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FOURIER TRANSFORM NMR INVESTIGATIONS OF ORGANOTIN COMPOUNDS

VIII *. PROPENYL- AND ISOPROPENYL-TIN COMPOUNDS; DETECTION AND IDENTIFICATION OF ISOMERS USING ^{119}Sn AND ^{13}C NMR

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Summary

Starting from the equilibrium mixture of *cis*- and *trans*-1-bromo-1-propene, isomeric mixtures of compounds $Me_nSn(CH=CHMe)_{4-n}$ (n = 0—3) have been prepared and studied. While proton NMR only allows distinction between the methyltin signals of the various isomers (except where n = 3), the ^{13}C spectra show separate signals for almost all isomeric carbons even when n = 0. In the ^{119}Sn spectra the signals due to the various isomers are separated by ca. 20 ppm for a given value of n; the peak areas can be used to estimate the proportions of *cis*- and *trans*-propenyl residues present in the mixtures. Addition of 2-bromopropene to the starting 1-bromo-1-propenes leads to the formation of further isomers, which can in all cases be observed and identified in the ^{119}Sn spectra; ^{119}Sn shifts can be calculated using the shifts for the $Me_3SnC_3H_5$ isomers as increments.

Introduction

Our interest in the NMR spectroscopy of organometallic compounds has recently led us to investigate tetraorganotins [2] and stannyl acetylenes [1] in some detail. Since the literature contains few data on alkenyltin compounds, we decided to carry out a more systematic study of these. While unsubstituted vinyltin compounds may be considered as typical alkenyltins, we decided to use propenyltins since these can exist in various isomeric forms which provide a probe of the sensitivity of ^{13}C and ^{119}Sn NMR.

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* For part VII see ref. 1.

Experimental

^{13}C and ^{119}Sn spectra were recorded in the pulse Fourier transform mode with proton noise decoupling as described in earlier papers of this series using Bruker-Physik spectrometers (WP-80 for ^{13}C and HFX-90 for ^{119}Sn). The digital resolution of the transformed spectra under the conditions used was ca. 3 Hz for ^{119}Sn at 35.546 MHz and ca. 1 Hz for ^{13}C at 20.155 MHz.

Propenyltin compounds $Me_nSn(CH{=}CHMe)_{4-n}$ (n = 0—3) were prepared as described by Seyferth and Vaughan [3], starting from the equilibrium mixture of *cis*- and *trans*-1-bromo-1-propene. The compounds with n = 1 and 2 had not previously been described in the literature; they gave satisfactory elemental analyses and had boiling points of 48°C/0.2 mmHg (n = 1) and 65°C/12 mmHg (n = 2). The more complex isomer mixtures containing isopropenyl residues were prepared in an analogous manner starting from a 3/1 mixture (w/w) of 1-bromo-1-propene and 2-bromopropene.

Results and discussion

The data obtained are presented in Tables 1—3; the normal sign convention is used for chemical shifts. It is known from the literature [4] that the starting 1-bromo-1-propene contains 68% of the *cis*-isomer; Seyferth and Vaughan [3] report that $Me_3SnCH{=}CHMe$ prepared from this mixture contains 64% of the *cis*-isomer whether prepared via the Grignard or organolithium route. This figure was determined by GLC, the assignment being made on the basis of the IR and PMR spectra; it has been confirmed by Delmas et al. [5], and forms the basis of the following discussion. We were able to confirm the report [3] that propenyltin mixtures are isomerised by UV light, but in our hands the isomerisation occurred much more slowly than described in the literature, so that we carried out irradiation only up to a *cis/trans* ratio of ca. 45/55.

The various features of the spectra will be discussed separately.

(a) ^{119}Sn chemical shifts

Trimethyl-*cis*-, -*trans*- and iso-propenyltin absorb at —58, —42 and —34 ppm, respectively, the peak areas of the *cis* and *trans* isomers in an unirradiated mixture comparing well with the literature *cis/trans* ratio of 64/36. It is known [6] that trimethylvinyltin absorbs at —40 ppm, so that substitution of vinyl protons by a methyl group can have an appreciable effect on the tin chemical shift. Compounds $Me_nSn(CH{=}CHMe)_{4-n}$ where n = 2, 1 or 0 show the expected three, four or five resonances, the ratio of the peak intensities again corresponding well to those expected on the basis of 64% *cis* residues; this indicates that the orientation at the double bond has little influence on the NOE or on the relaxation time t_1 of the ^{119}Sn nucleus.

The number of possible isomers increases when 2-bromopropene is added to the starting 1-bromo-1-propene. In all cases, however, the number of signals observed corresponded to the maximum numbers of possible isomers (see Table 1), except for n = 0 where only 14 signals were observed. The assignment of the additional signals to the various isomers was carried out on the following basis: in the series $Me_nSn(CH{=}CH_2)_{4-n}$ (n = 3—0), replacement of a methyl by a

TABLE 1

CALCULATED [a] AND OBSERVED ^{119}Sn CHEMICAL SHIFTS FOR COMPOUNDS $Me_nSn(C_3H_5)_{4-n}$ (in ppm) [b]

n	Isomer [c]	Calculated	Observed	n	Isomer [c]	Calculated	Observed
3	c	—	−58	0	cccc	−232	−234
	t	—	−42		ccct	−216	−211
	i	—	−34		cctt	−200	−191
2	cc	−116	−116		cttt	−184	−175
	ct	−100	−98		tttt	−168	−162
	tt	−84	−83		ccci	−208	−208
	ci	−92	−92		ccti	−190	−187
	ti	−76	−76		ctti	−176	−171
	ii	−68	−69		ttti	−160	−157
1	ccc	−174	−175		ccii	−184	−184
	cct	−158	−155		ctii	−168	−167
	ctt	−142	−139		ttii	−152	−153
	ttt	−126	−123		ciii	−156	−162
	cci	−150	−150		tiii	−144	−149
	cti	−134	−132		iiii	−136	−143
	tti	−118	−118				
	cii	−124	−127				
	tii	−110	−112				
	iii	−102	−106				

[a] For method of calculation see text. [b] Relative to internal Me_4Sn, negative shift to high field of reference. [c] c = *cis*-$CH_3CH{=}CH$, t = *trans*-$CH_3CH{=}CH$, i = $CH_2{=}C(CH_3)$.

vinyl group causes an upfield shift of 40 ppm [7], corresponding to the shift value for $n = 3$. Similarly, in the propenyltin series, the shift values for trimethyl-*cis*- and -*trans*-propenyltin can be used as increments to calculate the chemical shifts of the various isomers (e.g. $n = 2$, ct-isomer, observed −98 ppm, predicted −100 ppm). For isomers containing *cis*-, *trans*- and iso-residues or merely iso-residues we find that the shift for trimethylisopropenyltin can be taken as the third increment value for shift calculations. Table 1 shows the good agreement between calculated and observed resonance positions.

Since the theoretical background of tin chemical shifts is still far from clear [8], it seems unadvisable to speculate on the reasons for the extreme sensitivity of the tin chemical shift to relatively small structural variations. However, these results indicate once again that ^{119}Sn NMR can in some cases be a very powerful tool in studying the structures of organotin compounds.

(b) Carbon-13 chemical shifts (Table 2)

It can be seen from Table 2 that in the case of trimethylpropenyltin, the carbon signals from the predominant *cis* isomer lie partially to lower (Me_3Sn, C(1)) and partially to higher (C(2), C(3)) field of those from the *trans* isomer, the differences lying between 0.2 and 2 ppm. These assignments are unambiguous and were made on the basis of peak areas; they form the basis of the assignments for the more complex isomer mixtures. Kuivila [9] has reported the values found by us for the *trans* isomer, but has assigned them to the *cis* isomer.

For decreasing n, the carbon spectra become increasingly complex; where $n = 2$ the spectrum could consist of as many as 15, for $n = 1$ 22 and for $n = 0$ 24 signals. It is however found that the signals due to the methyl (C(3)) carbon

TABLE 2

^{13}C CHEMICAL SHIFT DATA FOR COMPOUNDS $Me_nSn(C_3H_5)_{4-n}$ (in ppm) [a]

n	$\delta(Me_3Sn)$	δ(C(1))	δ(C(2))	δ(C(3))	Isomer [b]
4	—9.6	—	—	—	—
3	—8.9	129.9	142.9	21.2	c
	—9.9	129.7	143.5	23.1	t
	—10.3	149.6	125.3		i [c]
2	—8.4	129.5	143.1	21.3	cc
	—9.4	129.2/129.0	143.3/143.9	21.1/23.2	ct
	—10.4	128.8	144.2	23.2	tt
1	—7.7	129.3	143.3	21.3	ccc
	—8.7	128.7/128.4	143.6/144.2	21.4/23.2	cct
	—9.8	128.4/128.0	143.8/144.6	21.5/23.2	ctt
	—10.9	128.0	145.0	23.2	ttt
0	—	128.5	143.8	21.3	cccc
	—	126.9 to 128.0	144.0/144.8	21.5/23.2	ccct
	—		144.2/145.2	21.6/23.2	cctt
	—	[d]/126.8	[d]/145.7	21.8/23.2	cttt
	—	[d]	[d]	23.2	tttt

[a] Relative to internal TMS, ±0.1 ppm. [b] Nomenclature as in Table 1. [c] $\delta(CH_3)$ 26.1 ppm. [d] Not observed. Where two values are given, the first is for *cis*-C_3H_5.

in a *trans* unit always lie at 23.2 ppm, while for $n = 1$ and 0 there is some overlapping of C(1) signals which makes exact assignment difficult or in some cases impossible. No spectra of mixtures containing isopropenyltin residues were recorded.

In the propenyltins the methyltin carbons are always clearly separated, the relative areas of the signals corresponding well to those found in the ^{119}Sn spectra. The separation of ca. 1 ppm between methyltin carbons in a closely related isomer pair (e.g. ccc, cct) must be contrasted with that of ca. 0.1 ppm observed for the corresponding protons. Proton NMR is an unsuitable tool for distinguishing between α, β or methyl protons in compounds containing two or more propenyl groups.

(c) Tin—carbon coupling constants (Table 3)

Because of line overlapping it is not possible to obtain the coupling constants for all isomers in the complex mixtures, so that in some cases only a range of coupling constant values can be given. However, the general trends can be clearly observed. No two-bond couplings could be observed (as has already been reported by Kuivila for tetravinyltin [9]); we must therefore reverse our previous assignment [2] for *trans*-$Et_3SnCH{=}CHPh$ to give a value of 10 Hz for ^2J(Sn—C) and 64 Hz for *trans*-^3J(Sn—C). As in proton NMR, the three-bond *trans* coupling is larger than the *cis* coupling. On going from $n = 4$ to $n = 1$, $^1J(Sn{-}CH_3)$ increases (by 11%) while on going from $n = 3$ to $n = 0$ ^1J(Sn—C(1)) also increases (by ca. 10%); in a comparable series of stannyl acetylenes, the corresponding increases are 81 and 129% respectively [1]. This indicates that the $-I$ effect of a propenyl group with respect to tin is relatively small. As in the stannyl acetylenes, ^1J(Sn—C(1)) is larger than $^1J(Sn{-}CH_3)$; this is not in fact at variance with the behaviour expected from Bent's postulate [10], since the carbons

TABLE 3

TIN—CARBON COUPLING CONSTANTS IN COMPOUNDS $Me_nSn(C_3H_5)_{4-n}$ (in Hz)

n	$^1J(Sn—CH_3)$	$^1J(Sn—C(1))$	cis-$^3J(Sn—C(3))$	trans-$^3J(Sn—C(3))$	Isomer [a]
4	338.0	—	—	—	—
3	346.9	464.6	49.2	—	c
	352.0	478.4	—	77.8	t
	339.9		—	—	i [b]
2	357.2	480—494	52.7	—	cc
	359.4		50.2	77.8	ct
	364.0		—	77.8	tt
1	377.8 [c]	491—497 [d]	48—52	81.2	
0	—	508—512 [e]	[f]	82.4	

[a] Nomenclature as in Table 1. [b] $^2J(Sn—C—CH_3)$ 11.4 Hz. [c] ctt isomer. [d] ccc, cct isomers. [e] cctt, cttt isomers. [f] Not measured.

involved are sp^2 and sp^3-hybridised respectively. According to the Pople—Santry treatment [11] the following equation applies for $^1J(Sn—C)$:

$$^1J(Sn—C) = \frac{16\beta^2}{9\gamma_{Sn}\gamma_C h} \cdot \psi^2_{5s(Sn)}(0) \cdot \psi^2_{2s(C)}(0) \cdot \alpha^2(Sn)\alpha^2(C) \cdot (\Delta E)^{-1}$$

Thus to allow for the dependence on $\alpha^2(C)$ (expressed in % s character of the Sn—C bond) we can "normalise" the value of $^1J(Sn—C(1))$ by multiplying by (0.25/0.33). The values of $^1J(Sn—CH_3)$ and $^1J(Sn—C(1))$ are then almost equal, indicating once more that the $—I$ effect of the propenyl group is small. This "normalisation" does not allow for variations in $\psi^2_{2s(C)}(0)$ for the two types of carbon, which are less readily quantified. However, a similar "normalisation" for compounds $Me_nSn(C{\equiv}CR)_{4-n}$ leads to much lower normalised values of $^1J(Sn—C(1))$ than those of $^1J(Sn—CH_3)$, as would be predicted by Bent's rule for the strongly electron-withdrawing acetylenic residue.

Dreeskamp [12] has observed that in methylvinyldichlorosilane $^1J(Si—C(1))$ is similarly larger (—92 Hz) than $^1J(Si—CH_3)$ (—71 Hz): the ratio of these values (1.30) compares well with the mean value of 1.34 for the mixed methylpropenyltins, as would be expected from the Pople—Santry model.

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