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^{13}C NMR STUDIES OF ORGANOSILANES

IV*. VINYL- AND ALLYL-SILANES

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Summary

The ^{13}C NMR spectra of 29 silanes containing vinyl and allyl groups have been recorded and assigned. The chemical shifts have been correlated using substiuent-chemical-shift factors for groups and atoms attached to the silicon atom. A high correlation is demonstrated between the spectral results for the vinyl compounds and the corresponding phenylsilanes.

Introduction

In a previous paper [1], we reported on the ^{13}C NMR spectra of a series of phenylsilanes and analyzed the results in terms of the interaction of the silicon atom and its substituents with the aromatic ring. The potential for dative π-bonding between the silicon and the substituents on the one hand, and the π-orbitals of the phenyl ring on the other was noted. Situations in which steric effects were important in determining the observed chemical shifts were discussed. These interpretations were made based on the phenyl—silicon system. If the analysis has any general validity, it should be applicable to other systems which are structurally and electronically similar. The vinylsilanes are such a class of compounds, wherein the carbon-1 of the vinyl group is analogous to the *ipso* carbon of the phenyl ring and the vinyl carbon-2 is related to the *ortho* phenyl carbon. Following this analogy, the allyl compounds should resemble the corresponding benzyl derivatives.

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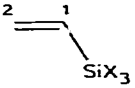
* For part III, see ref. 1.

A few previous, isolated reports of ^{13}C NMR spectra of vinyl- and allyl-silanes have appeared [2,3] but no systematic study has been undertaken *. For our purposes, in order for a valid comparison to be made with the phenyl results, spectral data for the vinyl- and allyl-silanes should be obtained under conditions which closely match those of the phenyl study. Accordingly, we have examined the ^{13}C NMR spectra of a series of vinyl- and allyl-silanes. The results indicate a high correlation between the spectral patterns observed for the vinyl and phenyl compounds.

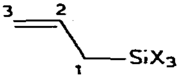
Results

^{13}C NMR spectra. The ^{13}C NMR spectra of fifteen vinyl- and fourteen allylsilanes of the type $RSiX_3$, where $X = CH_3$, C_2H_3, C_6H_5, H, Cl, OC_2H_5, $N(CH_3)_2$; $R = C_2H_3$ and C_3H_5, were recorded and assigned (Tables 1 and 2). Chemical shifts assignments were determined by off-resonance decoupling experiments conducted on numerous compounds as well as by comparing the spectra of related compounds and correlating systematic changes in shift with slight differences in structure. Where data were available, the values and assignments obtained for the chemical shifts agreed with those in the literature [2,3].

For the vinylsilanes, the chemical shift of carbon-1 covered a range of approximately 10 ppm; extending from 129.26 ppm (vinyltriethoxysilane) to 139.69 ppm (trimethylvinylsilane). Carbon-2 chemical shifts extended from 130.34 ppm (trimethylvinylsilane) to 139.20 ppm (vinyltrichlorosilane). The range for this carbon spanned approximately 9 ppm. The correlation coefficient between the two vinyl carbons was negative.



For the allylsilanes, the resonances of carbon-1, the saturated carbon, occurred upfield from those of the other carbons and spanned approximately 13 ppm, from 18.08 (allyltriethoxysilane) to 30.76 ppm (allyltrichlorosilane). The unsaturated carbons covered a smaller area of 8 ppm each. The signal of carbon-2 ranged from 127.24 (allyltrichlorosilane) to 135.08 ppm (trimethylallylsilane). The bounds of carbon-3 shifts extended from 112.65 (trimethylallylsilane) to 119.54 ppm (allyltrichlorosilane). No correlation between saturated and unsaturated carbon shifts was observed. However, the correlation between the chemical shifts of C-2 and C-3 was significant.



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* Subsequent to the submission of this manuscript we became aware of an NMR study of vinyl- and allyl-silanes by Schraml and co-workers [9]. There is substantial agreement between their results and those reported here although different substituents were included in the two studies. They note a correlation between the β-carbon resonance in the vinyl compounds and the *ortho* signal of the corresponding phenylsilanes. In our work, the only significant correlation for the β-carbon is with the *ipso* phenyl signal (vide infra).

TABLE 1

OBSERVED AND CALCULATED ^{13}C NMR CHEMICAL SHIFTS FOR VINYLSILANES, $C_2H_3SiX_3$

X_3 [a]	Carbon 1	Carbon 2
Me_3	139.69(139.70) [b]	130.34(130.55)
Vi_3	134.12(134.12)	135.33(135.33)
Me_2Cl	135.99(136.05)	133.89(133.84)
$MeCl_2$	133.22(133.23)	136.84(136.73)
Cl_3	131.24(131.24)	139.20(139.24)
Me_2OEt	137.46(137.40)	132.72(132.60)
$Me(OEt)_2$	133.79(133.91)	134.83(134.66)
$(OEt)_3$	129.26(129.24)	136.57(136.72)
Me_2Ph	137.93(137.81)	132.78(132.67)
$MePh_2$	135.80(135.92)	134.85(134.80)
MePhH	134.77(134.77)	134.70(134.70)
MePhCl	134.22(134.16)	135.80(135.96)
MePhOEt	135.48(135.50)	134.64(134.73)
$Ph(OEt)_2$	132.09(132.01)	136.83(136.79)
Ph_2OEt [c]	133.74(133.61)	136.62(136.85)
$Me(NMe_2)_2$ [c]	132.70	136.73
Rms deviation (ppm)	0.068	0.11

[a] Me = methyl, Ph = phenyl, Vi = vinyl, Et = ethyl. [b] Calculated values in parentheses. [c] Not included in regression analysis.

Regression analyses. The data for each of the carbons were analyzed separately using the equation:

$$\delta^a_{(X)} = k^a + \sum_{i=1}^{P} n_i \delta^a_i + \sum_{i=1}^{P} \sum_{j \geqslant i}^{P} n_{ij} \delta^a_{ij} \tag{1}$$

where $\delta^a_{(X)}$ is the chemical shift of the carbon being considered in the X-th com-

TABLE 2

OBSERVED AND CALCULATED ^{13}C NMR CHEMICAL SHIFTS FOR ALLYLSILANES, $C_3H_5SiX_3$

X_3 [a]	Carbon 1	Carbon 2	Carbon 3
Me_3	24.72(24.69) [b]	135.08(135.07)	112.65(112.63)
Me_2(allyl)	22.71(22.67)	134.74(134.81)	113.00(113.04)
Me_2Cl	26.42(26.67)	131.98(132.01)	115.23(115.18)
$MeCl_2$	28.59(28.64)	129.42(129.40)	117.54(117.48)
Cl_3	30.76(30.61	127.24(127.25)	119.54(119.52)
Cl_2(allyl)	26.57(26.52)	129.15(129.14)	117.77(117.89)
Me_2OEt	24.38(24.27)	133.98(133.97)	113.53(113.47)
$Me(OEt)_2$	21.69(22.05)	133.03(133.09)	113.95(114.02)
$(OEt)_3$	18.08(18.01)	132.41(132.42)	114.28(114.29)
$(OEt)_2$(allyl)	20.18(20.02)	132.92(132.83)	114.52(114.43)
Me_2Ph	23.66(23.44)	134.60(134.48)	113.36(113.42)
Ph_2(allyl)	20.01(20.16)	133.59(133.62)	114.68(114.61)
MePhH	21.02(21.02)	134.00(134.00)	114.00(114.00)
MePhOEt	23.11(23.02)	133.32(133.37)	114.17(114.25)
Rms deviation (ppm)	0.16	0.056	0.065

[a] Me = methyl, Et = ethyl, Ph = phenyl. [b] Calculated values in parentheses.

TABLE 3

REGRESSION PARAMETERS FOR VINYLSILANES, $C_2H_3SiX_3$ [a]

	Carbon 1	Carbon 2
k	139.70 ± 0.08	130.55 ± 0.11
δ(Ph)	−1.89 ± 0.05	2.12 ± 0.08
δ(Cl)	−3.66 ± 0.08	3.29 ± 0.12
δ(OR)	−2.31 ± 0.07	2.06 ± 0.06
δ(H)	−3.04 ± 0.12	2.03 ± 0.28
δ(Vi)	−1.86 ± 0.04	1.59 ± 0.06
δ(Cl—Cl)	0.83 ± 0.08	−0.39 ± 0.12
δ(OR—OR)	−1.18 ± 0.08	
Multiple regression coefficient	0.9996	0.998

[a] In ppm. Positive sign indicates downfield from TMS.

TABLE 4

REGRESSION PARAMETERS FOR ALLYLSILANES, $C_3H_5SiX_3$ [a]

	Carbon 1	Carbon 2	Carbon 3
k	24.69 ± 0.14	135.07 ± 0.05	112.63 ± 0.06
δ(Ph)	−1.25 ± 0.12	−0.59 ± 0.04	0.78 ± 0.05
δ(Cl)	1.97 ± 0.08	−3.06 ± 0.06	2.55 ± 0.08
δ(OR)	−0.42 ± 0.15	−1.10 ± 0.06	0.84 ± 0.07
δ(H)	−2.42 ± 0.25	−0.48 ± 0.09	0.58 ± 0.11
δ(allyl)	−2.02 ± 0.14	−0.26 ± 0.05	0.41 ± 0.06
δ(Cl—Cl)		0.46 ± 0.07	−0.25 ± 0.08
δ(OR—OR)	−1.80 ± 0.16	0.22 ± 0.06	−0.28 ± 0.07
Multiple regression analysis	0.999	0.9997	0.999

[a] In ppm. Positive sign indicates downfield from TMS.

pound; n_i the number of substituents of type i from a set of p different substituents; δ_i^a the SCS parameter for a substituent of i-type; n_{ij} the number of pairwise combinations of i and j; δ_{ij}^a the second order SCS parameter; and k^a a constant. In these series of silanes, $RSi(CH_3)_3$ was chosen as the reference compound. Both $\delta^a_{CH_3}$ and $\delta^a_{CH_3,j}$ were defined as zero. The final SCS parameters are given in Tables 3 and 4 and the calculated chemical shifts are listed with the observed shifts in Table 1 and 2.

Discussion

SCS parameters for vinyl- and allyl-silanes. It should be noted at the outset that the regression analyses of the vinyl and allyl carbons are not as extensive as those of the phenyl carbons. The number of compounds is considerably smaller, fourteen allyl- and fifteen vinyl-silanes, compared with fifty-five phenylsilanes

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* SCS = substituent chemical shift.

[1]. Moreover, fewer types of substituents were considered; in fact, the only alkoxy group included was the ethoxy group.

Because of the limited number of compounds studied, the SCS results should be viewed with some caution, particularly the second-order coefficients. Of the 15 possible non-zero second-order terms, examples of 11 different pairs were included in the vinyl compounds and 10 examples in the allyl series. However, two or more compounds containing a given pair of substituents occurred for only 7 pair of substituents in the vinyl case and 6 pair for the allyl compounds. Significant missing pairs of substituents included H—H, H—OEt, and H—Cl *. Care must, therefore, be taken in using the SCS parameters reported here to predict ^{13}C NMR spectra for vinyl- and allyl-silanes containing the above pairs of substituents.

In a ^{13}C NMR study of 17 vinyl compounds, Maciel [2] demonstrated a relationship between the C-1 and C-2 signals in $H_2C{=}CHX$ and the *ipso* and *ortho* signals in the corresponding C_6H_5X compounds. He ascribed the high correlation to a similarity of inductive, resonance, and neighbor effects due to similar electronic structures and molecular geometries in the vinyl—X and phenyl—X compounds. A homologous series of compounds like the vinyl- and phenyl-silanes might be expected to show such a correlation. Chemical shift data for eleven pair of compounds of the type $RSiX_3$ (R = vinyl and phenyl; X = CH_3, C_6H_5. Cl, OC_2H_5 and H) were correlated. Although most of the correlation coefficients were low (Table 5), the correlations between both vinyl carbons and the *ipso* carbon were high. The SCS parameters for carbon-1 showed a remarkable correspondence with those previously determined [1] for the *ipso* carbon of the phenyl compounds (Table 6). The expected [2,9] correlation between the C-2 and *ortho* shifts was not observed.

Allyl and phenyl chemical shifts were also correlated for nine compounds of the type $RSiX_3$ (R = allyl or phenyl; X = CH_3, C_6H_5, Cl, OC_2H_5 and H). Again most of the coefficients were low with the exception of that between carbon-2 and the *para* carbon and those between carbon-3 and both *meta* and *para* carbons. Since carbon-1 is a saturated carbon, its chemical shift was correlated with the corresponding methyl shift for eleven compounds of the type $RSiX_3$ (R = allyl or methyl; X = CH_3, C_6H_5, C_3H_5, Cl, OC_2H_5 and H). The correlation proved to be significant.

The effect of a substituent of the chemical shifts of vinyl and allyl carbons, As concluded in a previous study of the phenylsilanes [1], the trimethylsilyl substituent is a weak electron with drawing group and the trimethylsilylmethyl substituent, $—CH_2Si(CH_3)_3$, is a fairly good electron donor. Comparison of the vinyl and allyl carbon chemical shifts, especially those of the terminal carbons, verify this result. The carbon-2 chemical shift of each vinylsilane is approximately 20 ppm downfield from the carbon-3 shift of the respective allylsilane. Although the terminal carbon of the allylsilane has a greater electron density than that of the analogous vinylsilane, the substituents bonded to the silicon affect these carbons in a similar fashion.

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* Second-order terms for these pairs of substituents were found to be necessary for accurate correlations of phenyl- [1] and methyl-silane [5] data.

TABLE 5

CROSS-CORRELATIONS OF ^{13}C NMR CHEMICAL SHIFTS OF VINYL-, ALLYL-, PHENYL-, AND METHYL-SILANES

	Vinyl C-2	Allyl			Phenyl			
		C-1	C-2	C-3	C_i	C_o	C_m	C_p
Vinyl C-1	−0.900 (15) [a]	0.090	0.671	−0.594 (10)	0.992	−0.102	−0.342	−0.685 (11)
C-2		0.288	−0.880	0.853	−0.940	−0.001	0.640	0.866
Allyl C-1			−0.676	−0.694 (14)	−0.034	−0.846	0.850	0.686 (9)
C-2				0.986	0.753	0.477	−0.862	−0.999
C-3					−0.700	−0.474	0.913	0.994
Methyl CH$_3$		0.988 (11)						

[a] Number of compounds for this set of correlation coefficients given in parentheses.

TABLE 6

COMPARISON OF CARBON-1 AND *ipso* SCS PARAMETERS

	Carbon 1 (Vinyl)	*Ipso* (Phenyl)
k	139.70 ± 0.08	139.86 ± 0.14
δ(Ph)	−1.89 ± 0.05	−1.85 ± 0.07
δ(Cl)	−3.66 ± 0.08	−3.59 ± 0.14
δ(OR)	−2.31 ± 0.07	−2.37 ± 0.15
δ(H)	−3.04 ± 0.12	−2.57 ± 0.10
δ(Vi)	−1.86 ± 0.04	−1.91 ± 0.18
δ(Cl—Cl)	0.83 ± 0.08	0.81 ± 0.17
δ(OR—OR)	−1.18 ± 0.08	−1.27 ± 0.13
δ(H—H) [a]		−1.40 ± 0.13
δ(allyl)		−1.62 ± 0.14
δ(Bu) [a]		−0.55 ± 0.09
δ(β) [b]		0.51 ± 0.11
δ(β-β) [b]		0.40 ± 0.11

[a] Substituent pairs not included in vinyl series. [b] Vinyl series included only ethoxy groups.

Indeed the correlation coefficients among the unsaturated carbons of the vinyl- and allyl-silanes are much greater than those between both of the vinyl carbons and the saturated allyl carbon. Considering the series of silanes, $RSi(CH_3)_{3-n}X_n$ (where R = vinyl or allyl and X = Cl or OC_2H_5) in which substituents of type X successively replace methyl groups, the chemical shift of carbon-1 in the vinylsilane series always moves upfield, irrespective of the substituent replacing the methyl group *. However, the shift of carbon-1 in the allylsilane series moves upfield only if ethoxy substituents replace methyl groups and moves downfield if chlorine substituents replace them. Corresponding differences in substituents effects also occur for the chemical shift of the *ispo* carbon in a series of phenylsilanes and that of the methylene carbon of the analogous benzylsilanes [6].

Since the C-1 carbon of an allylsilane is saturated, it would be expected to behave (with respect to substitution on the silicon) like the methyl group of a methylsilane. The effect of the substitution of chlorine atoms for methyl groups in trimethylallylsilane should reduce the electron density of this carbon, and result in a downfield shift. For a similar reason, it might be expected that the substitution of polar ethoxy groups should also shift the carbon-1 resonance downfield. It must be remembered, however, that carbon-1 is three bonds removed from the alkoxy carbon directly to the oxygen and, therefore, subject to the upfield shift commonly termed a γ-effect [7,8]. Since the chemical shift of allyl carbon-1, like that of vinyl carbon-1, moves upfield with the substitution of ethoxy for methyl groups in the parent silane, it can be concluded that the γ-effect outweighs the inductive electron-withdrawing influence of the alkoxy substituents.

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* The downfield shifts for C-1 reported by Schraml [9] occur for bulky substituents and are likely due to steric effects.

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