^{13}C, ^{29}Si, ^{115}Sn, ^{117}Sn AND ^{119}Sn NMR SPECTRA OF SOME TRIPHENYL DERIVATIVES OF ELEMENTS OF IVB GROUP

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Received August 14th, 1980

^{13}C, ^{29}Si and Sn NMR spectra of ten compounds type $(C_6H_5)_3XY$, four compounds type $((C_6H_5)_3XO)_2CrO_2$ and — for comparison — two compounds type $(CH_3CH_2CH_2CH_2)_3SnY$ and $((CH_3CH_2CH_2CH_2)_3SnO)_2CrO_2$ (X are elements of IVB group) have been measured in deuteriochloroform. The respective chemical shifts, absolute values of coupling constants $^nJ(^{119}Sn^{13}C)$ and $^2J(^{119}Sn^{117}Sn)$ are given.

The compounds type $((C_6H_5)_3XO)_2CrO_2$ are used as polymerization catalysts for α-olefins[1,2]. These compounds are prepared either by conversion of the corresponding halogen derivative with Ag_2CrO_4, or by esterification of the corresponding hydroxy derivative with CrO_3, or by reaction of the ether with chromic acid[3]. Recently Ewing[4] published a review of ^{13}C substitution effects in monosubstituted benzenes. From the compounds type $(C_6H_5)_3XY$ used as the reaction substrates in preparation of the chromic acid esters literature only gives $(C_6H_5)_3SiCl$ (ref.[5]) and $(C_6H_5)_3.SnCl$ (ref.[6]). The ^{29}Si chemical shifts are published for triphenylsilanol and triphenylsilyl chloride[7]. Furthermore, ^{119}Sn chemical shifts were determined for the compounds $(C_6H_5)_3SnX$ where X = OH (ref.[8]), Cl (ref.[9]) and I (ref.[10]).

The aim of this work is a multinuclear NMR study of chromic acid esters which should confirm their presumed structure which has not yet been measured except for bis(triphenylsilyl) ester of chromic acid (X-ray structure analysis[11]). In this context also the compounds necessary for syntheses of the esters were measured. The results obtained will also be useful for verification of purity of the said compounds during their application as industrially important catalysts.

EXPERIMENTAL

The compounds *Ia* (ref.[12]), *Ib* (ref.[13]), *Ic,d* (ref.[14]), *Ie,f* (ref.[15]), *Ig* (ref.[16]), *Ih—j* (ref.[17]), *IIa* (ref.[18]), *IIb* (ref.[19]), *IIc,d* (ref.[3]), *IIIa* (ref.[20]), *IIIb* (ref.[21]) and *IV* (ref.[20]) were prepared, purified and identified according to the literature data.

The NMR spectra were obtained with the JNM-FX 100 (JEOL) apparatus equipped with multinuclear probe and working at 25·047 MHz(^{13}C), 19·788 MHz (^{29}Si), 32·60 MHz (^{115}Sn), 35·49 MHz (^{117}Sn) and 37·14 MHz (^{119}Sn) in pulse mode with Fourier transformation. The liquids and solids were measured as about 50% (v/v) and 25% (w/v) solutions in deuteriochloroform, respectively, the chromic acid esters were measured as saturated solutions (<25% (w/v)) in deuteriochloroform at the room temperature. Deuteriochloroform was used as an internal lock substance. The chemical shifts were related to internal $(CH_3)_4Si$ (^{13}C), external $(CH_3)_4Si$ (^{29}Si), and external $(CH_3)_4Sn$ (^{115}Sn, ^{117}Sn, and ^{119}Sn), and positive values denote down field shifts. For determination of $\delta(^{29}Si)$ of the compound *IIb* we added $Cr(acac)_3$ (0·03 mol l^{-1}). The solutions were measured in 10 mm (o.d.) NMR test tubes. In all the measurements 8k memory (before FT) was used. The ^{13}C chemical shifts were measured with digital resolution 1·22 Hz/point (~0·05 ppm) and the proton noise decoupling, the coupling constants $^nJ(^{119}Sn^{13}C)$ were measured with digital resolution better than 0·4 Hz/point. The ^{29}Si chemical shifts were measured with digital resolution 1·22 Hz/point (~0·07 ppm) and inverse gated decoupling (irradiation during the acquisition time). The ^{115}Sn, ^{117}Sn and ^{119}Sn chemical shifts were also measured with the use of inverse gated decoupling and digital resolution 0·45 to 2·44 Hz/point (~0·014 to 0·075 ppm).

RESULTS AND DISCUSSION

Four signals were observed in each carbon proton decoupled spectrum of the compounds *I*–*IV*. In the compounds *I* and *II* $C_{(1)}$ to $C_{(4)}$ denote the carbons of the phenyl groups, the numbering begins from the C—X carbon atom. The signals $C_{(1)}$ and $C_{(4)}$ of the compounds *I* and *II* were assigned on the basis of comparison of the proton decoupled and coupled spectra. The signal of the $C_{(2)}$ atom was differentiated from that of $C_{(3)}$ by the typical appearance of the coupled spectrum of the monosubstituted phenyl (due to two ($C_{(2)}$) or one ($C_{(3)}$) coupling constant $^3J(^{13}CH)$), and in some cases it was controlled by selective decoupling of the *ortho*-protons. The carbon signals in the compounds *III* and *IV* were assigned on the basis of the multiplicity (CH_3) and the known regularity for $^nJ(^{119}Sn^{13}C)$ (ref.[22]): $^1J > {}^3J > {}^2J$. The ^{13}C chem-

$(C_6H_5)_3X—Y$

Ia, X = C; Y = OH
Ib, X = C; Y = Cl
Ic, X = Si; Y = OH
Id, X = Si; Y = Cl
Ie, X = Ge; Y = $OGe(C_6H_5)_3$
If, X = Ge; Y = Br
Ig, X = Sn; Y = OH
Ih, X = Sn; Y = Cl
Ii, X = Sn; Y = Br
Ij, X = Sn; Y = I

$((C_6H_5)_3XO)_2CrO_2$

IIa, X = C
IIb, X = Si
IIc, X = Ge
IId, X = Sn

$(\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2)_3SnY$

IIIa, Y = $OSn(\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_3)_3$
IIIb, Y = Cl

$((\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2)_3SnO)_2CrO_2$

IV

ical shifts of the compounds *I* to *IV* are given in Table I. In the ^{13}C proton decoupled spectra of the compounds containing Sn atoms it is possible to observe the coupling constants $^{n}J(^{117}Sn^{13}C)$ and $^{n}J(^{119}Sn^{13}C)$. Table II gives absolute values of the coupling constants $^{n}J(^{119}Sn^{13}C)$. The values $^{n}J(^{117}Sn^{13}C)$ can be calculated from the relation $^{n}J(^{117}Sn^{13}C) = {^{n}J}(^{119}Sn^{13}C)/1{\cdot}0465$ (ref.[23]). The measured values $^{n}J(^{117}Sn^{13}C)$ fulfilled the said theoretical presumption within experimental error. With the chromic acid esters no simple dependence between ^{13}C chemical shifts and the nature of the atom X was found.

The ^{29}Si chemical shifts in triphenylsilanol and triphenylsilyl chloride were −11·9 and 1·9, respectively. The internal $(CH_3)_4Si$ in deuteriochloroform was shifted downfield by 0·7 ppm as compared with the external standard. After correction the measured ^{29}Si chemical shifts agree with the published values[7]. According to the ref.[7] values of the chemical shifts of these compounds are not affected by concentration and addition of $Cr(acac)_3$. The ^{29}Si chemical shift in the compound *IIb* (measured with addition of $Cr(acac)_3$) was −12·0, *i.e.* practically the same as in triphenylsilanol.

TABLE I

^{13}C Chemical shifts (in ppm related to internal $(CH_3)_4Si$; ±0·1 ppm) in Compounds *I* to *IV* in Deuteriochloroform

Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$
Ia[a]	146·7	127·8	127·8	127·1
Ib[b]	145·1	129·5	127·6	127·6
Ic	135·0	134·9	127·8	130·0
Id	132·8	135·1	128·0	130·7
Ie	137·4	134·3	128·0	129·3
If	134·6	134·2	128·6	130·4
Ig	140·4	136·4	128·5	129·4
Ih	137·1	136·0	129·0	130·4
Ii	136·9	136·0	129·0	130·3
Ij	136·2	136·2	128·9	130·1
IIa[c]	145·2	128·5	127·8	127·8
IIb	133·2	135·2	128·0	130·6
IIc	137·4	134·4	128·0	129·3
IId	139·2	136·5	128·7	129·8
IIIa	16·0	27·9	27·0	13·0
IIIb	17·3	27·6	26·5	13·3
IV	19·1	27·9	27·2	13·7

[a] δ(COH) = 81·9; [b] δ(CCl) = 81·3; [c] δ(CO—) = 101·3.

Spectra of individual Sn isotopes could be measured – thanks to multinuclear tunable probe – at identical experimental conditions (the same sample and standard, the same lock for all measurements of one sample). In determination of 90° angle for the FT measurements we measured pure tetramethyl stannate with external heavy water as a lock substance. The resonance frequencies of $(CH_3)_4Sn$ were determined: 32598278·6 ± 1·0 Hz (^{115}Sn), 35490171·8 ± 1·0 Hz (^{117}Sn) and 37141927·8 ± 1·0 Hz (^{119}Sn). The frequency values related to ^{119}Sn (and corresponding to relative γ values) are somewhat different from the data published recently[24]. It was stated that there is a difference in chemical shifts expressed in ppm for the isotopes ^{117}Sn and ^{119}Sn, which, however, was not proved by other authors[25]. Out of the compounds studied tris(n-butyl)stannyl chloride was measured by Sn NMR spectroscopy using the above-mentioned advantages of multinuclear tunable probe at digital resolution 0·45 Hz/point, and the Sn chemical shifts were related to external neat $(CH_3)_4Sn$. With this compound the primary isotope shielding shifts were not found ($\delta(^{115}Sn) = 152{\cdot}11 \pm 0{\cdot}03$; $\delta(^{117}Sn) = 152{\cdot}11 \pm 0{\cdot}03$; $\delta(^{119}Sn) = 152{\cdot}14 \pm 0{\cdot}03$). All the other compounds (except for *IId* which was only measured by ^{119}Sn NMR) were studied by using ^{117}Sn and ^{119}Sn NMR. Differences in chemical shifts expressed in ppm were always below 0·1 ppm and were thus within the experimental error due to digitalization. The half-widths of the ^{117}Sn and ^{119}Sn signals were of 100 Hz order of magnitude (only the compound *IId* has $w_{1/2} = 125 \pm 5$ Hz), being practically the same for the both isotopes. The ^{119}Sn chemical shifts are given

TABLE II

^{119}Sn Chemical Shifts (in ppm related to external $(CH_3)_4Sn$) and Absolute Values of Coupling Constants $^nJ(^{119}Sn^{13}C)$ (Hz) in Compounds *I* to *IV* in Deuteriochloroform

Compound	Shift	Coupling constants			
		$n = 1$	$n = 2$	$n = 3$	$n = 4$
Ig	– 82·5	—	—	—	—
Ih	– 44·7	614·3	50·0	64·5	13·4
Ii	– 59·8	595·0	49·7	63·7	13·9
Ij	–112·8	567·6	49·4	63·0	13·6
IId	– 81·5	677·1	48·7	66·3	[b]
IIIa	92·7	365·8	18·7	62·9	<5
IIIa[a]	82·4	370·4	20·3	58·1	<5
IIIb	152·8	339·5	23·4	64·5	<5
IV	141·8	386·7	23·5	71·6	<5

[a] In neat liquid (external ^{7}Li lock was used); [b] unresolved signals.

in Table II. The upfield shifts of $\delta(Sn)$ for a given substance (*e.g.* due to concentration or temperature changes) correspond to increase of coordination number of the tin atom and are usually accompanied by changes in $^nJ(^{119}SnH)$ (ref.[26]). In 50% solution of *IIIa* in deuteriochloroform we found the coupling constant $^2J(^{119}SnO.^{117}Sn) = 384{\cdot}9$ Hz by measuring both the ^{117}Sn and the ^{119}Sn NMR spectra. However, if the compound *IIIa* was measured without solvent, then the $\delta(Sn)$ was changed upfield by only 10 ppm (Table II), but the coupling constant $^2J(^{119}SnO.^{117}Sn)$ increased to the value 464·8 Hz. This finding could correspond to a far greater sensitivity of $^2J(^{119}Sn^{117}Sn)$ to structural change than that observed with $\delta(Sn)$. The values $^2J(^{119}SnO^{119}Sn)$ (calculated from $^2J(^{119}SnO^{117}Sn)$ by multiplication by the value 1·0465) are distinctly greater than $^2J(^{119}SnX^{119}Sn)$ where $X = C$ (ref.[27]) and $X = S$, Se, Te (ref.[28]). The above-mentioned concentration change of *IIIa* caused also small changes in the values $^nJ(^{119}Sn^{13}C)$ (Table II).

The multinuclear study confirmed the structures of the compounds presumed in the formulas *I* to *IV*. The attempts to measure analogous lead derivatives failed due to low solubility of these compounds in deuteriochloroform and hexadeuteriodimethyl sulphoxide.

Note added in proof: The correct ^{29}Si chemical shift in the compound *IIb* in deuteriochloroform (without $Cr(acac)_3$) is equal to 0·2. The above mentioned ^{29}Si chemical shift belongs to a trace of triphenylsilanol.

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Translated by J. Panchartek.