concluded that all four possible isomers are formed in the cohydrolysis reaction and not only three as thought before.

In the previous paper[1] successful chromatographic separation of the product (A) of cohydrolysis of dichlorodimethylsilane and dichloromethylvinylsilane into five fractions (B through F) was reported. The separation permitted the use of mass and IR spectra in solving the lasting problem of the structure of A (for pertinent references see[1]); combining the information obtained from the spectra with chromatographic properties it was concluded[1] that the product A consisted of decamethylcyclopentasiloxane (fraction B), 1-vinyl-1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane (fraction C), and *trans*-1,5-divinyl-1,3,3,5,7,7-hexamethylcyclotetrasiloxane (fraction D). The fractions E and F were shown [1] to contain the two isomers of 1,3-divinyl-1,3,5,5,7,7-hexamethylcyclotetrasiloxane. The remaining isomer of non-geminal divinylhexamethylcyclotetrasiloxane, *cis*-1,5-divinyl-1,3,3,5,7,7-hexamethylcyclotetrasiloxane was not found in A.

After the preparative chromatographic method had been modified the larger amounts of the isolated fractions allowed NMR investigation of the B, D, E and F fractions. The results and the modification of the chromatographic procedure are described in the present communication.

EXPERIMENTAL

NMR Measurements

The spectra were measured in the FT mode on a JEOL-PFT-100 spectrometer interfaced to a Nicolet 1085 data system. Fraction E was measured as a neat liquid, the other fractions in 30–50% (v/v) tetrachloromethane solutions. ^{29}Si-NMR spectra were recorded at 19·87 MHz and referenced to tetramethylsilane (TMS) line in a separate sample. The spectrometer was locked to ^{19}F-NMR signal of C_6F_6 in a capillary. The assignment of the lines of the proton noise decoupled spectra (gated decoupling with NOE suppressed) was aided by the spectra recorded without the decoupling. ^{13}C-NMR spectra were recorded at 25·15 MHz (with the spectrometer being locked to ^{2}D-NMR line of $CDCl_3$ in a capillary) relatively to the line of tetrachloromethane, the chemical shift of which was taken $\delta = 95{\cdot}98$, as determined in this laboratory. The chemical shifts were determined from the noise decoupled spectra.

Column Chromatography

Product A (3·06 g) was chromatographed on a column (3× 77 cm) containing 300 g of silica gel PHH (0·10–0·25 mm) with 15% (wt.) silver nitrate. The silica gel was activated at 120°C for 24 h and then its activity was modified by 10% of water. In order to faciliate the removal of the solvent without the losses of the substances, elution system dichloromethane–diethyl ether (99 : 1 (v/v)) was employed with a gradually increasing concentration of the latter component up to 10%. Prior to use, dichloromethane was shaken several times with water, dried over $CaCl_2$ and distilled, diethyl ether was dried over KOH and distilled. Since the individual fractions B-F contained small amounts of $AgNO_3$, each of them was rechromatographed with n-pentane on a small column (1× 8 cm) filled with the silica gel PHH (0·07–0·10 mm) which was not impregnated. Net yields were 0·33 g (10·8%) of fraction B, 0·013 g (0·4%) fraction C, 0·49 g (16·0%) fraction D, 1·47 g (48·0%) fraction E, and 0·55 g (18·0%) fraction F. The losses amounted to 0·21 g (6·8%).

RESULTS AND DISCUSSION

The chemical shifts are summarized in Table I.

In the fraction B both the silicon and carbon chemical shifts confirm the structure suggested previously for this compound. The following chemical shifts were reported for decamethylcyclopentasiloxane (abreviated as D_5): $\delta(\mathrm{Si}) = -22{\cdot}8$ (see[2]) and $-21{\cdot}93$ (see[3]) and $\delta(\mathrm{C}) = 0{\cdot}7$ (see[2]) while the shifts in octamethylcyclotetrasiloxane (D_4) are $\delta(\mathrm{Si}) = -20{\cdot}0$ (see[2]) or $-19{\cdot}51$ (see[3]) and $\delta(\mathrm{C}) = 0{\cdot}3$ (see[2]).

The mass spectra proved[1] that the fractions D, E, and F consisted of isomers of divinylhexamethylcyclotetrasiloxane; according to ^{29}Si-NMR spectra all these isomers are of the general $D_2D_2^{Vi}$ type. Thus the assignment[1] of *trans*-1,5-divinyl-1,3,3,5,7,7-hexamethylcyclotetrasiloxane structure to the compound D is further substantiated. The relative intensity ratio of the two silicone lines is in all cases close to 1 : 1 and not to 1 : 3 as would be the case if a redistribution reaction led to $D_3D^{Vi_2}$ type product. This conclusion is also supported by the pattern of the not decoupled ^{29}Si-NMR spectra which were used for the assignment of the two silicon chemical shifts in the compounds D and F to the silicon atoms in the D and D^{Vi} units. The signal of the D unit shows the expected symmetrical septett structure due to the coupling with the 6 methyl protons; the D^{Vi} signal consists of a nonsymmetrical pattern of many overlapping lines. The assymetry of this signal results from the fact that the X-part of the ABCX spin system (A, B, C = vinyl protons, X = silicon) is not of the first order. This was confirmed by the theoretical calculation of the ABCX spectrum with the proper chemical shifts and coupling constants. The chemical shift of about $\delta = -33{\cdot}5$ of the silicon atom in the D^{Vi} unit is in accord with the shift observed in *bis*(trimethylsiloxy)methylvinylsilane[4], $\delta(Si) = -35{\cdot}1$. The decrease of the shielding of the silicon atom in the D unit in $D_2D_2^{Vi}$ relatively to D_4 compound reflects the now recognized[5] sensitivity of the silicon in SiOR fragments to the nature of R. In the present case the substitution of the methyl group for vinyl group three bonds away from the silicon atom in question causes a shift of about 1 p.p.m.

The sensitivity of the silicon shielding is most strikingly demonstrated on the fraction E. Its ^{29}Si-NMR spectrum clearly indicates the presence of two isomers, denoted here *I* and *II*. Their approximative ratio is *I* : *II* = 2·5 : 1 as follows from the intensity ratios. The silicon chemical shift difference between the lines of the same unit in the two isomers is about 0·5 p.p.m., but their ^{13}C-NMR spectra coincide as documented on Fig. 1 by the expanded spectrum of the vinylic carbon atoms.

^{13}C-NMR lines were assigned to carbon atoms in the molecules according to the pattern of the not decoupled spectra, intensity ratio in the decoupled spectra, and comparison with the literature values. The methyl carbon chemical shift in octamethyl-

TABLE I

^{29}Si and ^{13}C-NMR Chemical Shifts[a]

D unit is $(CH_3)_2Si(O_{0.5})_2$, D^{Vi} is $(CH_3)(C_2H_3) . Si(O_{0.5})_2$.

	^{29}Si		^{13}C			
Fraction	D	D^{Vi}	D	D^{Vi}		
				CH_3	CH	CH_2
B	−21·72		0·75			
D	−18·28	−33·48	0·65	−0·94	136·31	132·77
E-*I*[b]	−19·04	−33·43	0·22	−1·28	136·02	132·43
E-*II*[b]	−18·65	−33·80	0·22	−1·28	136·02	132·43
F	−18·63	−33·11	0·65	−0·89	136·17	132·96

[a] Chemical shifts are in δ scale (p.p.m. units, relative to tetramethylsilane line, diamagnetic shifts are negative), estimated error ±0·10 p.p.m.; [b] the relative ratio of the corresponding lines is *I* : *II* = 2·5 : 1.

cyclotetrasiloxane (D_4) was quoted above, in *bis*(trimethylsiloxy)methylvinylsilane the methyl carbon on the central silicon atom is found at $\delta(C) = -0{\cdot}2$ and the vinylic carbons α and β at $\delta(C) = 137{\cdot}7$ and $\delta(C) = 132{\cdot}0$, resp. It should be mentioned here that literature data for vinyltrichlorosilane are not suitable for comparison with the spectra of the compounds studied here. The order of the shielding of the vinylic carbon atoms is reversed in vinyltrichlorosilane[4,6,7] and also $^{13}C—^{1}H$ coupling constants that can be determined by the first order analysis of the not decoupled spectra as indicated on Fig. 1 are different. The following values were reported for vinyltrichlorosilane couplings $^{1}J(^{13}C—^{1}H) = 155$ Hz (see[7]), $^{2}J(^{13}C—^{1}H_{trans\ to\ Si}) = -2{\cdot}5$ Hz (see[8]), and $^{2}J(^{13}C—^{1}H) = -6{\cdot}85$ Hz (see[8]). The coupling determined from the spectrum on Fig. 1 are, in the same order, 135, 5·5, and 10·9 Hz, resp., and $^{1}J(^{13}C—^{1}H) = 156$ Hz. The values of one-bond couplings are similar to those reported[9] for tetravinylsilane ($^{1}J(^{13}C—^{1}H) = 140{\cdot}28$ Hz and $^{1}J(^{13}C—^{1}H) = 156$ Hz).

The structure of the fractions E and F cannot be convincingly deduced from the spectra. But as it is known[1] that the fraction F is one of the 1,3-isomers, *cis*-1,5-divinyl isomer must be one of the two E fractions. It seems a good working hypothesis to assume that the silicon chemical shifts in a *cis-trans* pair of isomers are closer to each other than they are in the pairs of *cis* or *trans* positional isomers and that the shielding of the silicon atom in the D unit should differ from the shift in D_4 more in 1,5-isomer than in 1,3-isomer in which each D unit neighbors with only one D^{Vi} unit while in the 1,5-isomer it does so with two such units. These considerations lead us to assign tentatively E-*II* fraction the structure of *cis*-1,5-divinyl-1,3,3,5,7,7-hexamethylcyclo-

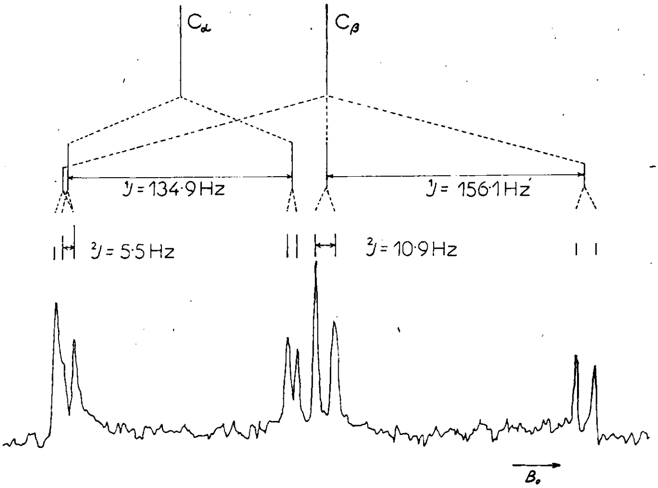

Fig. 1

^{13}C-NMR Spectrum of Vinylic Carbon Atoms of the Fraction E tetrasiloxane. As the spatial arrangement of the vinyl groups, which determines the R_F values of these compounds in a $AgNO_3$–SiO_2 system, is in the *cis*-1,5-divinyl derivative more similar to the *trans*-1,3-divinyl derivative than to its *cis*-isomer, it is very likely that the E-*I* fraction has the structure of *trans*-1,3-divinyl-1,3,5,5,7,7-hexamethylcyclotetrasiloxane. The only remaining isomer, *cis*-1,3-divinyl-1,3,5,5,7,7-hexamethylcyclotetrasiloxane must be identified with the fraction F. In this compound the two vinyl groups are sterically close and therefore they interact most strongly with Ag^+ ions and the compound has the lowest R_F value.

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