ORGANOSILICON COMPOUNDS. LXXIII.*
PMR SPECTRA OF VINYLAMINOSILANES

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Preparation of vinyltris(dimethylamino)silane, vinylmethylbis(dimethylamino)silane, and vinyl-dimethyl(dimethylamino)silane is reported. The PMR spectra of the vinylaminosilanes are measured and analysed. The spectra are compared with those of other vinylsilanes.

Various vinylsilanes have been studied by proton magnetic resonance spectroscopy in a number of papers (see *e.g.*[1-11]). Two reasons for such interest are apparent: first, the bonding situation in these compounds is still far from being well understood[1-7], second, vinylic proton spectra with their typical pattern of strongly coupled ABC systems (consisting of up to a maximum of fifteen lines) offer models on which NMR techniques can be conveniently tested and demonstrated[8-11].

Among the studied vinylsilanes the vinylsilanes of formula *I* have received the greatest attention

$$ \begin{array}{c} H_B \\ \\ H_A \end{array} C=C \begin{array}{c} H_C \\ \\ Si(CH_3)_{3-n}R_n \end{array} $$

I
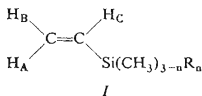
with a possible exception of vinylsilanes of the type $(CH_2=CH)_{4-n}SiR_n$ ($R = CH_3$, C_6H_5). In their study of vinylmethylsilanes, Hobgood, Goldstein, and Reddy[1] reported the spectrum of vinyltrichlorosilane (at 40 MHz) to consist of only one single slightly broadened line with a suggestion of structure. Later, Summitt and coworkers[3] studied this compound at 60 MHz with the same result except that the line was sharp with no structure save for ^{29}Si satelites.*** The latter authors also mentioned a puzzling observation that the chemical shift of this single line was almost exactly the same as that of Cl_3SiH. A study[5] of thirteen vinylsilanes revealed that the collaps of vinylic proton spectrum into a single line is a general feature for the vinylsilanes of formula *I* if $n = 3$ (or 2 in some cases) and $R = $ tert-OC_4H_9, $OSi(CH_3)_3$, OC_2H_5, and, of course, Cl.

Since for substituents other than chlorine the chemical shifts in R_3SiH silanes differed appreciably from the shifts of the vinylic protons on the corresponding vinylsilanes, the coincidence in trichloroderivatives was considered to be accidental[5].

The present work was initiated with the aim to shed some light on the causes that bring about the mentioned collaps in the spectra of trisubstituted vinylsilanes. For this reason vinyltris(dimethylamino)silane was prepared and its spectrum measured. Since the spectrum (see Fig. 1) which resembled very much the spectrum of methyltrivinylsilane[10] differed markedly from the spectra of other trisubstituted vinylsilanes the scope of this study was enlarged to include the whole series of vinylaminosilanes of formula *I* with $R = N(CH_3)_2$. These vinylsilanes are referred within this paper as vinylsilanes 0, *I*, *II* and *III* if $n = 0, 1, 2$, and 3, resp. Their PMR spectra were reported in the literature[12] only briefly, no analysis of vinyl proton region was given.

EXPERIMENTAL

Preparation of the Vinylsilanes

All the vinyl(dimethylamino)silanes were prepared by reactions of the corresponding methylvinylchlorosilanes with an excess of dimethylamine (Fluka AG, Switzerland). Vinyltrichlorosilane and vinylmethyldichlorosilane were commercial products (VCHZ Synthesia, Lučební závody, Kolín) which were redistilled before use. Vinyldimethylchlorosilane was prepared by the reaction of dimethyldichlorosilane with vinylmagnesium chloride in tetrahydrofurane[13]. The product contained some 10% of an impurity (most likely divinyldimethylsilane). The reactions with dimethylamine were carried out in cyclohexane in an atmosphere of dry nitrogen. The following procedure is that for preparation of vinyltris(dimethylamino)silane, the other vinylaminosilanes were prepared analogously.

Dimethylamine (20 g, 0·45 mol) dissolved in 100 ml of cyclohexane was placed into a 250 ml
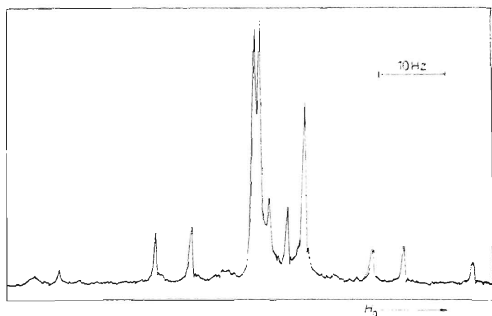

Fig. 1

Vinyl Region of 60 MHz PMR Spectrum of Vinyltris(dimethylamino)silane in 20% Solution

three-necked flask equipped with a stirred, dropping funnel, and a dry ice-aceton condenser and then the solution of vinyltrichlorosilane (10 g or 0·06 mol) in cyclohexane (30 ml) was added dropwise with stirring over one hour period. After all the chlorosilane had been added, stirring was continued and the reaction mixture warmed gradually for 4—5 hours under reflux untill the temperature reached the b.p. of cyclohexane. When cooled down, the liquid phase was separated from the precipitated dimethylamino hydrochloride by filtration through a glass frit using an overpressure of dry nitrogen. The cyclohexane was distilled off and the product purified by a fractionation under reduced pressure.

Vinyl tris(dimethylamino)silane distilled at 69°C/18 Torr, yield 75%; n_D^{20} 1·4467; d_4^{23} 0·866 (reported[12] b.p. 82°C/30 Torr, n_D^{25} 1·4447, d_4^{25} 0·863). IR spectrum 3049 cm^{-1} (antisymmetric stretching vibration =CH$_2$), 1594 cm^{-1} (stretching vibration C=C), 990 cm^{-1} (symmetric stretching vibration C—N—C), and 954 cm^{-1} (wagging vibration —CH=CH$_2$). For SiC$_8$H$_{21}$N$_3$ (187·4) calculated: 51·28% C, 11·31% H, 22·45% N; found: 50·93% C, 11·50% H, 23·3% N.

Vinylmethylbis(dimethylamino)silane distilled at 66°C/47 Torr; yield 71%; n_D^{20} 1·4351; d_4^{23} 0·828 (reported[12] b.p. 83°C/100 Torr; n_D^{25} 1·4337; d_4^{25} 0·824). IR spectrum 3050 cm^{-1} (antisymmetric stretching vibration =CH$_2$), 1594 cm^{-1} (stretching vibration C=C), 990 cm^{-1} (symmetric stretching vibration C—N—C), and 954 cm^{-1} (wagging vibration —CH=CH$_2$). For SiC$_7$H$_{18}$N$_2$ (158·3) calculated: 53·10% C, 11·47% H, 17·71% N; found: 53·06% C, 11·24% H, 17·6% N.

Vinyldimethyl(dimethylamino)silane distilled at 105°C; yield 63%; n_D^{20} 1·4177; d_4^{23} 0·763 (reported[12] b.p. 107°C; n_D^{25} 1·4170; d_4^{25} 0·773). The product contained some 5% of divinyldimethylsilane. IR spectrum 3051 cmΔ^1 (antisymmetric stretching vibration =CH$_2$); 1597 cm^{-1} (stretching vibration C=C), 990 cm^{-1} (symmetric stretching vibration C—N—C), and 954 cm^{-1} (wagging vibration —CH=CH$_2$). For SiC$_6$H$_{15}$N (129·3) calculated: 55·73% C, 11·70% H, 10·84% N; found: 56·8% C, 11·35% H, 10·1% N.

Measurements of the Spectra

The spectra were recorded on a modified Tesla BS 477 spectrometer operating at 60 MHz. The spectrometer was equipped with an internal locking system permitting double resonance experiments. Positions of lines were determined relative to the signal of an internal reference with the help of TESLA BM 445 E electronic counter. The individual positions could be read with an error ±0·1 Hz. Four recordings (two in each sweep direction) were used to calculate the average spectrum used further for analysis. The spectra were recorded in neat samples as well as in 50, 20, and 10% (volume) solutions in cyclohexane at ambient temperature. Spectrograde cyclohexane served both as a solvent and internal reference.

The assignment of the chemical shifts to CH$_3$Si and CH$_3$N protons was straightforward, the vinyl region of the spectra required an analysis. The chemical shifts obtained by the analysis were assigned using the established relation among the coupling constants $J_{gem} < J_{cis} < J_{trans}$[1–11]. It is worthy to note that the pattern of the spectra studied here (Figs 1—3) resembled much more the spectrum of divinyldimethylsilane[10] or the spectra of vinylphenylsilanes[2] than the spectrum of vinyltrimethylsilane[1,5] and other vinylsilanes of formula I studied previously[3,5].

Analysis of the Spectra

Various difficulties were encountered in the analysis. Beside those which have already been described by Freeman and Anderson[10] (these include the presence of ^{29}Si satelites superimposed on the spectrum, occurrence of weak lines difficult to distinguish from side bands) there was also a considerable overlap of central lines in all the spectra and in the spectrum of vinylsilane I the

lines from the impurity had to be distinguished from those of the main compounds. Using the same saturation and "tickling"[14] experiments as in ref.[10] the lines could be correctly assigned and adjusted sets[15] of self-consistent lines derived.

The adjusted sets were analysed by the method of Castellano and Waugh[16] as modified by Cavanaugh[17]. This method uses the frequencies of the adjusted set to generate ten energy-level systems from each of which four (at maximum) independent sets of coupling constants and chemical shifts are calculated. The actual solution of analysis may be ascertained by comparing the transition intensities predicted from these sets with the observed ones. The number of the sets of NMR parameters to be tested might be reduced if some of the energy-level systems do not satisfy certain conditions (conditions (a) and (b) of ref.[16]) or if an energy-level system which satisfies the conditions leads to complex quantities. In some cases, if the imaginary part is sufficiently small, it can be neglected or, in other cases, as reported by Cavanaugh[15], a slight change in the frequencies of the adjusted set might cause some of the imaginary parts vanish.

In the analysis of the spectra reported here some small (± 0.05 Hz) changes in the frequencies of the adjusted sets were necessary in order to get some solutions. Usually two solutions belonging to the same energy-level system (the same sum of the coupling constants) or four (at maximum) corresponding to two systems were obtained. In contrast to the previously published analyses[5,9] of other vinylsilanes the choice of the actual solution was quite unambiguous since the solutions differed markedly in the transition intensities as demonstrated on Fig. 4. In some cases, however, no reasonable changes in the frequencies led to real solutions. This is the reason why we report only the results obtained for 20% solutions, only at this concentration the spectra of all the compounds under study could be analysed. Also the required changes in the adjusted sets were minimal at this concentration so the spectra plotted by a computer fitted the experimental ones best. From the comparison shown on Fig. 3 it is apparent which lines were considered to belong to the impurity in the spectrum of vinylsilane *I*.

Concentration dependence. Again in contrast to our previous results on other vinylsilanes[5] the spectra of vinyldimethylaminosilanes showed a concentration dependence of both the chemical shifts and coupling constants. Since the concentration changes did not follow any clear pattern except for the changes being smaller at lower concentrations and for the center of gravity of the
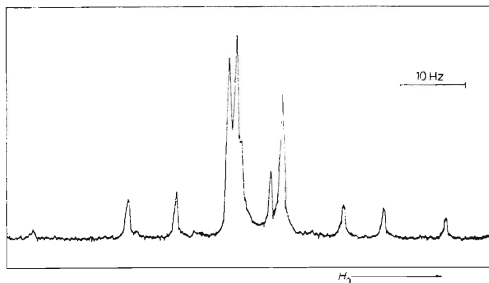

FIG. 2
Vinyl Region of 60 MHz PMR Spectrum of Vinylmethylbis(dimethylamino)silane in 20% Solution

vinyl region shifting to higher field with dilution and since not all 10% solutions could be analysed no justifiable values of parameters for infinite dilution could be derived. It is believed, however, that the parameters reported here for 20% solutions do not differ appreciably from infinite dilution values. For example the parameters for 10% and 20% solutions of vinylsilane *II* did not differ by more than 0·5 Hz in the chemical shifts and 0·1 Hz in the coupling constants.

RESULTS AND DISCUSSION

The results of measurements and analysis are given in Table I. The chemical shifts of protons in CH_3Si and CH_3N groups are, if converted into τ scale using the chemical shift of cyclohexane $\tau = 8 \cdot 56$ p.p.m., in a good agreement with the published data[12], similarly the shifts of the vinylic protons lie within the reported intervals.

As it was mentioned above the other than the reported solutions of the analysis did not fit the observed spectra (Figs 2, 3). For example the second solution plotted on Fig. *4b* corresponds to the following parameters: $\nu_A = 11 \cdot 58$, $\nu_B = -5 \cdot 13$, $\nu_C = 6 \cdot 44$; $J_{AB} = 2 \cdot 11$, $J_{AC} = 20 \cdot 68$, $J_{BC} = 16 \cdot 79$ Hz.

The coupling constants of this solution are very similar to those Castellano and
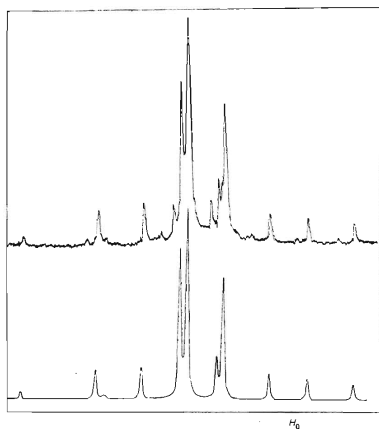

FIG. 3

Vinyl Region of 60 MHz PMR Spectrum of Vinyldimethyl(dimethylamino)silane in 20% Solution

    Upper trace — experimental spectrum, lower trace — theoretical spectrum. (Small differences in lines' positions are caused by nonlinearity and scale factors.)

Waugh[9] accepted as the correct ones for tetravinylsilane, the values which fit our spectrum are close to those the authors rejected on electronegativity grounds, despite that they could not distinguish the two corresponding spectra. In view of our results, irrespective of the difference in the molecules in question, it seems appropriate to assume that the discarded solution is the correct one. On the other hand values close to the average of the two solutions were obtained by other authors who used other methods to analyse tetravinylsilane spectrum[2,8].

The characteristic features of the PMR spectra of vinylsilanes were summarized previously[5], comparison with the present results (Table I and Fig. 5) reveals that these features are also common for the vinylsilanes studied here: *1)* Vinylic protons are shielded less in vinylsilanes than in carbon compounds, *2)* protons B are shielded less than protons A in vinylsilanes, which is in contradistinction to the situation encountered in the spectra of carbon compounds, *3)* the range of the chemical shifts of vinylic protons is smaller in vinylsilanes than in carbon compounds and decreases with increasing n, *4)* the trends in the chemical shifts are different in vinylaminosilanes,
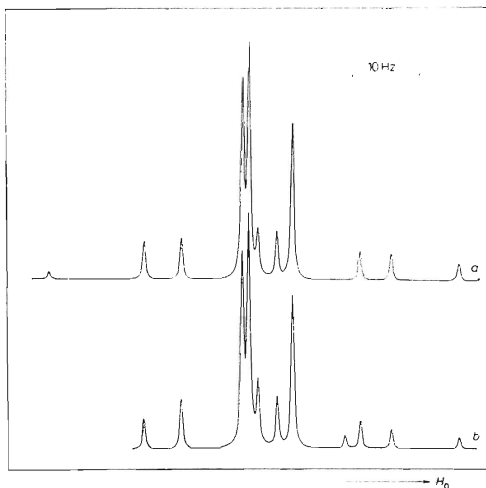

Fig. 4

Two Solutions of the Analysis of the Vinyltris(dimethylamino)silane Spectrum

Trace a — the accepted solution, trace b — rejected solution (compare with Fig. 1).

TABLE I

PMR Spectra of Vinylsilanes I [R = N(CH$_3$)$_2$] at 60 MHz in 20% Cyclohexane Solutions

	Chemical shift of the proton[a]						Coupling constants[a]			
n	A[b]	B[b]	C[b]	center of gravity[c]	CH$_3$Si[c]	CH$_3$N[c]	J_{AB}[d]	J_{AC}[d]	J_{BC}[d]	ΣJ
0[e]	14·42	−0·03	−13·39	−265·3	83·1	—	3·83	20·44	14·54	38·81
1	12·98	−1·67	−11·32	−264·1	82·2	−60·3	4·31	20·40	14·44	39·15
2	12·81	−2·71	−10·10	−263·9	83·5	−61·2	3·98	20·38	14·88	39·24
3	12·43	−3·42	−9·01	−262·9	—	−60·9	4·40	20·37	14·80	39·58

[a] All values are in Hz units. Negative chemical shift means shift to lower field (lower shielding) relative to the reference at 60 MHz. [b] Shift relative to the center of gravity of the vinylic multiplet, accuracy about ±0·06 Hz. [c] Shift relative to the line of cyclohexane, accuracy about ±0·1 Hz, [d] Accuracy about ±0·06 Hz. [e] Converted from ref.[5].

vinylchlorosilanes, and vinylsiloxanes, 5) the coupling constants are larger in vinyl-silanes than the corresponding constants in carbon compounds, 6) the coupling constants and their sum change slightly with the substituents on the silicon atom.

These features have already been interpreted[1,3,5] in the terms of the inductive effect and $(p - d)_\pi$ bonding between silicon atom and substituents. The low shielding of vinylic protons in vinylsilanes is considered to manifest $(p - d)_\pi$ bond between vinyl group and silicon. The $(p - d)_\pi$ bonding character of this linkage is further increased due to the inductive effect of chlorine atoms in vinylchlorosilanes while in siloxanes only the first oxygen atom attached to the silicon acts that way. When there are more oxygen atoms, then any further increase of $(p - d)_\pi$ character of the vinyl-silicon bond is compensated by the formation of competing O—Si $(p - d)_\pi$ bonds resulting in a neat decrease of $(p - d)_\pi$ bonding vinyl-silicon.

As no other interpretation has been offered since we should see what the present results mean in these terms. The fact that the vinylic protons in all the studied vinyl-aminosilanes are shield less than they are in *e.g.* 3,3-dimethyl-1-butene[18] would mean that the $(p - d)_\pi$ bond vinyl-silicon is preserved within the whole series.

In comparison to the related chloro-, tert-butoxy-, and trimethylsiloxy substituted vinylsilanes (see Fig. 5), the shifts of the protons A and B in vinylaminosilanes remain essentially unchanged in the series while the protons C are more shielded as n increases. This finding is rather surprising because the protons A and B are more influenced by the inductive effects of substituents[19] than the proton C. Due to the proximity of the substituents on the silicon atom to the proton C its chemical shift is certainly influenced by many factors difficult to interpret at this stage of our knowledge. The failure of dimethylamino groups to shift the protons A and B could mean

either that substitution by this group leaves the $(p - d)_\pi$ bond vinyl-silicon unchanged or that the shielding effect of any change in the $(p - d)_\pi$ bond is compensated by some other effects. This latter possibility seems unlikely because such compensating effects would have to counterbalance the effects of the $(p - d)_\pi$ bond in each of the three compounds where this bonding character would not change linearly.

Why the dimethylamino group does not cause the vinyl-silicon $(p - d)_\pi$ bond to change is not quite clear. In the other vinylsilanes (except vinylphenylsilanes) the first substituent always acted through its inductive effect[5]. Having in mind that the σ_I constant of $N(CH_3)_2$ group is about one fifth of that for Cl^{20} (irrespective of the same electronegativity of Cl and N atoms[21] the failure of this effect to show up can be understood. If the first dimethylamino group formed a $(p - d)_\pi$ bond to the silicon atom this bond did not compete with the vinyl group for the vacant $3d$ orbitals. The effect of further substitution depended on the nature of the substituent in the previously studied vinylsilanes[5]. Here, one can only speculate that if the other dimethylamino group also formed $(p - d)_\pi$ bonds the present results would mean that these bonds also did not compete with the vinylgroup. As there is no evidence of the formation of any $(p - d)_\pi$ bond Si—N in our results, answering the question how are the 3d-orbitals of the silicon distributed among the nitrogen atoms must
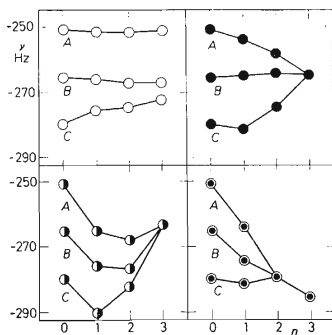

Fig. 5

Chemical Shifts of Vinylic Protons A, B, and C Plotted versus Number n of Substituents R in Vinylsilanes of Formula I

○ R = N(CH$_3$)$_2$, ● R = OC(CH$_3$)$_3$, ◑ R = OSi(CH$_3$)$_3$, and ⊙ R = Cl. The shifts are downfield relative to cyclohexane at 60 MHz. Data for other than dimethylamino derivatives are taken from ref.[5].

avait till the Si—N bond is better understood. At present this bond is subject of lasting contravresy.

The trends in the coupling constants are of little help as they are not very convincing (with increasing n in Formula *I*, the coupling J_{AC} decreases a little, the other two seem to increase) except for the sum of the coupling constants which increases with n. In view of the currently available correlations of the coupling constants in vinyl derivatives[22,23], this increase can be interpreted as indicating a small decrease of the electronegativity of the silicon atom in $Si(CH_3)_{3-n}[N(CH_3)_2]_n$ groups with increasing n. This is in accord with the trend in the internal chemical shift of ethyl-groups in $(C_2H_5)_{4-n}Si[N(CH_3)_2]_n$ series[24].

In the context of the chemistry of silicon–nitrogen compounds the fact that the $(p - d)_\pi$ bond failed to manifest itself in the present study is not surprising. The dimethylamino group is apparently capable of donation of the electrons needed to form such a bond in $SiH_3N(CH_3)_2$ (see ref.[25]) but it is known[26] that both physical and chemical properties of silylamines change as the size and nuber of the groups attached to the silicon atom are increased. This change is perhaps best illustrated[26] by coplanarity of $(SiH_3)N$ and $(CH_3SiH_2)_3N$ (which is attributed to the Si—N $(p - d)_\pi$ bond) in contrast to nonplanarity of $[(CH_3)_3Si]_3N$. Therefore it seems probable that the N—Si $(p - d)_\pi$ bond might be more developed in $CH_2 : CHSi.$ $.H_2N(CH_3)_2$ and perhaps even in $CH_2 : CHSiH[N(CH_3)_2]_2$ than in the vinylsilanes studied here. That will be the subject of our future study.

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Translated by the author (J. S.).

Note added in proof: In a private communication P. J. Green reported a successful analysis of the 220 MHz spectrum of this compound.