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HIGH RESOLUTION NMR STUDIES OF ALLYLIC DERIVATIVES OF GROUP IVB ELEMENTS

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SUMMARY

The high resolution NMR spectra of certain Group IVB allyl compounds, $R_3M-(CH_2)_n-CH=CH_2R'$ (where R = Me, Et, Ph; R' = H, Ph; M = Sn, Si, Ge; $n=1$ or 2), have been studied in an attempt to detect manifestations of ground state $p_\pi-d_\pi$ overlap. Analyses, using sub-spectral techniques for $ABMX_2$ and ABX_2 systems, were confirmed using computer iteration methods. The emphasis has been placed here on the sensitivity of the coupling constants of the allyl group towards anticipated steric and electronic perturbation or towards the interaction between the Group IVB atom d orbitals and the olefinic p_π orbitals. Some ^{119}Sn chemical shifts have also been recorded. The conclusions reached do not support the existence of ground state $d_\pi-p_\pi$ overlap in these compounds.

INTRODUCTION

The kinetic behaviour in the reactions of allyl derivatives of Group IVB elements with electrophilic reagents has led to the postulate of a cyclic transition state stabilised by intramolecular overlap of empty d orbitals of the heteroatom and the occupied p_π orbital of the double bond[1]. The infrared, Raman and ultraviolet spectra of a similar series of compounds have been interpreted as favouring such $d_\pi-p_\pi$ overlap as an important ground state phenomenon particularly for the allyl series. NMR and Mössbauer data have, however, been interpreted as providing evidence against the ground state existence of such $d_\pi-p_\pi$ overlap in alkenyl–tin compounds[2] and norbornenyl–tin compounds[3]. Much of the NMR evidence has been mainly concerned with the chemical shifts of protons[2] and carbon-13 nuclei[3] since intramolecular complex formation involving $d_\pi-p_\pi$ overlap would tend to deshield the olefinic nuclei[4].

There is reason to expect that the coupling constants associated with the allyl group would also be affected by, and prove sensitive probes for, the overlap of low-lying d and olefinic p_π orbitals[5]. The high resolution NMR spectra of a number of the

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series of compounds, $R_3M-(CH_2)_n-CH=CHR'$ (R = Me, Ph; M = Si, Sn; n = 0, 1, 2 and R' = H, Ph) have been obtained in varying solvents and analysed to second order, where appropriate, to provide the coupling constant data necessary to check the conclusions of other work.

EXPERIMENTAL

The compounds were prepared in these laboratories and the preparative methods have been described[1].

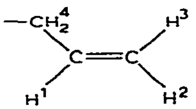
The proton spectra were obtained using a Varian A60A spectrometer operating at 60 MHz and 100 MHz spectra were provided by the S.R.C. service centred in University of East Anglia.

RESULTS

The spectra of $R_3M-CH_2-CH=CH_2$ compounds have been analysed as $ABMX_2$ systems. The spectra of $R_3M-(CH_2)_n-CH=CH_2$ (n = 1, 2) compounds have similarly been analysed as far as the olefinic protons are concerned. The cinnamyl compounds $R_3M-CH_2-CH=CH-Ph$ have been analysed as ABX_2 systems. The chemical shifts and coupling constants are given in Tables 1 and 2.

TABLE 1

CHEMICAL SHIFTS FOR $R_3M-(CH_2)_n-CH=CHR'$ COMPOUNDS[a]



Compound	δ_1	δ_2	δ_3	δ_4
$Ph_3Sn-CH_2-CH=CH_2$	6.04	4.75	4.90	2.38
$Et_3Si-CH_2-CH=CH_2$	5.76	4.73	4.77	1.52
$Me_3Si-CH_2-CH=CH-Ph$	6.42		6.48	1.86
$Et_3Ge-CH_2-CH=CH_2$	6.13		6.18	1.80
$Me_3Sn-(CH_2)_2-CH=CH_2$	5.85	4.86	4.95	2.26
$Ph_3Ge-CH_2-CH=CH_2$	5.87	4.82	4.90	2.42
in CS_2	5.88	4.79	4.88	2.30
in benzene	5.96	4.85	4.94	2.38
$Bu_3Sn-CH_2-CH=CH_2$	5.85	4.58	4.73	1.75

[a] CCl_4 solution, 30% v/v, except when stated otherwise.

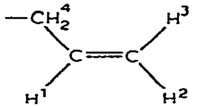
DISCUSSION

Chemical shifts

The factors which may be expected to contribute to the chemical shifts and any differences observed within the series include: (*i*) change in the magnetic susceptibility between Si, Ge and Sn; (*ii*) diamagnetic anisotropies of Si–C, Ge–C, Sn–C and C=C bonds. It has been suggested[4] that the anisotropy of the Sn–C bond should

TABLE 2

COUPLING CONSTANTS[a] DERIVED FOR $R_3M-(CH_2)_n-CH=CHR'$ COMPOUNDS AND RELATED MOLECULES



Compound	J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}
$Me_3Sn-CH_2-CH=CH_2$	8.9	15.8	7.8	2.1	−1.1	−0.6
$Me_3Sn-(CH_2)_3-CH=CH_2$	9.0	16.4	6.2	2.4	−1.3	−1.1
$Ph_3Sn-CH_2-CH=CH_2$	9.4	17.8	8.2	2.1	−1.2	−0.8
in acetone	9.8	17.4	8.5	2.2	−1.2	−0.8
in benzene	9.8	17.4	8.4	2.2	−1.2	−0.8
in CS_2	9.4	17.9	8.3	2.1	−1.2	−0.8
$Et_3Sn-CH_2-CH=CH-Ph$						
in acetone at 38°		+15.4	+8.8			−1.3
at 10°		+15.4	+8.9			−1.4
at −10°		+15.3	+9.0			−1.1
at −30°		+15.4	+8.9			−1.2
at −50°		+15.3	+8.8			−0.7[b]
at −70°		+15.3	+9.0			−0.4[b]
$Me_3Si-CH_2-CH=CH_2$	9.2	17.4	7.7	2.4	−1.3	−0.9
$Et_3Si-CH_2-CH=CH_2$	9.2	17.3	7.8	2.5	−1.3	−0.9
$Me_3Si-CH_2-CH=CH-Ph$		16.1	8.4			−1.5
$Et_3Si-CH_2-CH=CH-Ph$		15.3	8.4			−1.4
$Et_3Ge-CH_2-CH=CH_2$	10.2	17.4	8.3	2.4	−1.3	−0.8
$Ph_3Ge-CH_2-CH=CH_2$	10.1	16.5	8.0	2.2	−1.1	−0.9
in benzene	9.4	17.8	8.0	2.3	−1.3	−1.0
$Bu_3Sn-CH_2-CH=CH_2$	9.8	17.3	8.4	2.1	−1.2	−0.7
$Et_3Ge-CH_2-CH=CH-Ph$		15.7	8.5			−1.3
$CH_3-CH=CH_2$[c]	10.0	16.8	6.4	2.1	−1.3	−1.8
$CH_3-CH_2-CH=CH_2$[c]	10.3	17.2	6.2	2.0	−1.3	−1.7
$C_3H_7-CH_2-CH=CH_2$[c]	10.2	17.0	6.6	2.2	−1.2	1.5

[a] CCl_4 solution, ±0.1 Hz, except when stated otherwise. [b] ±0.3 Hz. [c] Ref. 7.

result in a general shielding of the olefinic protons of tetraallyltin relative to tetravinyltin and the shielding increases in the order *gem* > *cis* > *trans*. Further, for π interactions, the geminal proton chemical shift has been anticipated as showing the greatest downfield displacement on changing the solvent from carbon tetrachloride to dimethyl sulphoxide[2]. Dimethyl sulphoxide has not been used in this work because DMSO solutions give broad lines[2]. Alternative solvents such as acetone and benzene which might be expected to behave in a similar way to DMSO in competing for the empty *d* orbitals of the M atom, have been used instead. The results are reported for a limited number of compounds, sufficient to support past conclusions[2,3]. The variation in chemical shifts between protons in comparable positions in different molecules is small, that is, not greater than 0.3 ppm. This variation can be attributed to contributions from the effects listed above. The effects of bond anisotropy are difficult to quantify because of the lack of molecular geometry and susceptibility data in these compounds. The insensitivity of chemical shifts to benzene as solvent excludes a competition for the void M *d* orbitals. It does not exclude a strong intramolecular effect.

^{119}Sn chemical shifts

The ^{119}Sn chemical shifts of three compounds have been measured[5] where d_π–p_π interaction may be considered possible. The results are summarised here:

Me_4Sn	0
$Me_3Sn{-}CH_2{-}CH{=}CH_2$	$+5.4 \pm 0.4$ ppm
$Me_3Sn{-}(CH_2)_2{-}CH{=}CH_2$	-1.6 ± 0.2 ppm
$Me_3Sn{-}(CH_2)_3{-}CH{=}CH_2$	0.5 ± 0.2 ppm

Overlap of the Sn *d* orbitals and C–C π orbitals would be expected to lead to a shielding of the Sn nucleus. The Sn nucleus in the allyl compound is the most shielded of those studied but the magnitude of the effect is not great enough to be considered significant.

Coupling constants

Proton–proton. The sensitivity of vinylic coupling constants to substituents which perturb the electron distribution is well established[6,7]. Significantly the sum of the vinylic coupling constants in trimethylvinylsilane is 38.8 Hz[6] compared with 29 Hz in propene[7]. This difference has been attributed to d_π–p_π bonding between directly bonded carbon and silicon[6]. It is reasonable to expect that a d_π–p_π interaction between silicon and the π electrons of a carbon–carbon double bond would produce qualitatively a similar result. A comparison of the sum of coupling constants in the vinyl part of the allyl groups studied with the same parameter in propene 1-butene and 1-hexene (Table 2) reveals no significant difference. This result does not support the postulate of ground-state p_π–d_π interaction.

Variable temperature studies on triethylcinnamyltin (Table 2) provide no significant new information.

The coupling constant most susceptible to stereochemical changes which may be associated with the pseudo-cyclic form involving intramolecular p_π–d_π interaction is the vicinal coupling constant, J_{14}. An equation has been derived which, it is claimed[9], provides a "semiquantitative" measure of the fraction of *cis* conformer where the X substituent in $CH_2{=}CH{-}CH_2X$ is spatially adjacent to the double bond contributing to the observed equilibrium position. That equation was applied to allyl halides in the form: $n = 1.2\text{–}0.16\,J_{14}$, to give n, the fraction of *cis* conformer. The authors emphasised that the equation would probably not hold for all allyl compounds, a point born out for values of J_{14} outside the range 1.25 to 7.5 Hz, but having been derived from the Karplus equation it seems likely that for another self consistent series of allyl compounds the Karplus constants will be different and in general[10] the lower the value of J_{14} the greater the value of n.

A large value for n would be consistent with p_π–d_π interaction. The only significant result observed from this point of view relates to trimethyl-1-pentenyltin where J_{14} at 6.2 Hz is 20% lower than in trimethylallyltin. This can be explained in terms of an increased fraction of *cis* conformer but the values of the vinyl coupling constants do not differ sufficiently between the two compounds to attach any real significance to the result.

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