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# INFRARED, RAMAN AND NMR STUDY OF $(CH_2{=}CH)_3SnX$ COMPOUNDS ($X = Cl, Br, I$)

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## Summary

The infrared, Raman and ($^1H$, $^{13}C$) NMR spectra of trivinyltin chloride, bromide and iodide have been analyzed and discussed. The vibrational assignment has been confirmed by an approximate normal coordinate analysis. Evidence has been found for a marked influence of the X substituent on the tin–carbon bond due to isovalent rehybridization. Variations in the $\pi$ electron system of the vinyl group are hardly significant.

## Introduction

This account deals with the compounds $(CH_2{=}CH)_3SnX$ ($X = Cl, Br, I$). The chloride, $(CH_2{=}CH)_3SnCl$, is frequently used as a catalyst for olefin polymerization, as stabilizer for PVC or as bactericide [1] while $(CH_2{=}CH)_3SnI$ shows insecticidal action [2]. However, spectroscopic data for these compounds are scarce and so we now present the results of a complete infrared, Raman and ($^1H$, $^{13}C$) NMR spectroscopic investigation and discuss them in terms of the molecular structure and chemical bonding.

## Experimental

### *Synthesis*

Seyferth and Stone reported the synthesis of $(CH_2{=}CH)_3SnCl$ by a dismutation reaction between $(CH_2{=}CH)_4Sn$ and $SnCl_4$ at ca. 100°C [3] 43.6% yield, $(CH_2{=}CH)_2SnCl_2$ was a by-product. However, Rosenberg and Gibbons later showed that $(CH_2{=}CH)_3SnCl$ can be prepared in virtually quantitative yields by the same reaction at low temperatures [4]:

$$3(CH_2{=}CH)_4Sn + SnCl_4 \xrightarrow{35-40°C} 4(CH_2{=}CH)_3SnCl \qquad (1)$$

Fractionation of the crude product under reduced pressure yields a colourless liquid with strong lachrymatory properties and a very irritating smell. As noted by Rosenberg and Gibbons [4], $(CH_2{=}CH)_3SnCl$ tends to rearrange rapidly to form $(CH_2{=}CH)_2SnCl_2$ and $(CH_2{=}CH)_4Sn$, according to eq. 2.

$$2(CH_2{=}CH)_3SnCl \rightarrow (CH_2{=}CH)_2SnCl_2 + (CH_2{=}CH)_4Sn \qquad (2)$$

As for the synthesis of $(n\text{-}Bu)_3SnBr$ [5], $(CH_2{=}CH)_3SnBr$ was prepared by the direct bromination of $(CH_2{=}CH)_4Sn$ with $Br_2$ at −78°C, and obtained as a colourless liquid. Similarly [5] the reaction of equimolecular amounts of $(CH_2{=}CH)_4Sn$ and $I_2$ under reflux (20 h) in dry ether, gave $(CH_2{=}CH)_3SnI$ as a colourless liquid.

The purity of each compound was checked by a GC analysis using helium as carrier gas. For $(CH_2{=}CH)_3SnBr$ and $(CH_2{=}CH)_3SnI$ the intensity of peaks originating from other products were negligible. For $(CH_2{=}CH)_3SnCl$ additional peaks originating from $(CH_2{=}CH)_4Sn$ and $(CH_2{=}CH)_2SnCl_2$ arising from the rearrangement reaction (eq. 2), are observed, in accordance with observations in ref. 4.

### *Spectra*

The IR spectra were recorded with pure liquid samples between CsI windows on a Perkin–Elmer Model 580 double-beam spectrometer. The Raman spectra of the pure liquids were recorded on a Coderg PH1 spectrometer, with He/Ne gas laser.

All the NMR spectra were obtained from nearly saturated solutions in $CDCl_3$. The $^1H$ NMR spectra were recorded at 360 MHz on a Bruker WH-360 FT NMR spectrometer. The proton-decoupled $^{13}C$ NMR spectra were recorded at 50.29 MHz on a Bruker WP-200 FT NMR spectrometer: the chemical shifts are relative to TMS.

## Results and discussion

### *Infrared and Raman spectra*

The vibrational irreducible representation of the $(CC)_3SnX$ skeleton is $\Gamma_{vib}^{C_{3v}} = 5A_1 + A_2 + 6E$. With regard to the IR and Raman activity selection rules, the latter

TABLE 1

OBSERVED SKELETAL FREQUENCIES OF $Vi_3SnX$ IN $cm^{-1}$

| Mode description | X = Cl [30] | | X = Br | | X = I | |
|---|---|---|---|---|---|---|
| | IR | R | IR | R | IR | R |
| $\nu_s(CC)$ ($A_1$) | 1584w | 1585p | 1584w | 1586p | 1582w | 1584p |
| $\nu_{as}(CC)$ ($E$) | | | | | | |
| $\nu_s(SnC_3)$ ($A_1$) | 514sh | 521p | 513s | 520p | 512s | 518p |
| $\nu_{as}(SnC_3)$ ($E$) | 543s | 548 | 541s | 547 | 538 | 542 |
| $\nu(SnX)$ ($A_1$) | 333m | 333p | 231w | 232p | | 188p |
| $\delta_s(C_3SnX)$ ($A_1$) | | | | | | |
| $\delta_{as}(C_3SnX)$ ($E$) | | | | | | |
| $\delta_{as}(CSnC)$ ($E$) | | | | | | |
| $\delta_s(ip)(SnCC)$ ($A_1$) | | 292p | | 292p | | 292p |
| $\delta_{as}(ip)(SnCC)$ ($E$) | 300w,sh | ~ 300sh | 300w | ~ 300sh | 300w | ~ 300sh |
| $\delta(op)(SnCC)$ ($E$) | | | | | | |

transforms into $\Gamma^{C_{3v}}_{IR,R} = 5A_1 + 6E$. A tentative description and assignment of the 11 active normal modes is summarized in Table 1.

The assignment of the $\nu_s$ and $\nu_{as}(SnC_3)$ is straightforward. In the IR spectra the $\nu_s(SnC_3)$ is partly obscured by the strong and broad CH wag vibrational band (±380 cm$^{-1}$) and is only observed as a shoulder band. The strong polarized and mass-dependent Raman band (medium IR band) in the low frequency region can be safely ascribed to the $\nu$(Sn–X).

The strong, polarized Raman band at invariably 292 cm$^{-1}$ and the weak shoulder band at ~ 300 cm$^{-1}$, corresponding to a medium to weak IR band at 300 cm$^{-1}$, are respectively assigned to the $\delta_s$(SnCC) and $\delta_{as}$(SnCC). Only one band is observed for the $\nu$(C=C) in the range 1580–1590 cm$^{-1}$. The fact that an unique C=C stretching band and almost coinciding $\delta$(SnCC) vibrational bands are observed, is strong evidence that, due to the heavy tin atom, dynamic interaction among the various vinyl groups is weak. This results in an accidental degeneracy of the inner vibrations of the vinyl groups attached to tin, leading to the coincidence of $\nu_s$ and $\nu_{as}$(CC) on the one hand and of $\delta_{as}$(ip) and $\delta$(op) SnCC on the other hand. Thus, for simplicity, the interpretation of the vibrational frequencies arising from the vinyl group are based on a model of an individual vinyl group attached to a heavy mass. The other vibrations are treated in the $XSnC_3$ skeleton.

In order to confirm the band assignments an approximate normal coordinate analysis is carried out separately for the Sn–C=C and $C_3SnX$ skeletons. A rigorous treatment is impossible since the structural data are lacking. Good estimates for bond distances and angles are used in the calculations: $d$(Sn–C) 2.16 Å, $d$(C=C) 1.34 Å, $d$(Sn–Cl) 2.19 Å, $d$(Sn–Br) 2.49 Å, $d$(Sn–I) 2.72 Å, $\alpha$(Sn-C=C) 120°, $\alpha$(CSnX) 109.5°.

The calculation is based on general vibrational analysis programs [6] utilizing the Wilson GF matrix method for a "general unsymmetrized molecule". The relevant internal coordinates and the optimized set of force constants are summarized in Table 2. Observed and calculated frequencies and the potential energy distribution, PED, are listed in Table 3.

The fact that the force constant for the C=C bond does not vary with the halogen on tin indicates that there is no marked interaction between the vinyl $\pi$ system and the tin $d$-orbitals. Furthermore, the increase of the Sn–C force constant on X substitution, in the sequence I < Br < Cl, is in accord with the increasing $s$-content of the Sn hybrid orbital directed towards carbon. Thus the more effective overlap with the carbon $sp^2$ orbital results in a strengthening of the Sn–C bond.

TABLE 2

RELEVANT INTERNAL COORDINATES AND VALENCY FORCE CONSTANTS (mdyn/Å)

| Designation | Description | | X = Cl | X = Br | X = I |
|---|---|---|---|---|---|
| $r_1$ | Sn–X stretch | $fr_1$ | 1.78 | 1.38 | 1.031 |
| $r_2 = r_3 = r_4$ | Sn–C stretch | $fr_2$ | 1.96 | 1.95 | 1.93 |
| $r_5$ | C=C stretch | $fr_5$ | 9.96 | 9.96 | 9.96 |
| $\alpha_{12} = \alpha_{13} = \alpha_{14}$ | C–Sn–X bend | $f\alpha_{22}$ | 0.08 | 0.08 | 0.05 |
| $\alpha_{23} = \alpha_{24} = \alpha_{34}$ | C–Sn–C bend | $f\alpha_{23}$ | 0.07 | 0.07 | 0.07 |
| $\beta_{25} = \beta_{35} = \beta_{45}$ | Sn–C=C bend | $f\beta_{25}$ | 0.24 | 0.24 | 0.24 |

### *NMR spectra*

In older literature considerable difficulties were encountered in the analysis of the $^{1}$H NMR spectra of $SnVi_4$, due to their second order degeneracy [7–10]. This was

TABLE 3

OBSERVED AND CALCULATED FREQUENCIES AND POTENTIAL ENERGY DISTRIBUTION (PED)

| Description | Observed | | | Calculated | | | PED ( > 5%) |
|---|---|---|---|---|---|---|---|
| | X = Cl | X = Br | X = I | X = Cl | X = Br | X = I | |
| $\nu$(C–C) | | 1584 | | | 1584 | | $\Delta r_5$ (100) |
| $\nu_{as}$(Sn–C) | 543 | 541 | 538 | 541.8 | 540.4 | 538 | $\Delta r_2$ (100) |
| $\nu_s$(Sn–C) | 514 | 513 | 512 | 516.3 | 514.4 | 511 9 | $\Delta r_2$ (100) |
| $\delta$(Sn–C–C) | | 300 | | | 300 | | $\Delta \beta_{25}$ (100) |
| $\nu$(Sn–X) | 333 | | | 333 | | | $\Delta r_1$ (97) |
| | | 231 | | | 231 | | $\Delta r_1$ (82) |
| | | | 188 | | | 188 | $\Delta r_1$ (58) $\Delta \alpha_{12}$ (22) $\Delta \alpha_{23}$ (20) |
| $\delta_{as}$(C-Sn-C) | | | | 163 | | | |
| | | | | | 162 | | |
| | | | | | | 160 | |
| $\delta_s$($C_3$SnX) | | | | 161 | | | |
| | | | | | 156 | | |
| | | | | | | 132 | |
| $\delta_{as}$($C_3$SnX) | | | | 140 | | | |
| | | | | | 134 | | |
| | | | | | | 112 | |

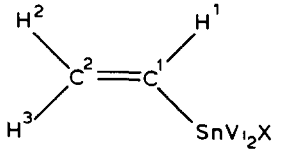
TABLE 4

EXPERIMENTAL NMR CHEMICAL SHIFTS $\delta$ (ppm) AND COUPLING CONSTANTS $J$ (Hz) FOR $(CH_2{=}CH)_3SnX$ COMPOUNDS

| Method | Parameter | $(CH_2{=}CH)_3SnCl$ | $(CH_2{=}CH)_3SnBr$ | $(CH_2{=}CH)_3SnI$ |
|---|---|---|---|---|
| $^{1}$H NMR | $\delta(^{1}H(1))$ | 6.50 | 6.51 | 6.49 |
| | $\delta(^{1}H(2))$ | 6.33 | 6.30 | 6 24 |
| | $\delta(^{1}H(3))$ | 5.96 | 5.93 | 5 88 |
| | $2J(^{1}H(2)–^{1}H(3)) = J_{gem}$ | 2.4 | 2.4 | 2.3 |
| | $3J(^{1}H(1)–^{1}H(2)) = J_{cis}$ | 13.3 | 13.3 | 13.1 |
| | $3J(^{1}H(1)–^{1}H(3)) = J_{trans}$ | 20.1 | 20.1 | 20.1 |
| | $^{2}J(^{119}Sn–^{1}H(1))$ | 143.8 | 146.7 | 145.7 |
| | $^{2}J(^{117}Sn–^{1}H(1))$ | 136.7 | 140.3 | 139.1 |
| | $^{3}J(^{119}Sn–^{1}H(2))$ | 235.4 | 237.8 | 237.0 |
| | $^{3}J(^{117}Sn–^{1}H(2))$ | 224.4 | 227.2 | 226.4 |
| | $^{3}J(^{119}Sn–^{1}H(3))$ | 116.1 | 117.6 | 118.0 |
| | $^{3}J(^{117}Sn–^{1}H(3))$ | 110.8 | 112.4 | 113.1 |
| $^{13}$C NMR | $\delta(^{13}C(1))$ | 134.9 | 134.5 | 133.8 |
| | $\delta(^{13}C(2))$ | 137.8 | 138.0 | 138.0 |
| | $^{1}J(^{119}Sn–^{13}C(1))$ | 594.7 | 575.2 | 546.6 |
| | $^{1}J(^{117}Sn–^{13}C(1))$ | 568.2 | 549.3 | 522.3 |

almost completely overcome in this study because $^{1}H$ and $^{13}C$ spectra were recorded at 360 MHz and 200 MHz, respectively.

The experimental NMR chemical shifts and coupling constants for the $(CH_2{=}CH)_3SnX$ compounds are listed in Table 4. The labeling of the nuclei in Table 4 is as follows:



*$^{1}$H NMR spectra.* The first order $^{1}H$ NMR spectra of the $(CH_2{=}CH)_3SnX$ compounds consist of three quadruplets with $^{117,119}Sn$ satellite spectra (Fig. 1). The assignment of each of these quadruplets to the H(1), H(2) or H(3) proton is based on the rule of the repeated spacings between the lines within each quadruplet and on the well-known [10] classification of the proton–proton coupling constants in vinylic derivatives: $J_{trans} > J_{cis} > J_{gem}$.

*$^{1}$H chemical shifts.* The vinyl $^{1}H$ chemical shifts may be influenced by inductive effects, anisotropy effects, Van der Waals forces, and electric field effects [11]. For

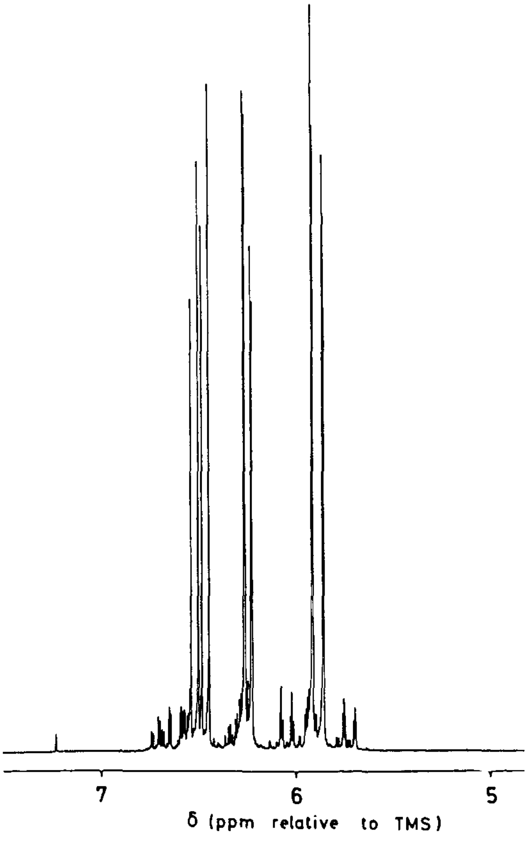
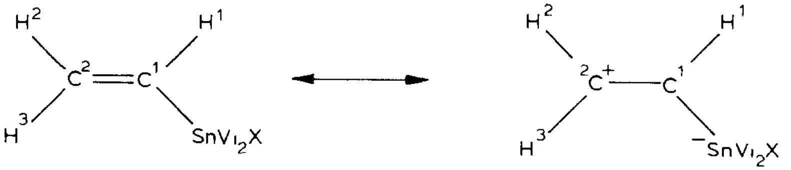


Fig. 1. 360 MHz $^{1}H$ NMR spectrum of $(CH_2{=}CH)_3SnI$.

the present series of compounds the discussion can be restricted to the dominant effects.

(i) The inductive effect of the halogen atom, operating through the $\sigma$ bonds and falling off very rapidly with an increasing number of intervening bonds. Therefore, with increasing electronegativity of the halogen atom, the H(1) proton will be slightly deshielded, and the deshielding for the H(2) and H(3) proton will be even lower.

(ii) Resonance interactions between the $\pi$ electron system of the vinyl group and the Sn(5*d*) orbitals, operating through the $\pi$ bonds (eq. 3). Such $\pi$ interactions are favoured when the quite diffuse Sn(5*d*) orbitals contract sufficiently to make an overlap with the vinylic $\pi$ electron system suitable. Consequently the more electronegative halogens favour this $\pi$ interaction, causing a deshielding of the H(2) and H(3) protons, leaving the H(1) proton almost unaltered.



(3)

(iii) Anisotropy effects of the Sn–X bond, operating through space, causing a deshielding of the H(1), H(2) and H(3) protons and decreasing in the order I > Br > Cl [12].

Accordingly the H(1) proton chemical shift remains practically constant on increasing electronegativity of the halogen substituent, while the H(2) and H(3) protons undergo nearly equal deshieldings (Table 4). In view of the theory outlined above, this proves that the $^{1}$H chemical shifts are dominated by the $(\pi(\mathrm{Vi}) \rightarrow d(\mathrm{Sn}))\pi$ contribution. This statement is further evidenced by the non-additivity of the deshielding for the H(2) and H(3) protons. Indeed the chemical shift differences roughly parallel the electronegativity differences between the substituents ($\chi_{\mathrm{I}} = 2.5$, $\chi_{\mathrm{Br}} = 2.8$, $\chi_{\mathrm{Cl}} = 3.0$) [13]. Furthermore, the small $^{1}$H chemical shift variations on substitution prove that the variations in these $\pi$ bonding contributions are only minor, in accordance with the conclusions reached from our IR and Raman data.

*$^{1}H$–$^{1}H$ coupling constants.* The $^{1}$H–$^{1}$H coupling constants for the $(CH_2{=}CH)_3SnX$ derivatives vary in the order $J_{trans} > J_{cis} > J_{gem}$ (Table 4), as observed for most vinyl compounds [10,14–16]. Karplus predicted this sequence on theoretical grounds [17]. These coupling constants are all of the same sign [14] (assumed positive [7]). In general a slight increase of $J_{trans}$, $J_{cis}$ and $J_{gem}$ is observable on increasing the electronegativity of the halogen substituent, thus on increasing the group electronegativity of the $SnVi_2X$ group.

Banwell, Sheppard [18] and Schaefer [19] also found a correlation between the electronegativity of the X substituents and the $^{1}$H–$^{1}$H coupling constants in $(CH_2{=}CH)_nX$ compounds. However, in contrast with the results from this study, they observed an inverse relationship. Since for the $(CH_2{=}CH)_3SnX$ compounds only minor variations of the $J(^{1}H{-}^{1}H)$ data can be observed (Table 4), it does not seem appropriate to comment these data.

*$^{119,117}Sn$ satellite spectra.* The first complete analysis of the $^{119,117}$Sn satellite spectra of $Sn(CH{=}CH_2)_4$ was reported by Lunazzi and Taddei [9]. The high

resolution NMR spectra obtained in the present study simplify markedly the analysis of the $^{119,117}Sn$ satellite spectra. Assignment of signals to $J(^{119}Sn-^{1}H)$ and $J(^{117}Sn-^{1}H)$ is based on the fact that the ratio of these parameters should be equal to $\gamma(^{119}Sn)/\gamma(^{117}Sn) = 1.046$ [9,20].

According to Lunazzi and Taddei [9] it is likely that all the tin–hydrogen coupling constants for both isotopes have identical relative signs. Furthermore Krebs and Dreeskamp [15] showed them all to be positive. The data of Table 4 show that $J(Sn-H(2)) > J(Sn-H(1)) > J(Sn-H(3))$, in accordance with the findings of Delmas, Maire and Santamaria for $Sn(CH=CH_2)_4$ [10]. As for the homonuclear proton–proton coupling constants, the variations of the heteronuclear tin–proton coupling constants are also minor, proving again that the electron distribution in the vinyl system remains practically unaltered on halogen substitution.

*$^{13}C$ NMR spectra.* The $^{13}C$ NMR data for $Sn(CH=CH_2)_4$ have been published previously [21–23], but no data for the $(CH_2=CH)_3SnX$ derivatives have been reported. The proton decoupled NMR spectra of the $(CH_2=CH)_3SnX$ derivatives are composed of two singlet peaks belonging to the C(1) and C(2) carbon atom, with

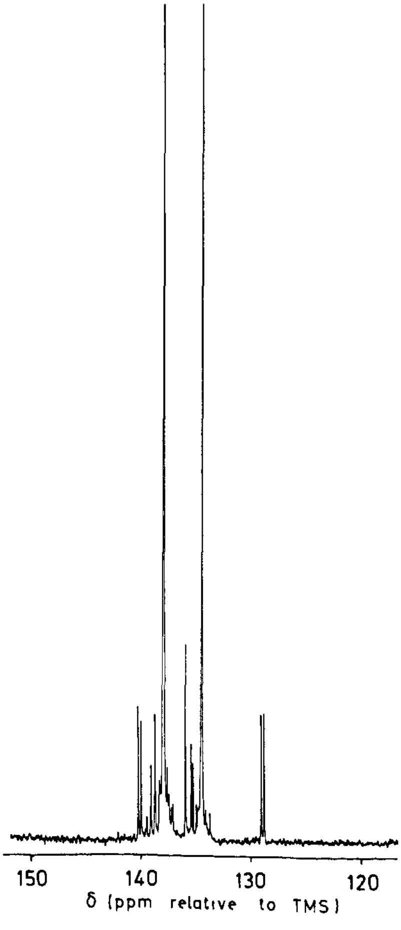


Fig. 2. 200 MHz $^{13}C$ NMR spectrum of $(CH_2=CH)_3SnBr$.

the C(1) signal clearly surrounded by $^{119,117}$Sn satellites (Fig. 2). The assignment of these singlets to the respective carbon atoms is based on the nuclear Overhauser effect in proton decoupled $^{13}$C NMR spectra, the largest signal to noise (S/N) increase being associated with the carbon atom bearing the largest number of protons, i.e. C(2).

*$^{13}$C chemical shifts.* The $^{13}$C chemical shift is mainly governed by changes in the paramagnetic screening term $\sigma^p$ [24,25] (eq. 4), where $\Delta E$ represents the mean

$$\sigma^p = -\frac{e^2\hbar^2}{2m^2c^2}\cdot\frac{1}{\Delta E}\cdot\langle\frac{1}{r^3}\rangle_p\cdot P \qquad (4)$$

excitation energy of the electrons, $\langle\frac{1}{r^3}\rangle_p$ is the mean value of $\frac{1}{r^3}$ for the $p$ electrons, $P$ represents the electron unbalance in the $p$ orbitals.

In the compounds of this study the probably dominating effects influencing the $^{13}$C chemical shifts are discussed below.

(i) Isovalent rehybridization around tin. On substitution with a more electronegative X atom, according to Bent's theory [26], the Sn–X orbital gains $p$ character while in the Sn–C(1) orbitals more $s$ character is induced. Since the electronegativity of an orbital is enhanced on increasing $s$ character [27], the orbital electronegativity of the Sn hybrid orbital directed to C(1) will rise, influencing the factor $\langle\frac{1}{r^3}\rangle_p$ in eq. 4. Consequently the C(1) carbon atom will be deshielded, and C(2) will not be seriously affected.

(ii) Resonance interactions between the $\pi$ electron system of the vinyl group and the Sn($5d$) orbitals, according to eq. 3. These interactions increase in the order $\mathrm{I} < \mathrm{Br} < \mathrm{Cl}$ (see above) and cause a deshielding of C(2), leaving C(1) practically unaltered. As stated above, these $\pi$ interactions are small.

The chemical shift for the C(2) atom remains practically unaltered on increasing electronegativity of the halogen atom, while the C(1) resonance is clearly deshielded (Table 4). Obviously the dominant factor in determining the $^{13}$C parameters for $(CH_2{=}CH)_3SnX$ compounds is the rehybridization around tin. Since the degree of isovalent rehybridization is proportional to the electronegativity difference between the altered substituents, it follows that the largest deshielding of C(1) should be observed on substitution of iodine by bromine.

*$^{119,117}$Sn satellite spectra.* It is generally accepted [28,29] that the Fermi-contact interaction, which is linearly related to the $s$ character in the bond, constitutes the dominant factor in the spin–spin coupling mechanism. According to Bent's theory (see above), on increasing electronegativity of the halogen atom, more $s$ character is induced in the Sn–C(1) orbitals, which enhances the Fermi-contact interaction and generates higher values of $^1J$(Sn–$^{13}$C(1)) (Table 4). This is further evidenced by the observation that the largest increase in these couplings occurs on substitution of iodine by bromine.

*NMR evidence for the rearrangement of $(CH_2{=}CH)_3SnCl$.* In the $^1$H and $^{13}$C NMR spectrum of $(CH_2{=}CH)_3SnCl$ additional peaks are observed because of the presence of $(CH_2{=}CH)_4Sn$ and $(CH_2{=}CH)_2SnCl_2$ impurities. The data in Table 5 for $(CH_2{=}CH)_2SnCl_2$ were directly deduced from these spectra.

Obviously the sample analyzed in the NMR spectrometer was a mixture of $(CH_2{=}CH)_3SnCl$, $(CH_2{=}CH)_4Sn$ and $(CH_2CH)_2SnCl_2$. This is evidence for the

TABLE 5

NMR CHEMICAL SHIFTS (ppm) AND COUPLING CONSTANTS (Hz) FOR $(CH_2{=}CH)_2SnCl_2$

| Method | Parameter | $(CH_2{=}CH)_2SnCl_2$ |
|---|---|---|
| $^1$H NMR | $\delta(^1H(1))$ | 6.54 |
| | $\delta(^1H(2))$ | 6.42 |
| | $\delta(^1H(3))$ | 6.16 |
| | $^2J(^1H(2)-^1H(3)) = J_{gem}$ | 1.4 |
| | $^3J(^1H(1)-^1H(2)) = J_{cis}$ | 12.6 |
| | $^3J(^1H(2)-^1H(3)) = J_{trans}$ | 19.3 |
| $^{13}$C NMR | $\delta(^{13}C(1))$ | 134.4 |
| | $\delta(^{13}C(2))$ | 139.3 |
| | $^1J(^{119}Sn-^{13}C(1))$ | 760.8 |
| | $^1J(^{117}Sn-^{13}C(1))$ | 726.9 |

rearrangement reaction (eq. 2). From the low intensity of these additional peaks it can be deduced that the decomposition of $(CH_2{=}CH)_3SnCl$ is fairly slow.

## Conclusion

The combined results from this IR, Raman and NMR study on the chemical bonding in $(CH_2{=}CH)_3SnX$ (X = Cl, Br, I) compounds have shown that on halogen substitution on tin it is primarily the tin–halogen and the tin–carbon bonds which are altered, in accordance with the theory of isovalent rehybridization. It has also been demonstrated that variations in the $(\pi(Vi) \rightarrow d(Sn))\pi$ bond are rather weak.

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