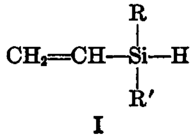
The Structures of the Polymers and Cyclic Dimers Obtained from Diorganovinylsilanes

James W. Curry

Received July 21, 1960

In 1956 Curry[1] reported the polymerization and cyclization of certain diorganovinylsilanes (I) *via* Si-H addition. The resulting products were designated as polysilethylenes (II) and 1,4-disilacyclohexanes (III) on the basis of infrared spectral analysis. Subsequently, however, it was called to our attention[2] that certain of these structural assignments might not be correct. Accordingly, in an effort to gain additional information, new samples of the materials were prepared and studied by NMR spectroscopy.

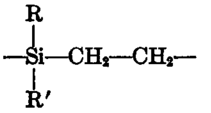


$CH_2{=}CH{-}\overset{R}{\underset{R'}{Si}}{-}H$

I

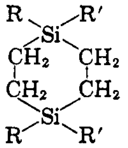
a. R = R′ = CH_3 c. R = R′ = C_6H_5

b. R = R′ = C_2H_5 d. R = CH_3; R′ = C_6H_5



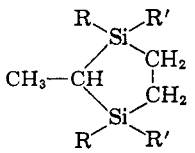
$-\overset{R}{\underset{R'}{Si}}{-}CH_2{-}CH_2{-}$

II a–d



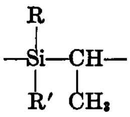
IIIa, b, c, d

For the dimethylvinylsilane cyclic dimer, the results indicated the presence of both structure IIIa and the five-membered ring compound, 1,1,2,3,3-pentamethyl-1,3-disilacyclopentane (IVa). There was found in the nmr spectrum, at relatively low field, a doublet, arising from the protons of the C-methyl group in IVa. The observed splitting was due to spin coupling with the proton at the tertiary carbon atom. The next peak was attributed to the equivalent methylene groups in IIIa, and at slightly higher field was a peak from the protons of the CH_2 groups in IVa. Next, there appeared two signals from the two pairs of nonequivalent methyls attached to silicon in IVa, the one pair being above the plane of the five-membered ring, and the other pair, below the plane of the ring. A third CH_3—Si peak at somewhat higher field represented the equivalent methyl groups in IIIa. Finally, a low, broad pattern appearing at still higher field was due to the tertiary proton in IVa. The pattern would normally appear as a quartet because of splitting by the protons of the attached methyl group. In this case, however, the first peak of the quartet was obscured by the CH_3—Si resonance from IIIa. By comparing the areas of the two CH_2 peaks, it was possible to determine that the cyclic dimer consists of 27% IIIa and 73% IVa.



IVa, b, c, d

The corresponding polymer was shown to be predominantly polydimethylsilethylene (IIa), although the presence of a small amount of the alternate structure (Va) was also indicated. In the nmr spectrum there was a low intensity signal from the methyl protons in CH_3—CH, split into a doublet by the proton at the tertiary carbon. At higher field there was a single peak arising from the equivalent CH_2 groups in IIa, and at still higher field there appeared the CH_3—Si resonance. From the relative areas of the three sets of signals the composition of the polymer was estimated approximately as 75% IIa and 25% Va.



$-\overset{R}{\underset{R'}{Si}}{-}\underset{CH_3}{CH}{-}$

V a–d

Examination of the spectrum from the diethylvinylsilane cyclic dimer revealed the presence of a very small amount of 1,1,3,3-tetraethyl-2-methyl-1,3-disilacyclopentane (IVb). The tertiary proton present therein gave rise, at high field, to a weak signal, which was split into a quartet by the attached methyl group. Thus, from the evidence it was concluded that the major component is 1,1,4,4-tetraethyl-1,4-disilacyclohexane (IIIb). The resonance peaks were not, however, sufficiently well defined to permit a quantitative estimate of the relative amounts of the two isomers. Interestingly enough, the multiplicity of CH_2 peaks in the spectrum indicated that the individual protons in these groups are not equivalent and suggested that compound IIIb may exist in a fixed conformation (chair form).

The spectrum of the polymer from diethylvinylsilane was difficult to interpret because all of the resonance peaks were crowded into a small region. However, no quartet, which would be expected from the tertiary proton in Vb, could be found, and it was concluded, therefore, that IIb best represents the structure of this product.

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(1) J. W. Curry, *J. Am. Chem. Soc.*, **78**, 1686 (1956).

(2) A. J. Barry, Dow Corning Corp., private communication.

Spectral analysis of the diphenylvinylsilane cyclic dimer showed clearly the presence of 1,1,3,3-tetraphenyl-2-methyl-1,3-disilacyclopentane (IVc) to the exclusion of the other possible isomer (IIIc). The expected quartet and doublet from HC—CH_3 appeared at relatively low and high field, respectively, and bracketed neatly the single resonance peak from the two equivalent methylene groups.

The results from the related polymer were not so definite. However, the apparent absence of a doublet signal from CH_3—CH indicated that Vc is probably not present, thereby suggesting that the most likely structure is IIc.

The spectrum of the methylphenylvinylsilane cyclic dimer showed a split phenyl signal at low field, indicating the presence of both of the two possible structures. At high field were observed, successively, an incompletely resolved multiplet due to all the methylene groups present, a group of low peaks, probably from CH_3—CH, and another multiplet due to non-equivalent protons in the CH_3—Si groups. The multiple splittings were attributed to *cis* and *trans* isomers of both IIId and IVd. By comparing the relative areas of the two portions of the phenyl signal, it was established that this dimeric material is a 60:40 mixture of the two ring structures. However, the resonance peaks from CH_2 and CH_3—CH were not sufficiently well resolved to permit a conclusion as to which isomer constitutes the larger portion.

On the basis of the meager information available from the spectrum of the methylphenylvinylsilane polymer, structure IId is favored over the isomeric Vd, although the latter cannot be completely ruled out. Even in carbon tetrachloride solution the resonance peaks were viscosity broadened, and while the small quartet pattern from CH_3—CH did not appear to be present in high field, it might have been obscured by the other broad signals near this region.

In summary, the NMR evidence, while not always clear cut, did show that both five- and six-membered ring structures are represented among the various cyclic dimers, and in the main, appeared to reaffirm the earlier assigned[1] polysilethylene structure for the polymers.

EXPERIMENTAL[3,4]

Nuclear magnetic resonance spectra. The NMR spectra were determined using the Varian Associates High Resolution Spectrometer (V-4300-C), operated at 60 mc. and 14090 gauss. The spectra of all of the polymers and of diphenylvinylsilane cyclic dimer were run in carbon tetrachloride solution. The other cyclics (liquids) were run without solvent.

Physical properties. In Tables I and II are listed certain physical properties. The values shown have either not been reported previously or constitute revisions of those recorded earlier.[1]

TABLE I

Reaction product	n_D^{25}	d_4^{25}	R_D, Calcd.	R_D, Found
Dimethylvinylsilane:				
Polymer	1.4903	0.8827	0.3263	0.3277
Diethylvinylsilane:				
Polymer	1.4988	0.8970	0.3276	0.3272

TABLE II

Reaction Product	Mol. Wt., Calcd.	Mol. Wt., Found	Average Degree of Polymerization
Dimethylvinylsilane:			
Polymer	—	2340, 2190, 2110	25.6
Cyclic Dimer	172	178, 177	—
Diethylvinylsilane:			
Polymer	—	992, 980	8.6
Cyclic Dimer	228	239, 237	—
Diphenylvinylsilane:			
Polymer	—	647, 661	3.1
Methylphenylvinylsilane:			
Polymer	—	847, 864	5.8
Cyclic Dimer	297	283, 286	—

Acknowledgment. The author gratefully acknowledges the financial support of this work by the Dow Corning Corporation. He also wishes to thank Mr. LeRoy F. Johnson of Varian Associates, Palo Alto, Calif., and Mr. Paul C. Lauterbur of Mellon Institute of Industrial Research, Pittsburgh, Pa., for their aid in running and interpreting the nmr spectra discussed in this paper.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA, SANTA BARBARA
GOLETA, CALIF.

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[3] Calculated specific refractivities were computed from bond refractivity values listed in the following references: A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *Chem. & Ind.* (*London*), 358 (1950), and A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

[4] All molecular weight determinations were carried out cryoscopically in benzene.

An Evaluation of the Gilman-Haubein Determination of Alkyllithium

KENNETH C. EBERLY

Received August 18, 1960

The question arose concerning the application of the double titration of Gilman and Haubein[1] to assay of pure butyllithium under oxygen- and moisture-free conditions. It was felt that quantitative experiments were in order to confirm the method.

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[1] H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515–16 (1944).