NMR ANALYSIS OF THE STEREOISOMERS OF METHYLVINYLPHENYLCYCLOTRISILOXANES AND CYCLOTETRASILOXANES

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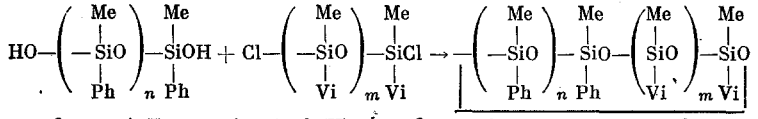
UDC 541.632:547.1'128:543.422.25

It has been reported [1-3] that chemical shifts for methyl group protons can be correlated with geometrical structures in cyclosiloxanes containing a CH_3 and a C_6H_5 group, or an H atom and a CH_3 group, as substituents at the silicon atom. In fact, it has been shown that the chemical shift (CS) can be rather precisely predicted through a system of increments, each describing the number, orientation, and distance of separation of the various substituents relative to the CH_3 group.

It was the aim of the present work to identify the stereoisomers of methylphenylvinyl-substituted cyclosiloxanes, and, at the same time, review the principles basic to analyses of this kind. Study was made of six- and seven-membered siloxane rings with various numbers of methylphenyl and methylvinyl radicals attached to the Si atoms. These compounds were prepared by heterofunctional condensation of methylphenylsilanediol, or α,ω-dihydroxymethylphenylsiloxanes, with α,ω-dichloromethylvinylsiloxanes, or methylvinyldichlorosilane, according to the following reaction scheme:



$n = 0$, $m = 1$ (I); $n = 1$, $m = 0$ (II); $n = 2$, $m = 0$ (III); $n = 0$, $m = 2$ (IV); $n = 1$, $m = 1$ (V)

The reaction with n = 0 and m = 0 yields 1,3,5,7-tetramethyl-1,5-diphenyl-3,7-divinylcyclotetrasiloxane (VI) [4], a compound differing from (V) insofar as the phenyl and vinyl radicals are attached to Si atoms located at the extremities of a ring diagonal.

Elementary analyses, and certain properties of the chromatographically pure compounds, are shown in Table 1.

EXPERIMENTAL

The ^1H NMR spectra of 10% solutions of compounds (I)-(VI) in CCl_4 were obtained with a Hitachi–Perkin–Elmer R-20 spectrometer, operating at a frequency of 60 MHz with TMS as an internal standard. Chemical shifts (δ) were measured in ppm.

1,3,5-Trimethyl-1,3-divinyl-5-phenylcyclotrisiloxane (I). To a solution of 18.0 g (0.23 mole) of pyridine dissolved in 180 ml of abs. ether there was added dropwise from separate funnels at 0-10°C 17.5 g (0.11 mole) of methylphenylsilanediol dissolved in 80 ml of ether and 25.8 g (0.11 mole) 1,3-bis(methylvinylchloro)-disiloxane dissolved in 50 ml ether. The resulting mixture was agitated for 3 h at 20°C, filtered, the solvent evaporated off with a water aspirator, and the residue distilled under oil-pump vacuum.

1,3,5-Trimethyl-1,3-diphenyl-5-vinylcyclotrisiloxane (II). Proceeding similarly, solutions containing 57.7 g (0.20 mole) of 1,3-bis(methylphenyloxy)disiloxane dissolved in 250 ml ether and 28.0 g (0.20 mole) methylvinyldichlorosilane dissolved in 60 ml ether were added simultaneously and dropwise to a solution containing 31.4 g (0.40 mole) of pyridine dissolved in 150 ml ether.

* Deceased.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 843-850, April, 1978. Original article submitted January 4, 1977.

0568-5230/78/2704-0728$07.50

TABLE 1. Physicochemical Constants for Compounds (I)-(V)

Compound	Yield, %	bp, °C (p, mm Hg)	d_4^{20}	n_D^{20}	MR Found/calculated	Mol. mass, found/calculated	Empirical formula	Found/calculated C	H	Si
(I)	21	80-83 (1)	1,0135	1,4710	85,10 84,54	298,3 308,5	$C_{13}H_{20}Si_3O_3$	27,52 27,31	6,49 6,53	50,37 50,60
(II)	28	150-152 (1)	1,0630	1,5095	100,81 100,20	354,2 358,5	$C_{17}H_{22}Si_3O_3$	56,33 56,94	6,14 6,18	23,70 23,49
(III)	55	180-183 (1)	1,1010	1,5268	138,28 138,82	488,1 494,7	$C_{24}H_{30}Si_4O_4$	58,34 58,25	6,12 6,10	22,25 22,70
(IV)	47	109-111 (1)	1,0270	1,4688	107,01 107,50	384,1 394,6	$C_{16}H_{26}Si_4O_4$	48,32 48,68	6,57 6,64	28,49 28,46
(V)	72	164-165 (2)	1,0753	1,4992	122,17 122,52	436,2 444,4	$C_{20}H_{28}Si_4O_4$	54,12 54,01	6,32 6,35	25,18 25,26

1,3,5,7-Tetramethyl-1,3,5-triphenyl-7-vinylcyclotetrasiloxane (III). Proceeding similarly, solutions containing 37.4 g (0.09 mole) 1,3,5-trimethyl-1,3,5-triphenyl-1,5-dihydroxytrisiloxane dissolved in 190 ml ether and 12.4 g (0.09 mole) methylvinyldichlorosilane dissolved in 25 ml ether were added simultaneously and dropwise to a solution containing 13.9 g (0.18 mole) pyridine dissolved in 140 ml ether.

1,3,5,7-Tetramethyl-1,3,5-trivinyl-7-phenylcyclotetrasiloxane (IV). Proceeding similarly, solutions containing 6.2 g (0.04 mole) methylphenylsilanediol dissolved in 60 ml ether and 9.2 g (0.04 mole) 1,3,5-trimethyl-1,3,5-trivinyl-1,5-dichlorotrisiloxane dissolved in 20 ml ether were added simultaneously and dropwise to a solution containing 6.3 g (0.08 mole) pyridine dissolved in 60 ml ether.

1,3,5,7-Tetramethyl-1,7-diphenyl-3,5-divinylcyclotetrasiloxane (V). Proceeding similarly, solutions containing 16.5 g (0.06 mole) 1,3-bis(methylphenyloxy)disiloxane dissolved in 25 ml ether were added simultaneously and dropwise to a solution containing 9.5 g (0.12 mole) pyridine dissolved in 100 ml ether.

1,3,5,7-Tetramethyl-1,5-diphenyl-3,7-divinylcyclotetrasiloxane (VI). Proceeding similarly, solutions containing 15.4 g (0.1 mole) methylphenylsilanediol dissolved in 75 ml ether and 14.1 (0.1 mole) methylvinyldichlorosilane dissolved in 30 ml ether were added simultaneously and dropwise to a solution containing 15.8 g (0.2 mole) pyridine dissolved in 150 ml ether.

DISCUSSION OF RESULTS

NMR identification of the various stereometric forms of the organocyclosiloxanes involved an analysis of the positions and intensities of the CH_3 group proton signals. Analysis in the present case was carried out on mixtures of the isomers of the compounds. Here one must calculate the CS's for the CH_3 protons of the individual stereoisomers, obtain the most probable values of the isomer ratios, and then compare the actual spectra with superpositions of the calculated spectra.

The additive scheme of calculating CH_3 group proton shifts requires further discussion [1-3] before being applied to compounds (I)-(VI).

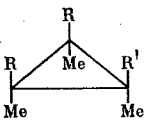
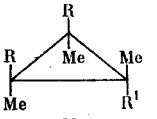
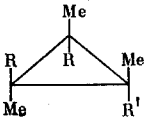
In general, the CS's of these protons depend on both the electronic structure and local effects from the fields of the ring and substituent bonds. The role played by individual factors in fixing the proton CS's in the nonequivalent CH_3 groups of the six-membered cyclosilazanes, compounds similar to the cyclosiloxanes, at least from the point of view of the analysis contemplated here, has been discussed in [5]. There it was shown that the CS's between protons of CH_3 group which differ only in geometrical position are largely determined by the local fields of the ring substituents and bonds, these, in turn, being fixed by the position of the point of conformational equilibrium. The effect from the ring bonds will differ from zero only if the conformational energies of the substituents are different, and the point of conformational equilibrium shifted toward one or the other of the two conformers. The effect of the local fields on the CS's of the cis and trans CH_3 group protons is also determined by the conformer content, but in such way that it cannot be described in terms of a single set of $\Delta\delta_{cis}$ and $\Delta\delta_{trans}$ values.

The local ring bond fields will not contribute to the CS's of the CH_3 protons when the conformer energies are identical, and the substituent contribution to the cis and trans CH_3 group CS average out to a constant value.

TABLE 2. Contribution of the Vinyl Group to the Chemical Shift of the CH_3 Group Protons in the Organocyclosiloxanes

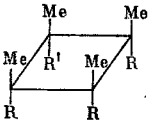
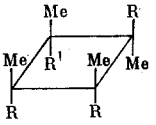
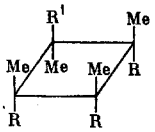
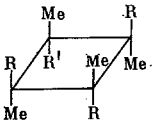
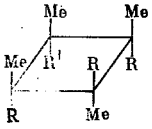
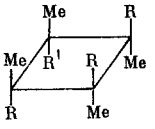
Compound	$\Delta\delta_1$	$\Delta\delta_2$ cis	$\Delta\delta_2$ trans	$\Delta\delta_3$ cis	$\Delta\delta_3$ trans
Cyclotrisiloxane	0,076	0	0,015	–	–
Cyclotetrasiloxane	0,06	0,004	0,019	−0,006	0,008

TABLE 3. Fractions of the Various Isomers in the Methylphenylcyclotrisiloxanes (I) (R = Vi; R' = Ph) and (II) (R = Ph; R' = Vi)

Isomer No.	Configuration	n*
1		0,25
2		0,25
3		0,50

* n is the mole fraction of the isomer in the mixture.

TABLE 4. Isomer Ratios in the Methylphenylvinylcyclotetrasiloxanes (III) (R = Ph; R' = Vi) and (IV) (R = Vi; R' = Ph)

Isomer No.	Configuration	n	Isomer No.	Configuration	n
1		0,125	4		0,250
2		0,125	5		0,125
3		0,125	6		0,250

From this it can be concluded that the substituents will contribute additively to the CS's only if there is no difference in the conformational energies of the substituents at the ring Si atoms.

Study of the six-membered organocyclosilazanes [5] has shown that the difference in conformational interactions amounts to no more than 0.1 kcal/mole, even in the case of groups differing as radically in size as the CH_3 and the C_6H_5. In fact, the conformational interactions are so slight that a shift in the position of the point of conformational equilibrium has no appreciable effect on the CS. Thus the spectra of the methyl-

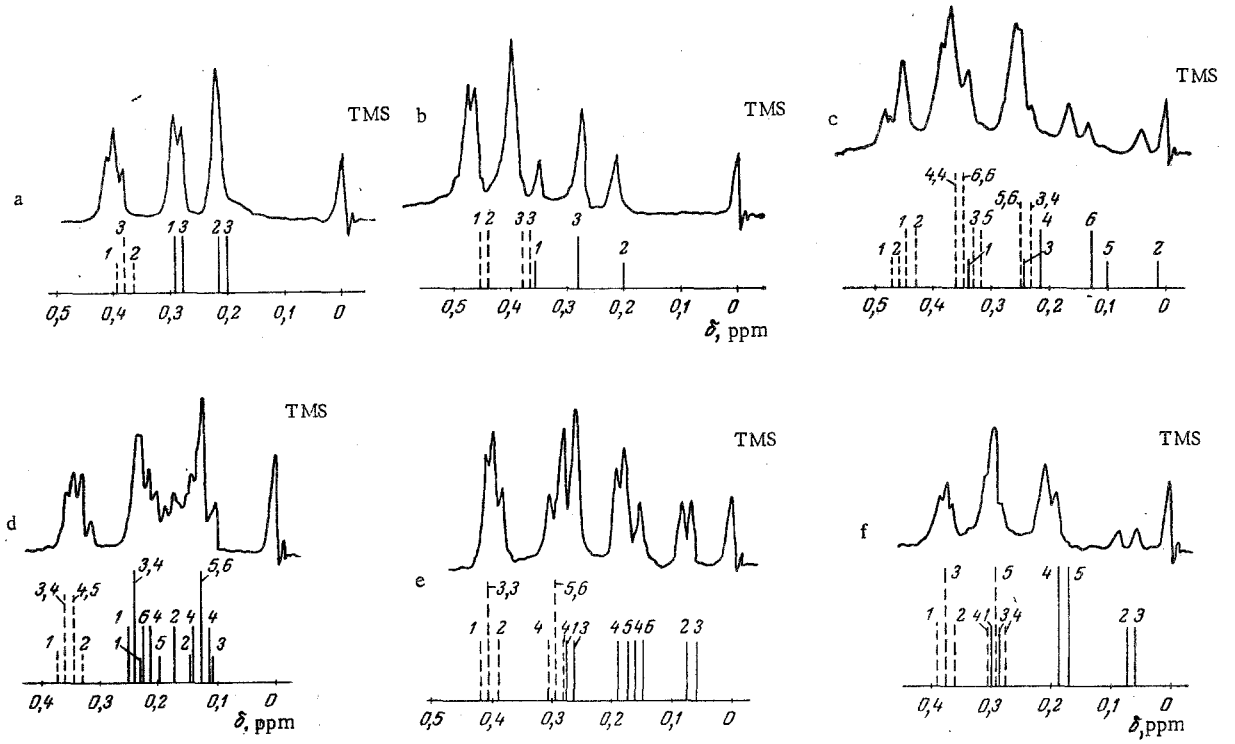


Fig. 1. Experimental and calculated methyl proton spectra: a) 1,3,5-trimethyl-1,3-divinyl-5-phenylcyclotrisiloxane (I); b) 1,3,5-trimethyl-1,3-diphenyl-5-vinylcyclotrisiloxane (II); c) 1,3,5,7-tetramethyl-1,3,5-triphenyl-7-vinylcyclotetrasiloxane (III); d) 1,3,5,7-tetramethyl-1,3,5-trivinyl-7-phenylcyclotetrasiloxane (IV); e) 1,3,5,7-tetramethyl-1,7-diphenyl-3,5-divinylcyclotetrasiloxane (V); f) 1,3,5,7-tetramethyl-1,5-diphenyl-3,7-divinylcyclotetrasiloxane (VI). The numbers attached to the lines in the theoretical spectra correspond to the order numbers in Tables 3-6.

phenyl-substituted cyclotrisilazanes shows the same ordering of signals as the hypothetical spectra, but with equality of the conformational energies of the substituents.

The Si—O—Si angle in the organocyclotetrasiloxanes (~140° [6]) is considerably greater than the Si—N—Si angle in the organocyclotrisilazanes (117°, [7]), and the distance between the substituents is accordingly greater as well. Since the nonvalent interactions, which are determinant in fixing the conformer stabilities, fall off rapidly with increasing distance of separation, it would seem that the conformational energies would be a much less significant factor in the organocyclotetrasiloxanes than in the organocyclotrisilazanes. The conformational contribution cannot be of appreciable magnitude, even in the organocyclotrisiloxanes, for the ring folding there is slight [6, 8].

Thus it can be concluded that it is possible to use an incremental scheme for calculating the CS's of the CH_3 group protons in cyclosiloxanes with various sets of substituents at the Si atom. The one requirement here is certainly that the substituents be no larger than the C_6H_5 group.

These requirements are satisfied by our compounds (I)-(VI), each of which contains CH_3, C_5H_6, or $CH=CH_2$ groups. We have, therefore, calculated the CS's through an additive scheme of the form:

$$\delta = \delta_0 + \Delta\delta_1 + \sum_i \Delta\delta_i^{vi} \cdot n_i + \sum_j \Delta\delta_j^{ph} \cdot n_j$$

Here $\Delta\delta_1$ is the contribution to the CS's of the CH_3 group protons from substituents attached to the same Si atom; $\Delta\delta_i^{vi}$ is the contribution to the CS's of the CH_3 group protons from $CH=CH_2$ groups attached to a neighboring Si atom in cis or trans orientation to the CH_3 group ($\Delta\delta_{2cis}$ or $\Delta\delta_{2trans}$), or to a distant Si atom in cis or trans orientation to the CH_3 group ($\Delta\delta_{3cis}$ or $\Delta\delta_{3trans}$); n_i is the number of vinyl groups in the ith position, and $\sum_j \Delta\delta_j^{ph} \cdot n_j$ is a similar term for the contribution from C_6H_5 groups.

TABLE 5. Isomer Ratios in 1,3,5,7-Tetramethyl-1,7-diphenyl-3,5-divinylcyclotetrasiloxane (V)

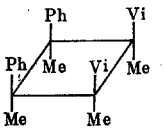
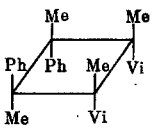
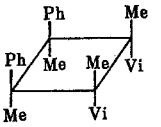
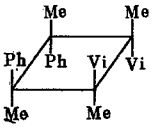
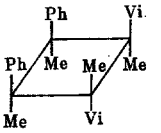
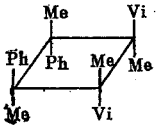
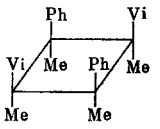
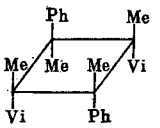
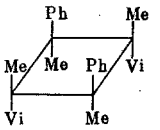
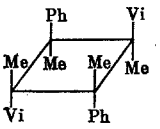
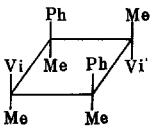
Isomer No.	Configuration	n	Isomer No.	Configuration	n
1		0,125	4		0,250
2		0,125	5		0,125
3		0,250	6		0,125

TABLE 6. Isomer Ratio in 1,3,5,7-Tetramethyl-1,5-diphenyl-3,7-divinylcyclotetrasiloxane (VI)

Isomer No.	Configuration	n	Isomer No.	Configuration	n
1		0,125	4		0,250
2		0,125	5		0,250
3		0,250			

The set of C_6H_5 group increments developed in [3] was used for calculating the signal positions for compounds (I)-(VI). The corresponding set of vinyl group increments was obtained from the spectra of the heptamethylvinylcyclotetrasiloxane, the isomers, 1,3,3,5,7,7-hexamethyl-1,5- and 1,3,5,5,7,7-hexamethyl-1,3-divinylcyclotetrasiloxane, and 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane. Data are summarized in Table 2.

The most trustworthy value available for the organocyclotrisiloxanes is the difference in the vinyl group contributions to the CS's of the cis and trans CH_3 groups ($\Delta\delta_{trans} - \Delta\delta_{cis} = 0.015$ ppm). The vinyl group shielding of the cis-CH_3 group protons was arbitrarily set equal to zero, assuming the effects of the CH_2=CH and C_6H_5 groups in the cyclotrisiloxanes to be identical [3].

Signal intensities were calculated from the number of equivalent CH_3 groups in the isomer and the most probable isomer distribution in each compound. Only statistical factors were taken into account in determining the isomer populations, which is to say that the problem was treated as one of determining the number of combinations of asymmetrical Si atoms leading to the given configuration. Energetic factors were not taken into account here since it would seem that the substituents are so far separated in the organocyclosiloxanes that steric hindrances would no longer affect the formation of the various isomeric forms. The results of these calculations are summarized in Tables 3-6.

The spectra of compounds (I)-(VI) obtained from these calculations are shown below the experimentally developed spectra in Fig. 1. The signals for the CH_3 group protons of the MeSiPh and MeSiVi fragments are indicated by dashed and full lines, respectively. The calculated spectra give a good representation of the general aspects of the spectra of compounds (I)-(VI). The maximum deviation between the signal positions in the two types of spectra is no more than 0.03 ppm. These figures largely refer to the entire signal group. Thus in the calculated spectrum for compounds (I) and (II), all of the proton signals for the CH_3 groups of the MeSiPh fragment are moved upfield by 0.02-0.03 ppm, comparison being with the positions in the experimental spectrum. The separation of signals within the group is maintaned more closely. The actual signal ratio is also close to the calculated, as can be clearly seen from the spectra of the organocyclotrisiloxanes and the separate components in the spectra of the organotetrasiloxanes.

Thus analysis of the signal positions and intensities in the ^1H NMR spectra of the organocyclooxanes can be successfully carried out by assuming steric interactions to be of minor significance in the ground state of the molecule and in the reactive transition states.

CONCLUSIONS

1. Certain methylphenylvinylcyclosiloxanes have been synthesized.

2. Study of the PMR spectra of mixtures of the stereoisomers of the organocyclosiloxanes shows that steric interaction is of little significance in the ground state and in the reactive transition states of these compounds.

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ASYMMETRICAL UNBRIDGED NITROGEN

16.* THE OPTICALLY ACTIVE N-ALKOXYISOXAZOLIDINES AND THE STRUCTURE OF THE TETRAAMIDE OF 2-METHOXYISOXAZOLIDINE-3,3,5,5-TETRACARBOXYLIC ACID

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UDC 541.65:541.6:547.786

The high configurational stability of the nitrogen atom in the N-alkoxyisoxazolidines has been demonstrated by separating the geometrical isomers and studying the isomerization of the dimethyl ester of 2-methoxy-5-cyanoisoxazolidine-3,3-dicarboxylic acid [2], and other derivatives [3]. This work has laid the basis for synthesizing the first optically active N-alkoxyisoxazolidines with a single asymmetrical center on the nitrogen

* See [1] for Communication 15.

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 850-859, April, 1978. Original article submitted January 4, 1977.

0568-5230/78/2704-0733$07.50