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FOURIER TRANSFORM NMR INVESTIGATIONS ON ORGANOTIN COMPOUNDS

VII *. CARBON-13 AND TIN-119 SPECTRA OF STANNYL ACETYLENES

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Summary

The ^{13}C and ^{119}Sn NMR spectra of compounds of the type $Me_nSn(C{\equiv}CR)_{4-n}$ (n = 0--4) have been studied. As n decreases, the methyltin carbon resonance is shifted to low field, while C(1) in the acetylenic fragment is shifted to high field; at the same time, the tin-119 resonance is shifted monotonically to high field. Tin—carbon coupling constants increase with decreasing n, but the observed values cannot be correlated with changes in carbon hybridisation. Variation of R has little influence on the NMR parameters.

Introduction

During a study of tetraorganotins [2] we made some preliminary NMR measurements on triorganostannyl acetylenes. These were characterised by very large substituent chemical shifts (SCS) for the acetylenic carbons, as well as by large direct and indirect tin—carbon coupling constants. We therefore decided to make a more systematic study of these compounds, including tin-119 measurements. The results are presented here.

Experimental

Spectra were recorded in the PFT mode with proton noise decoupling as described in earlier papers of this series using Bruker-Physik spectrometers (HFX-90 for ^{119}Sn and WP-80 for ^{13}C). The digital resolution of the transformed spectra under the conditions used was ca. 3 Hz for ^{119}Sn at 33.546 MHz and ca. 1 Hz for ^{13}C at 20.155 MHz.

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* For part VI see ref. 1.

TABLE 1

TIN-119 AND CARBON-13 CHEMICAL SHIFTS IN COMPOUNDS $Me_nSn(C{\equiv}CR)_{4-n}$ (in ppm; for ^{119}Sn, δ(Me_4Sn) 0 ppm, and for ^{13}C, δ(TMS) 0 ppm)

Compound	*n*	*R*	δ(^{119}Sn)	δ(Me)	δ(C(1))	δ(C(2))	δ(C(3))	δ(C(4))	δ(C(5))	δ(C(6))
I	4	—	0,0	−9,6						
II	3	n-C_4H_9 [a]	−73,0	−8,1	81,4	110,4	19,9	31,4	22,1	13,7
					(12,8)	(26,4)	(1,3)	(0,3)	(−0,3)	(−0,4)
III	3	n-C_5H_{11} [b]	−73,1	−8,1	81,4	110,4	20,3	29,0	31,2	22,4
					(12.8)	(26,3)	(1,4)	(−0,3)	(−0,7)	(−1,2)
IV	3	t-C_4H_9	−72,2	−8,0	78,8	118,7	28,2	31,5		
					(11,8)	(26,4)	(0,8)	(0,5)		
V	3	Ph [c]	−66,3	−8,0	93,0	109,2	124,2	127,7	128,0	131,7
					(15,5)	(25,4)	(1,8)	(−0,6)	(0,0)	(0,0)
VI	2	n-C_4H_9	−156,7	−6,6	79,6	110,6	19,8	31,1	22,0	13,6
VII	1	n-C_4H_9	−248,6	−5,0	78,2	111,6	19,9	31,0	22,1	13,7
VIII	0	n-C_4H_9 [d]	−345,9		76,7	110,0	19,8	30,8	22,1	13,8

[a] ^{13}C data agree well with Lit. [4]. [b] δ(C(7)) 13,9. [c] Lit. [11] −69,0. [d] The tin signal is negative under the conditions of measurement (temp. ca. 40°C). The numbers in parentheses indicate the SCS when the acetylenic proton is replaced by $SnMe_3$.

The substances investigated were prepared by published procedures; the following equations illustrate the methods used.

$$RC{\equiv}CH + Me_3SnNEt_2 \rightarrow Me_3SnC{\equiv}CR + HNEt_2$$

$$(R = Ph, alkyl)$$

$$(4\text{-}n)\ RC{\equiv}CH \xrightarrow{BuLi} (4\text{-}n)\ RC{\equiv}CLi \xrightarrow{Me_nSnCl_{4-n}} Me_nSn(C{\equiv}CR)_{4-n}$$

$$(R = alkyl, n = 0\text{—}2)$$

Only compounds with n = 3 or 2 were prepared pure. $Sn(C{\equiv}CBu)_4$ exploded when vacuum distillation was attempted, and therefore distillation of $MeSn(C{\equiv}CBu)_3$ was not carried out.

Results and discussion

The data obtained are presented in Tables 1 and 2; the normal sign convention is used for chemical shifts. Chemical shifts and coupling constants will be discussed separately.

(a) Carbon-13 chemical shifts (Table 1)

The compounds studied consist of two groups, compounds II—V of the type $Me_3SnC{\equiv}CR$ in which R is varied, and compounds I, II and VI—VIII of the type $Me_nSn(C{\equiv}CBu)_{4-n}$ in which n is varied. It can be seen that in the first group variation of R has little effect; this is perhaps not surprising since R is a substituent at the β carbon. A direct comparison of the carbon shifts in R is not possible, but we can compare the substituent chemical shifts (*SCS*) observed when the acetylenic proton is replaced by Me_3Sn. *SCS* of appreciable magnitude occur only for C(1) (α-*SCS*), C(2) (β-*SCS*) and C(3) (γ-*SCS*). We have previously [3] observed *SCS* in trimethyl-n-alkyltins of ca. —2 (α), +4 (β) and +2 (γ) ppm, while Kuivila's measurements [4] indicate that the α-*SCS* in alkenyltins lies between 10 and 15 ppm, the β being 10—13 ppm. In the alkynyltins the values are 12—15 (α) and 25—26 (β) ppm. A rationalisation of these values is difficult: it appears that $(p - d)_\pi$ interactions between tin and the acetylenic bond are not important, since the α-*SCS* in silyl- and germyl-acetylenes (where such interactions should be more important) is also ca. 15 ppm, while the β-*SCS* is ca. 21 ppm in silyl and ca. 16 ppm in germylacetylenes. Bond polarisation effects probably also play no major role: replacement of the acetylenic proton of phenylacetylene by a methyl group leads to α- and β-*SCS* of 3 ppm, so that $\Delta\delta$, the difference between the acetylenic carbon shifts, remains 6 ppm. In compound V, $\Delta\delta$ is 16 ppm, while in compound IV where the substituents t-Bu and $SnMe_3$ are both electron-donating $\Delta\delta$ is 40 ppm. It thus seems that the observed *SCS* values in the stannyl acetylenes must be due to changes which are not readily qualitiable in the paramagnetic term caused by introduction of the stannyl group.

In the second group of compounds in which n is varied, decrease in n corresponds to a low-field shift of the methyltin carbons, readily understandable in terms of electronegativity of the substituents at tin. At the same time, C(1) in the acetylene fragment is shifted to high field, though the electronegativity of

TABLE 2

TIN—CARBON COUPLING CONSTANTS IN COMPOUNDS $Me_nSn(C{\equiv}CR)_{4-n}$ (in Hz)

Compound	n	R	^1J(Sn—Me)	^1J(Sn—C(1)	^2J(Sn—C(2)	^3J(Sn—C(3))
I	4	Me	338.0			
II	3	n-C_4H_9	404.3	506.6	105.2	[a]
III	3	n-C_5H_{11}	405.1	505.8	105.3	10.3 [b]
IV	3	t-C_4H_9	405.1	510.4	100.7	9.2
V	3	Ph	404.0	444.1	92.7	13.1 [c]
VI	2	n-C_4H_9	495.5	661.5	137.4	12.6
VII	1	n-C_4H_9	613.2	877.8	180.8	14.9 [d]
VIII	0	n-C_4H_9		1160.4	235.3	20.0

[a] Not observed. [b] $^4J(Sn—C_4)$ 20.6 Hz. [c] $^4J(Sn—C_4)$ 49.2 Hz. [d] $^4J(Sn—C_4)$ 8.0 Hz.

the organostannyl group attached to C(1) increases. Thus this high-field shift must be due to small changes in the paramagnetic term.

(b) ^{119}Sn chemical shifts (Table 1)

All the compounds studied show shifts to high field of Me_4Sn; for compounds $Me_3SnC{\equiv}CR$ the shift shows little variation with R, so that hexynyltins can be considered as typical stannylacetylenes when $R \neq H$. McFarlane et al. [5] have previously examined three ethynyltins, for which they observed somewhat different shifts ranging from —52 ppm (Et_4SnC_2H) to —279 ppm ($Sn(C_2H)_4$ in Et_2O, a donor solvent). In common with them, we observe a linear dependence of δ(Sn) on n in compounds $Me_nSn(C{\equiv}CR)_{4-n}$. They explained the high-field shift in terms of $(d - p)\pi$ interactions; Radeglia and Engelhardt [6] have proposed a model for estimating tin chemical shifts which does not rely on the inclusion of such interactions, but in its simplest form takes into account only the electronegativities of the atoms directly bound to tin. Its application thus becomes difficult for mixed tetraorganotins such as mixed methylphenyltins, mixed methylalkenyltins or mixed methylaklynyltins, all of which show the same trend in tin chemical shift [7], since the calculated shielding constant values depend on the value assumed for the carbon electronegativity EN_C in the organic residues. EN_C for alkynyl groups probably has a similar value to that of sulphur (taken [6] as 2.70); however, compounds $Me_nSn(SR)_{4-n}$ show an opposite trend in their chemical shift to the unsaturated carbon compounds. It is clear that the simple model cannot be used for such substances, but must be refined to include other factors; it seems unlikely that bond angle corrections at tin [8] are sufficient to eliminate the discrepancies mentioned above.

(c) Tin—carbon coupling constants (Table 2)

The following trends are clearly visible from Table 2 (i) ^1J(Sn—C(1)) is always larger than ^1J(Sn—Me), (ii) both ^1J values increase with decreasing n; the correlation coefficient r between these J values is 0.988, (iii) there is a linear correlation ($r = 0.999$) between $^1J(Sn—C_1)$ and $^2J(Sn—C_2)$, the line passing through the origin.

The first these features can be explained on the basis of Bent's postulate [9], the second on the basis of increasing electron demand at tin (changes in Z_{eff}, corresponding to changes in the value of the valence *s*-electron wave-function at the nucleus). The correlation between $^{1}J(\mathrm{Sn{-}C(1)})$ and $^{2}J(\mathrm{Sn{-}C(2)})$ would intuitively be predicted; it is interesting to note that in compounds $\mathrm{Me}_n\mathrm{SnR}_{4-n}$ (R = alkyl), no such dependence is observed. However, a comparison between two such different systems is not valid.

The Muller—Pritchard correlation [10] of $^{1}J(\mathrm{CH})$ with the *s*-character of the bonding orbital has often been criticised; while the exact nature of the Sn—C bonding orbital in alkenyl- and alkynyl-tins is not clear, we felt it would be of interest to compare $^{1}J(\mathrm{Sn{-}C})$ in closely related compounds in which the carbon is sp^3, sp^2 and *sp*-hybridised. The following values are obtained: $\mathrm{Me_3SnCH_2CH_2CH_3}$ 369, $\mathrm{Me_3SnCH{=}CHCH_3}$ 478, $\mathrm{Me_3SnC{\equiv}CC}{\leqq}$ 507 Hz; $\mathrm{Sn(CH_2CH_2CH_3)_4}$ 314, $\mathrm{Sn(CH{=}CHCH_3)_4}$ 524, $\mathrm{Sn(C{\equiv}CC{\leqq})_4}$ 1160 Hz. Thus in both series $^{1}J(\mathrm{Sn{-}C})$ cannot be correlated with carbon hybridisation, and the values in the two series are not self-consistent. This indicates again that no one factor is solely responsible for variations in direct coupling constants when the hybridisation at one of the atoms involved varies.

A comparison between compound V and the other compounds studied is not readily possible, since the acetylene and phenyl systems are conjugated. However, the decrease in ^{1}J and ^{2}J values suggests that the electron demand of the C≡CPh residue from tin is less than that of C≡C-alkyl.

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