

$^1\text{H-NMR}$ SPECTRA OF SOME CHLORO-ALKENES

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$^1\text{H-NMR}$ spectra and electric dipole moments of a series of propene derivatives, $(\text{CH}_3)_{3-n}\text{Cl}_n\text{CCH}=\text{CH}_2$ ($n = 0-3$), were measured and the spectra analysed. Discrepancies in literature data on compounds with $n = 0$ and 3 are probably due to systematic spectrometer errors. Vinylic proton chemical shifts are found to vary linearly with n in the direction expected on the electronegativity ground (the variations with n occurs in the order $H_A > H_B \geq H_C$). Calculations show that even with the extreme reported values of C—C and C—Cl bond magnetic anisotropies, the shift variations with n cannot be accounted for by magnetic anisotropy effects of a freely rotating $(\text{CH}_3)_{3-n}\text{Cl}_n\text{C}$ group. Similar calculations rule out electric field effects as the dominant factor. On the other hand, the electron charge distribution, as obtained from CNDO/2 calculations, including d -orbitals and employing Del Bene-Jaffé parametrization, is linearly related to the vinylic proton shifts. This finding supports the earlier interpretation of NMR spectra of vinylsilanes in terms of back-bonding. The vinyl proton-proton coupling constants decrease with increasing n , the changes being larger in the constants which couple proton A (*cis*) to the other two.

Despite numerous studies, the interpretation of $^1\text{H-NMR}$ spectra of substituted alkenes is not yet generally agreed upon and, hence, the interpretation of the spectra of vinylsilanes¹⁻¹⁰ and vinyl derivatives of other elements¹¹⁻¹⁷, is still viewed as more or less speculative. Recently, interpretations in the terms of back bonding received additional support from measurements of the NMR spectra of other nuclei, *e.g.* ^{13}C (refs¹⁶⁻²⁰), ^{29}Si (ref.¹⁸) and others (refs^{16,17}). To date, however, data on a full series of corresponding carbon analogues of the above organometallic compounds which would make direct comparisons possible, has not been available. The present work attempts to bridge the gap with data on $^1\text{H-NMR}$ spectra of a series of compounds of the type $(\text{CH}_3)_{3-n}\text{Cl}_n\text{CCH}=\text{CH}_2$ (where $n = 0, 1, 2$, and 3), analogous to vinylsilanes studied under the same conditions earlier^{7,21}. We are concerned mainly in these studies with chemical shifts of the vinyl group protons because the (assumed) planarity of the vinyl group in all these compounds permits us to simultaneously probe the environment of the central atom at three different sites fixed with respect to each other and thus elucidate nature of the joint and

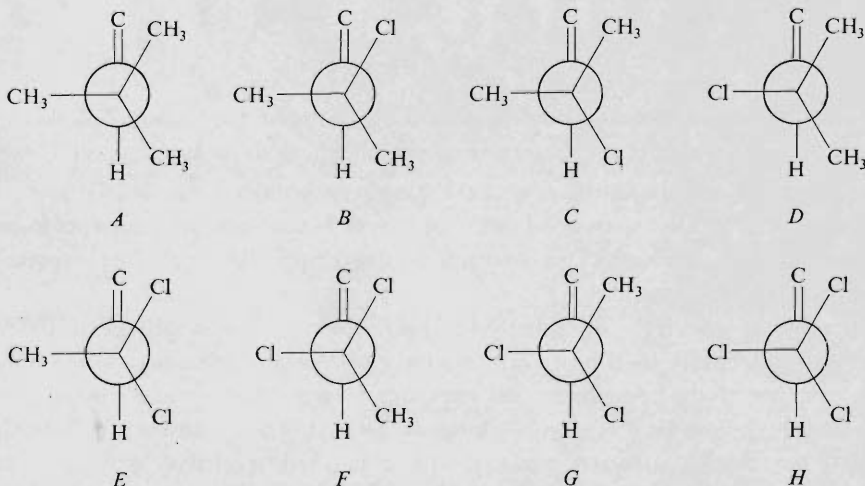
separate effects of the central atom and ligands on the proton-NMR parameters of the vinyl group.

EXPERIMENTAL

Materials: The preparations and properties of the compounds studied were reported elsewhere²². Redistilled carbon tetrachloride, benzene and hexamethyldisiloxane (HMDSO) were used.

Dipole moments: Dipole moments were calculated according to Halverstadt and Kumler²³ from the concentration dependences of dielectric constant and density of benzene solutions. Dielectric constants were measured by a resonance method at 0.545 MHz using an apparatus similar to that described by Le Fèvre and Russell²⁴. Measurements were carried out at temperature of $25.0 \pm 0.1^\circ\text{C}$ with the relative accuracy $\Delta\epsilon/\epsilon = \pm 3.4 \cdot 10^{-4}$. Density of the solutions was determined by pycnometry at the same temperature with the accuracy of $\pm 2 \cdot 10^{-5}$.

Quantum chemistry: Quantum chemical calculations for each of the vinyl compounds were carried out by the standard CNDO/2 method^{25,26} using idealized geometry with standard²⁵ and experimental bond lengths ($r_{\text{Si-C}} = 1.87 \text{ \AA}$ and $r_{\text{C-Cl}} = 1.78 \text{ \AA}$) (ref.²⁷). Only those conformations around the $\text{C}(sp^3)\text{-C}(sp^2)$ bond the Newmann projections of which are shown below were considered. To estimate the possible role of d orbitals, the calculations were carried out both with their neglect and with their inclusion. Modified calculations employing reduced integrals of π type in the sense of parametrization of Del Bene and Jaffé²⁷ were also performed with the factor $\kappa = 0.58$ (again both with and without d orbital inclusion) in order to get more adequate description of π interactions.



Spectroscopy: The spectra were recorded on a modified Tesla BS 477 spectrometer operating at 60 MHz with internal frequency lock stabilisation. The probe temperature was 32°C . Resonance frequencies were obtained with respect to the signal of HMDSO, 2–3 drops of which were added to the compounds contained 5 mm o.d. NMR tubes. Line positions were monitored by a Tesla BM 445E counter and were accurate to within about 0.05 Hz. The line width varied from less than 0.2 to 0.5 Hz. The spectra of 3,3-dimethylbutene-1 and 3-chloro-3-methylbutene-1 were measured also at 100 MHz on a Varian HA spectrometer.

0.2 Hz while the 40 MHz spectrum³⁵ showed an observable geminal splitting. The results of our analysis agree substantially with previous work³².

Solvent effects: All of the spectra reported here at 60 MHz were studied as a function of concentration in carbon tetrachloride. The effects were so small as to be of little chemical significance. However, a representative line of each quartet was measured at concentration intervals down to 3% by volume. Extrapolation to infinite dilution yielded the dilution shifts of these lines. To a first approximation these are the concentration shifts of the corresponding proton shifts (Table II).

TABLE I
¹H-NMR parameters in Hz

Compound ^a	Freq. ^b	ν_{Me}^c	ν_A^c	ν_B^c	ν_C^c	J_{AB}^d	J_{AC}^d	J_{BC}^d	$\sum J^e$
Me ₃ CVi	60	60.5	293.41	287.48	347.57	1.37	17.33	10.68	29.39
Me ₂ ClCVi	60	98.2	310.74	297.73	361.83	0.69	17.08	10.57	28.34
MeCl ₂ CVi	60	132.7	328.15	307.73	371.83	0.03	16.72	10.42	27.17
Cl ₃ CVi	60	—	345.22	316.08	383.11	-0.49	16.06	10.07	25.65
Me ₃ CVi	100	100.3	486.53	477.34	577.43	1.36	17.50	10.69	29.55
Me ₂ ClCVi	100	164.6	518.08	497.57	602.63	0.79	17.20	10.62	28.61

^a Me means CH₃, Vi means CH=CH₂; ^b spectrometer frequency in megahertz; ^c chemical shifts to lower field are given relative to tetramethylsilane for neat samples, using $\nu(\text{HMDSO}) = 3.2$ Hz for conversion at 60 MHz. The shifts are accurate to ± 0.5 Hz; ^d coupling constants are accurate to $\pm 1\%$; ^e the sum of coupling constants is accurate to ± 0.1 Hz.

TABLE II
Vinyl proton infinite dilution shift corrections in CCl₄ at 60 MHz

Compound ^a	$\Delta\nu_A^b$	$\Delta\nu_B^b$	$\Delta\nu_C^b$
Me ₃ CVi	-1.9	-1.4	-1.8
Me ₂ ClCVi	+0.2	+1.0	-0.6
MeCl ₂ CVi	+0.3	+0.1	+0.3
Cl ₃ CVi	+1.1	+1.2	+0.4

^a See footnote ^a in Table I; ^b units of Hz. The sense of these corrections is as follows; a neat solution having a chemical shift of 300.0 and a correction of ± 1.0 would have an infinite dilution shift of 301, *i.e.* a lower resonance field.

Accuracy. Two useful criteria of the reliability of the calculated parameters for ABC-spin systems are 1) the sum of the squares of the errors in the eigenvalues (obtained from a least squares fit of the frequencies to an eigenvalue spectrum) and 2) the difference between the sum of the observed spacings and the sum of the coupling constants. The first is a measure of random errors and the second depends very much on some types of systematic errors *e.g.* a scale factor introduced in recording the spectrum. When the first criterion is poorly met, unpredictable errors arise in the ratios of the parameters, in particular, in the ratios of the calculated coupling constants. Introduction of a scale factor leads to a consonant scaling of all the parameters and to incorrect spacings in the spectrum but does not alter the ratios of the calculated parameters.

To illustrate the point, at least seven analyses of the spectrum of 3,3-dimethylbutene-1, at spectrometer frequencies from 31.6 to 100 MHz are reported in the literature²⁹⁻³⁴ in which the sum of the calculated J 's and therefore the spacings vary between 28.7 and 29.7 Hz while this quantity can be determined with an accuracy better than 0.2 Hz. The variation arises mostly from linear scale factor errors.

It follows that reported errors in published parameters, based on the agreement between calculated and observed frequencies or energy levels alone may be inadvertently low.

Dipole moments and CNDO/2 calculations. Experimental dipole moments are summarized in Table III. For the purpose of comparison, dipole moments calculated

TABLE III
Dipole moments^a

Compound ^b	Experimental ^c	CNDO/2 calculated ^d			
		no parametrization		parametrized	
		without d	with d	without d	with d
Me ₃ CVi	0.0 ^e	0.42	0.42	0.48	0.48
Me ₂ CiCVi ^f	2.04	2.91	2.33	2.81	1.86
MeCl ₂ CVi ^g	2.05	3.13	2.47	2.97	1.92
Cl ₃ CVi	1.66	2.57	2.01	2.38	1.57

^a In Debye units; ^b see footnote^a in Table I; ^c accurate within ± 0.05 D; ^d for the explanation see Experimental. ^e Possible error ± 0.2 D; ^f calculated data for conformation B; ^g calculated data for conformation E.

by different modifications of the CNDO/2 method are also given. It is obvious that both inclusion of d orbitals and parametrization according Del Bene-Jaffé improves the agreement between experimental and theoretical dipole moments. Therefore, we shall only consider results obtained with parametrized CNDO/2 calculations including d orbitals. The calculated valence electron densities on vinylic hydrogen atoms are collected in Table IV, including data for trimethylvinylsilane.

DISCUSSION

Chemical shifts. The chemical shifts of vinylic protons vary linearly with n (the number of chlorine atoms in the molecule), with infinite dilution corrections made,

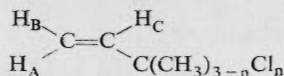
TABLE IV
Valence electron densities^a

Compound ^b	H _A ^c	H _B ^c	H _C ^c
Me ₃ CVi	0.0198	0.0115	0.0108
Me ₂ ClCVi ^d	0.0289	0.0151	0.0441
MeCl ₂ CVi ^e	0.0318	0.0222	0.0299
Cl ₃ CVi	0.0352	0.0267	0.0346
Me ₃ SiVi	0.0165	0.0160	0.0212

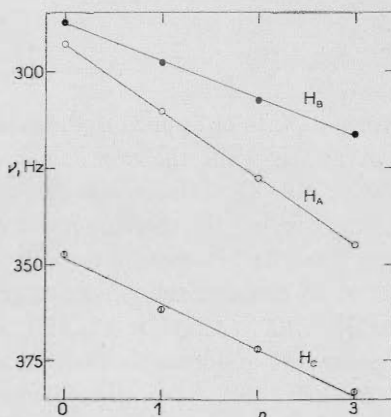
^a Calculated by the CNDO/2 method including d orbitals and employing Del Bene-Jaffé parametrization; ^b see footnote^a in Table I; ^c vinylic hydrogen atoms labelled as in the text (Results); ^d conformation B; ^e conformation E.

FIG. 1

The dependence of vinylic proton chemical shifts on the number n of chlorine atoms in compounds of the type



(The chemical shifts are in Hz units at 60 MHz down-field from TMS)



the linearity is very good (Fig. 1). The slopes for protons H_A , H_B and H_C are -0.30 , -0.17 , and -0.17 ppm per substitution of CH_3 group by Cl atom, resp. The low-field shift with increasing n is consistent with predictions based on inductive effects of electronegative substituents. It can be conceived that also magnetic anisotropy effects, electric field effects or any other related property of the substituents which is additive, could account for the observed trend.

Magnetic anisotropy effects. Assuming free rotation of the whole $(CH_3)_{3-n}Cl_nC$ group around the $C(sp^3)-C(sp^2)$ bond and geometry of propene³⁷ the contributions of the magnetic anisotropy of the rotating $(CH_3)_{3-n}Cl_nC$ group to the shielding of vinylic protons were calculated according to the formula derived earlier³⁸, using bond anisotropies compiled by Bothner-By and Pople³⁹. Calculations have shown that substitution of one CH_3 group by one Cl atom brings, at maximum, the following shifts for protons H_A , H_B , and H_C -0.008 , -0.014 , and -0.004 ppm, respectively.

Not only are such values by an order of magnitude smaller but also their ratios are in disagreement with the experimentally observed slopes. Hence the difference in magnetic anisotropy between $C-Cl$ and $C-CH_3$ bonds must be discharged as the possible cause of the observed trend.

Electric field effects. According to Buckingham⁴⁰ the effect of electric field E on the proton screening constant is approximately given by

$$\sigma_{elec} = -2 \cdot 10^{-12} E_z - 10^{-18} E^2,$$

where E_z is the electric field component in the direction of the $C-H$ bond. The electric field due to a distant dipole μ (for the dipole vector oriented from negative to positive charge) is⁴¹

$$E = -\frac{\mu}{r^3} + \frac{3(\mu \cdot r)r}{r^5}.$$

The formulas can be applied to the evaluation of the effects of the substituents on protons A and B while the approximations involved do not justify their application to the proton C. Calculations for compounds with $n = 1$ and 2 would require averaging over all the conformations of $C(CH_3)_{3-n}Cl_n$ groups around the $C(sp^3) - C(sp^2)$ bond; in compounds with $n = 0$ and 3 averaging is not necessary, it is sufficient to consider the effects of group moments which are 0 and 1.6 D (1 D = $0.33356 \cdot 10^{-29}$ Cm) for $C(CH_3)_3$ and CCl_3 groups⁴², respectively. For the idealized geometry we obtain the electric field contributions to the shielding of protons A and B:

$$\sigma_{elec,A} = -9.8 \cdot 10^{-8} \mu - 0.06 \cdot 10^{-8} \mu^2$$

$$\sigma_{\text{elec,B}} = -8.06 \cdot 10^{-8} \mu - 0.16 \cdot 10^{-8} \mu^2$$

(for dipole moments in Debye units defined as mentioned above). These expressions predict correctly the direction of substituent effects (increased deshielding in the compound with $n = 3$), but the calculated shifts are at least one order of magnitude smaller than observed.

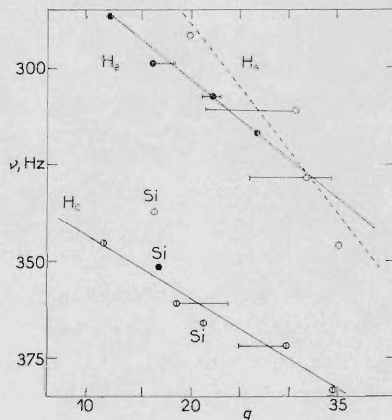
Chemical shifts of protons A and B in vinyl derivatives were correlated with the group dipole moments of the substituents⁴³. The present results for 3,3-dimethylbutene-1 fit the correlations quite well. The chemical shifts in 3,3-trichloropropene-1 deviate considerably, resembling the observations for acrylonitrile and styrene before they were corrected for magnetic anisotropy⁴³.

Q-Factor. ^1H chemical shifts in some substituted ethenes were shown to correlate with the so-called Q -factor⁴⁴ ($Q = P/Ir^3$, where P is the polarizability of the C—X bond, r is the C—X bond length and I is the first ionization potential of X). If the present results are combined with the Q values for $\text{C}(\text{CH}_3)_3$ and CCl_3 groups as determined by Smith and coworkers⁴⁵, the corresponding points fall off from the correlations, though the correlations again predict correctly the direction of the trend.

Correlation with electron densities. As it is apparent from Fig. 2 the chemical shifts of the proton B and C protons correlate well with the valence electron densities ($r = 0.991$ and 0.983 , respectively, the correlations are significant at 5% significance level), the slopes in the two correlations being not significantly different ($170 \pm \pm 55 \text{ Hz/e}$ or 3 ppm per electron). Analogous correlation for the proton A is not significant (at 5% significance level), but it is clear from Fig. 2 that the electron densi-

FIG. 2

The dependence of vinylic proton chemical shifts on the valence electron densities q calculated with the inclusion of d orbitals and parametrization. (The points correspond to the values given in Table IV for the most stable conformation, the intervals cover the conformational dependence of the densities. The solid lines are the least-squares fits). The points corresponding to trimethylvinylsilane are also included (Si). Values of q are $q \cdot 10^3$



ties on this proton are most sensitive to conformational changes around the $C(sp^3) - C(sp^2)$ bond. It appears that the correlation could be improved by some averaging of the valence electron density. All the correlations noted would improve if the electron densities on hydrogen atoms were properly combined with the density on the adjacent carbon atom. Such improvements were described for other systems⁴⁶⁻⁴⁸ but our limited set of data could not justify such an approach.

In view of the failure of other interpretations to account sufficiently for the observed trend and the fact that the slope found in the correlations is about one third of that found in aromatic systems⁴² the described correlations described above justify discussion of the B and C proton chemical shifts in the terms of the effects of substituents on electron distribution in vinyl derivatives.

Comparison with vinyl derivatives of other group IV elements. The differences between the corresponding chemical shifts in various substituted vinylsilanes and in their Ge, Sn or Pb analogues are relatively small and have been shown to depend largely on the metal-vinyl bond magnetic anisotropy¹³. At the same time there is a large difference between the vinyl proton shifts of the present carbon derivatives and their silicon analogues^{7,21}. The difference involves three distinct features: (i) overall lower shielding in vinylsilanes, (ii) inverted order of shielding of β vinylic protons, and (iii) a lower sensitivity to substitution of methyl group by chlorine atoms in vinylsilanes compared with their carbon analogues. The features (i) and (ii) have already been noted^{1,3,7,21} though not for the full series of exact analogues. Lower shielding in vinylsilanes has been attributed to back bonding^{1,3,7,21}, inverted order ("ABC" spectra of vinylsilanes as compared to "BAC" spectra of their carbon analogues) has been assigned to be due to the magnetic anisotropy of $M - C(\text{vinyl})$ bond and/or to preferential *trans* delocalization³. The CNDO/2 result of our study do not support such assertions, but it is possible that they do not treat adequately interactions between silicon and ethene. The lower sensitivity to substitution in vinylsilanes reflects the attenuation of inductive effects by silicon and it may be also affected by back bonding between chlorine and silicon. The correlations between chemical shifts and electron densities of vinylic protons B and C supports the earlier interpretations of these shifts in vinylsilanes in terms of substituent interactions.

Coupling constants. All the coupling constants in the present series of compounds decrease approximately linearly with increasing n number of chlorine atoms. The sum, $\sum J$, is reduced from 29.39 to 25.65 Hz, *i.e.* about 1.2 Hz per substitution. The direction of the changes and their magnitude are in perfect agreement with the dependence of proton couplings in monosubstituted ethenes, on the inverse of substituent electronegativity as described by Schaefer and Hutton⁵⁰. Using Müller, Pritchard⁵¹ electronegativities of $C(\text{CH}_3)_3$ and CCl_3 groups the dependences⁵⁰ give the following predictions for the changes in the coupling constant when n is changed from 0 to 3:

$\Delta J_{AB} = -1.05$ Hz, $\Delta J_{AC} = -1.27$ Hz, and $\Delta J_{BC} = -1.55$ Hz and the sum $\Delta\Sigma = 3.875$ Hz *i.e.* 1.29 Hz per substitution. The smaller variation in silicon analogues is in agreement with the aforementioned attenuation of substituent effects by silicon.

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