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NMR STUDY (^{1}H, ^{13}C and ^{29}Si) OF $(CH_3)_{4-x}Si(CH{=}CH_2)_x$ COMPOUNDS WHERE x = 0, 1, 2, 3, 4

L. DELMULLE and G. P. VAN DER KELEN

Laboratory for General and Inorganic Chemistry-B, University of Gent, Krijgslaan 271, B-9000 Gent (Belgium)

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ABSTRACT

The ^{1}H, ^{13}C and ^{29}Si NMR spectra of the various methylvinylsilanes have been analysed with the aid of a special simulation program. From considerations of the chemical shifts and of the coupling constants $^{2,3}J_{^1H-^1H}$, $^1J_{^{13}C-^1H}$, $^1J_{^{29}Si-^{13}C}$ and $^2J_{^{29}Si-C-^1H}$ it is shown that a mesomeric —M effect from the vinyl group to the Me—Si group is important, in very good agreement with previously published PES results [1—3]. The mesomeric interaction in this series is ascribed to a $\{d, \sigma^*-\pi\}$ hyperconjugation in accordance with theoretical considerations [4].

INTRODUCTION

As part of a systematic physicochemical study of the bonding characteristics in compounds of the type $R_xMR'_{4-x}$(R:$CH_2{=}CH-$, $CH_2{=}CH-CH_2-$; R':CH_3-, Cl, Br, I; M: C, Si, Sn) this study presents the results of the NMR analysis of the compounds with M = Si, R' = CH_3- and R = $CH_2{=}CH-$.

Since the vinyl group has a multiple bond, the formation of a dative $(d-p)\pi$ bond is possible if M is an acceptor. The idea of partial double bonding involving Si *d*-levels goes back to Brockway and Wall [5] and the concept of $(d-p)\pi$ conjugation being introduced by Pauling [6] to account for the contraction in Si—halogen and Si—O bonds. Later, quantum-chemical data became available which also supported the concept of $(d-p)\pi$ interaction in Si—aryl and Si—vinyl bonds [7, 8]. In a recent PES study on vinyl, allyl, phenyl and benzylbutylphosphines and vinyl and allylmethylsilanes, Schmidt and Schweig [1] concluded from calculation of the interaction integrals $H_{\pi\pi} = \{\delta E(\delta E + \Delta E)\}^{1/2}$ that $(d-p)\pi$ interaction is important in the vinylmethylsilanes.

EXPERIMENTAL

All products were prepared by a standard Grignard synthesis with freshly dried THF and ViBr. Purification of the methylvinylsilanes was by column chromatography on Al_2O_3. The THF-free Me_xSiVi_{4-x} was obtained in 60% yield.

All spectra were recorded on a Bruker HFX-90 pulse spectrometer. The analysis was carried out by a simulation and iteration procedure. For this purpose the SPECSY program, specially written for a PDP 8E-computer with a 12K memory, was developed.

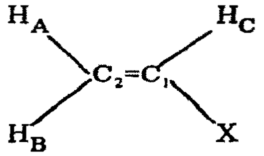
The parameters obtained are summarized in Tables 1—3.

RESULTS AND DISCUSSION

It can be seen from Table 1 and Fig. 1 that the vinylic ^{1}H chemical shifts for trimethylvinylsilane are rather unusual when compared to those for 3,3-dimethyl-1-butene and for vinyl chloride. The measured vinylic ^{1}H chemical shifts suggest a sequence which indicates an electron-withdrawing effect from the vinyl group towards the methylsilyl group, in contrast to the 3,3 dimethyl-1-butene compound where the vinylic ^{1}H chemical shifts are indicative of a +I effect, resulting in a drift of valency electrons towards the double bond. The reversed sequence cannot be explained in terms of electronegativity or anisotropy, for Bock and Seidl [9, 10] showed that the electron-supplying inductive effect (+I) of Me_3Si— is greater than that of Me_3C—. The changes observed in the vinylic proton chemical shifts of the vinylmethylsilanes, in

TABLE 1

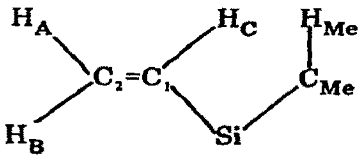
^{1}H and ^{13}C chemical shifts in δ ppm for



ViX	H_A	H_B	H_C	C_1	C_2
X = Cl	5.018	5.239	5.938		
t-Bu	4.848	4.941	5.854	148.40	110.40
Me_3Si	5.871	5.628	6.117	138.70	129.57

TABLE 2

^{1}H, ^{13}C and ^{29}Si chemical shifts (δ p.p.m.) in Me_xSiVi_{4-x}



$4-x$	H_{Me}	H_A	H_B	H_C	C_1	C_2	C_{Me}	Si
0	0	—	—	—	—	—	0	0
1	0.044	5.871	5.628	6.117	138.70	129.57	−1.97	−10.68
2	0.122	5.923	5.662	6.098	136.76	130.67	−3.56	−17.35
3	0.146	6.000	5.717	6.106	134.65	132.23	−5.12	−24.06
4	—	6.083	5.750	6.167	134.11	135.01	—	−30.31

TABLE 3

Coupling constants (Hz) in Me_xSiVi_{4-x}

$4-x$	J_{gem}	J_{cis}	J_{trans}	$^1J_{^{13}C_{Me}-H}$	$^1J_{^{13}C_2-H_A}$	$^1J_{^{13}C_2-H_B}$	$^2J_{^{13}C_2-H_C}$	$^1J_{^{29}Si-^{13}C_{Me}}$	$^1J_{^{29}Si-^{13}C_1}$	$^2J_{^{29}Si-C-H_{Me}}$
0	—	—	—	118.0	—	—	—	50.7	—	6.6
1	3.75	14.75	20.42	119.0	156.2	155.2	−7.2	52.0	64.0	6.6
2	3.54	14.70	20.58	119.8	156.4	155.2	−7.2	53.7	66.0	6.5
3	3.36	14.78	20.68	120.2	156.3	155.7	−7.3	55.9	68.0	6.7
4	3.65	14.62	20.50	—	156.2	156.5	−6.8	—	72.8	—

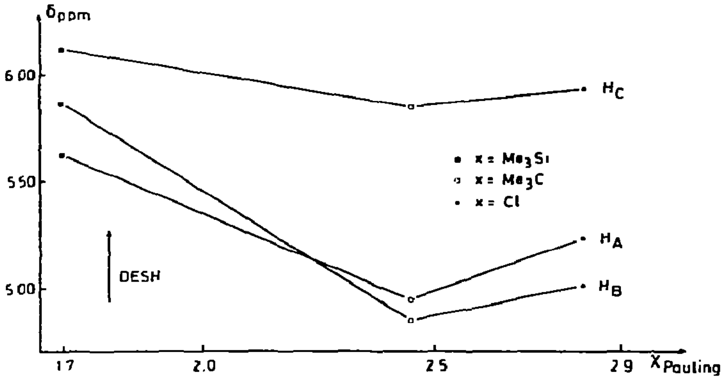


Fig. 1. ^{1}H chemical shifts as function of the Pauling electronegativity of the central atom in ViX.

comparison with those of their isostructural hydrocarbon analogues, can eventually be explained by considering the main difference between the Si and C atoms, i.e. the lower electronegativity of Si and the presence of vacant 3*d* orbitals. In organometallic compounds of this type, the energy gap between σ and π electronic levels is rather small, as can be seen from Table 4. Thus, an interaction between these levels is possible and an MO description is more appropriate. Pitt [4] calculated the interaction between σ and π orbitals for some aryl and benzylmethylsilanes. He considered both conjugation and hyperconjugation effects and concluded that the Me_3Si group acts as an electron acceptor when bonded directly to the π system.

A possible explanation for the NMR behaviour of the vinylmethylsilanes is a hyperconjugation mechanism. Pitt calculated that hyperconjugation of this type results in stabilization of the π-levels. This results in polarization of the π electron density towards the empty *d*-orbitals or the σ^* orbitals of the silyl group. This is in accordance with theoretical results obtained by Zeeck [11] and with PES measurements by Weidner and Schweig [3]. This mechanism is called the $\{d, \sigma^*—\pi\}$ hyperconjugation.

The change of the ^{13}C chemical shifts as a function of the number of vinyl substituents can be due to the same hyperconjugative mechanism that reduces the π electron density mainly at the C_2 atom, resulting in a decrease of the

TABLE 4

IP values (eV) for σ M—C orbitals in Me_4M (M = C, Si, Ge, Sn) and for some π systems from ref. 4

σ	IP	π	IP
C—C	11.2	$CH{\equiv}CH$	11.4
Si—C	10.6	$CH_2{=}CH_2$	10.5
Ge—C	10.2		
Sn—C	9.7		

shielding. The C_1 atom is subject to a field displacement owing to the inductive effect of the Si atom (the electronegativity of which is less than that of C) and to the $\{d, \sigma^*—\pi\}$ hyperconjugation mechanism. $SiVi_4$, however, seems to deserve a special mention in this series. NMR measurements at variable temperature showed that not only resonance stabilization of the partial π bond but even steric interactions were responsible for the values of the ^{13}C NMR parameters.

It can be seen from Table 2 that the Si atoms are highly shielded and that there is a remarkable linearity in the progressive shielding — about 6.5 ppm per vinyl group. This shielding is in contrast to the change in electronegativity expected on varying the number of vinyl groups. It fits well, however, with the idea of a $\{d, \sigma^*—\pi\}$ hyperconjugation mechanism. Infrared studies [9, 12] and PES measurements by Mollère and Bock [2] also led to the hypothesis of a $\{d, \sigma^*—\pi\}$ hyperconjugation. There is little change in coupling constants. The influence on J_{gem} of the various substituent interactions can be accounted for by the MO model of Pople and Santry [13]. The trend of J_{gem} is decreasing, but is too small to be interpreted (Table 3). The same remark holds for the *vicinal* coupling constants. If, however, the α parameter is considered, from the criterion of Brügel et al. [14], $\alpha = J_{trans}/\Delta\nu$, where $\Delta\nu$ is the frequency separation between the two *trans*-interacting hydrogen atoms, the α values listed in Table 5 increase on progressive vinyl substitution, indicating an increase of the —I and of the —M effects. The latter confirms the previously suggested importance of $\{d, \sigma^*—\pi\}$ hyperconjugation.

It can be seen in Table 3 that the carbon—hydrogen coupling constants are scarcely affected by variation of the number of substituents. In contrast, the silicon—carbon spin—spin coupling constant increases on going from mono- to tetra-vinyl substitution. This can be ascribed to a decrease of the relative importance of the $\sigma—\pi$ conjugation and an increase of the $\{d, \sigma^*—\pi\}$ hyperconjugation, for Pitt calculated that hyperconjugation causes a stabilization of the π level that counteracts its destabilization caused by $\sigma—\pi$ conjugation. Hence ΔE decreases, resulting in an increase of the coupling constant.

The variation of the $^2J_{^{29}Si—C—^1H}$ coupling constants is very small and cannot be explained for lack of geometrical information. This variation is probably a function of the changing H—C—Si angle since it was found that the methyl hydrogens were influenced by steric interactions.

TABLE 5

α values ($\alpha = J_{trans}/\Delta\nu$) for Me_xSiVi_{4-x}

$4-x$	J_{trans}	$\Delta\nu = \lvert\nu_B - \nu_C\rvert$(Hz)	α
1	20.42	44.0	0.46
2	20.58	39.2	0.53
3	20.68	35.0	0.59

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