A ^{13}C and ^{119}Sn NMR Study of Tin(II) Chloride–Vicinal Diol Systems in Polar Organic Solvents

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The interactions of $SnCl_2$ with 1,2-ethanediol, cis- *and* trans-*1,2-cyclohexanediol and methyl* α-L-*rhamnopyranoside have been studied by ^{13}C and ^{119}Sn NMR spectroscopy. In acetone, the major reaction with compounds containing* cis-*vicinal OH groups, is an acid catalysed formation of a cyclic acetal, whereby an isopropylidene moiety bridges the vicinal O atoms. In addition, evidence was found of a donor interaction between the OH groups of the unreacted diols and $SnCl_2$, providing further information on the mechanism for the catalytic monoalkylation of vicinal diols by the $SnCl_2/CR_2N_2/MeOH$ system. In methanol, N,N-dimethylformamide and dimethylsulphoxide, no interaction between $SnCl_2$ and the diols was observed, presumably due to preferential coordination by these donor solvents to the tin atom.*

Introduction

An investigation of the interaction of tin compounds with carbohydrates and related molecules is of considerable importance in connection with their use as wood preservatives [1, 2], homogeneous catalysts for the selective alkylation of polyhydroxylated compounds [3], and as potential flame-resist treatments for cellulosic fibres, such as cotton [4, 5].

As part of a continuing study into the nature of these interactions [3], we now report ^{13}C and ^{119}Sn NMR spectroscopic data on solutions containing tin(II) chloride and the vicinal diols, 1,2-ethanediol, and *cis-* and *trans-*1,2-cyclohexanediol, in acetone and methanol. Additionally, the recent report by Alföldi *et al.* [6], that methyl α-*L*-rhamnopyranoside forms a complex with $SnCl_2$ in acetone, has prompted us to communicate our own results on this system.

Experimental

NMR Spectra

^{119}Sn NMR spectra were recorded in 10 mm tubes on a JEOL FX60Q spectrometer. ^{13}C NMR spectra were obtained on JEOL FX60Q or JEOL GX270 instruments in 10 mm or 5 mm tubes, respectively. Field frequency lock was to external D_2O.

Syntheses

cis-*1,2-isopropylidenedioxycyclohexane*

This compound was prepared according to the method of Wilson and Read [7].

*methyl 2,3-O-isopropylidene-*α*-L-rhamnopyranoside*

This compound was synthesised as previously reported by Jarý *et al.* [8].

cis-1,2-cyclohexanediol was obtained from ICN Pharmaceuticals Inc., Plainview, New York, and *2,2-dimethyl-1,3-dioxolane* was obtained from Lancaster Synthesis Ltd., Morecambe, U.K. Both chemicals were used as supplied, without further purification.

Results and Discussion

The ^{13}C chemical shifts of 1,2-ethanediol (I), equimolar $SnCl_2$/(I) mixtures in acetone and methanol, and of some related systems, are given in Table I.

It is found that, in acetone, in addition to the solvent peak {$(CH_3)_2CO$, $\delta(^{13}C) = 30.6$ p.p.m.}, four other resonances are present in the $SnCl_2$/(I) solution, and those at 108.6, 64.7 and 25.8 p.p.m. may be assigned to the cyclic acetal, 2,2-dimethyl-1,3-dioxolane (II):

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TABLE I. ^{13}C NMR Chemical Shifts for $SnCl_2$/(I) and Related Systems.

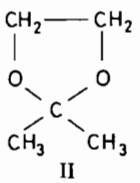
Solution	Solvent	Approximate Concentration (*M*)	R, R, C, O–, O–	^{13}C Chemical Shifts[a]		
				-OCH_2CH_2O-	$HOCH_2CH_2OH$	CH_3
(I)	acetone	0.5			64.1	
(I)/$SnCl_2$	acetone	0.5	108.6	64.7	63.5	25.8
(I)/$SnCl_4$	acetone	0.5	108.6	64.8	61.6	25.8
(I)/HCl[b]	acetone	0.5	108.6	64.9	64.2	25.9
(II)	acetone	0.5	108.6	64.9		25.9
(I)	methanol	0.9			64.2	
(I)/$SnCl_2$	methanol	0.9			64.0	

[a] In p.p.m. (±0.1) downfield from Me_4Si. [b] Solution contains 0.05 ml of 37% w/v HCl in 3 ml acetone.

TABLE II. ^{119}Sn NMR Chemical Shifts for $SnCl_2$/Diol Systems.

Solution	Solvent	Approximate Concentration (*M*)	^{119}Sn Chemical Shift[a]
$SnCl_2$	acetone	0.5	−242.0[b]
$SnCl_2$	acetone	0.4	−223.5[b]
$SnCl_2$/(I)	acetone	0.5	−279[c]
$SnCl_2$/(III)	acetone	0.5	−243[c]
$SnCl_2$/(V)	acetone	0.5	−279[c]
$SnCl_2$/(VI)	acetone	0.4	−255[c]

[a] In p.p.m. relative to Me_4Sn. [b] Error = ±0.5 p.p.m. [c] These peaks are considerably broader than those given by $SnCl_2$ alone in acetone and, consequently, the error in $\delta(^{119}Sn)$ is ±1 p.p.m.



II

since they are, within experimental error, identical to those given by an acetone solution of the pure compound (Table I). The fourth peak, at 63.5 p.p.m., is due to the unreacted diol (I), since the addition of excess (I) to the same solution results in an increase in the relative intensity of this peak, compared to those of the cyclic acetal (II). It is found that only approximately 50% of (I) is converted to (II) by the addition of an equimolar amount of $SnCl_2$, and this suggests the existence of the following equilibrium in solution:

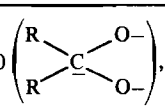
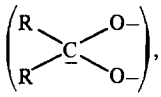
$$(I) + (CH_3)_2CO \overset{SnCl_2}{\rightleftharpoons} (II) + H_2O$$

This is confirmed by the addition of $SnCl_2$ to an equimolar mixture of the acetal (II) and water, in acetone, which results in the appearance of a peak at 63.5 p.p.m., characteristic of (I). It is known [9] that the reaction of vicinal diols with ketones to produce cyclic acetals may be acid catalysed, and, when 0.05 ml of 37% w/v HCl solution was added to 0.1 g of (I) in 3 ml of acetone, the ^{13}C NMR spectrum revealed, as expected, the presence of (II); the peak attributed to (I) appeared at 64.2 p.p.m., which is, within experimental error, identical to that found for the free diol (Table I). The small shift of the ^{13}C resonance of (I) in the presence of $SnCl_2$ (−0.6 p.p.m.), is consistent with a weak interaction between these two species in acetone. In line with this, the addition of an equimolar amount of (I) to a 0.5 *M* solution of $SnCl_2$ in acetone, results in a broad resonance with a shift in $\delta(^{119}Sn)$ of 37 p.p.m. to high field of the uncomplexed $SnCl_2$ (Table II).

Although the $\delta(^{119}Sn)$ value of $SnCl_2$ in acetone is known to be concentration dependent (varying from *ca.* −200 to −245 p.p.m.) [10], the recorded value of −279 p.p.m. for the $SnCl_2$/(I) solution, exceeds the range attributed to this phenomenon. Since the ^{13}C NMR spectrum of this system reveals a mixture of approximately equal amounts of diol (I) and acetal (II), it would be expected in principle that the ^{119}Sn NMR spectrum should show at least two peaks depending on whether or not $SnCl_2$ is complexed to diol (I). However, since only one resonance is observed, this suggests that chemical exchange is occurring, leading to an averaging of ^{119}Sn chemical shifts. It is of interest to note that $\delta(^{119}Sn)$ of 0.5 *M* $SnCl_2$ in DMSO (which is likely to contain the species

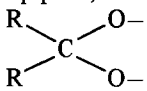
TABLE III. ^{13}C NMR Chemical Shifts for $SnCl_2$/(III) and $SnCl_2$/(V) Systems.

Solution	Solvent	Approximate Concentration (*M*)	^{13}C Chemical Shifts[a]		
			C-1,2	C-3,6	C-4,5
(III)	acetone	0.5	71.1	30.8	22.4
(III)/$SnCl_2$[b]	acetone	0.5	74.1	28.8	21.3
(IV)[c]	acetone	0.3	74.3	29.0	21.5
(III)	methanol	0.9	71.9	30.9	22.7
(III)/$SnCl_2$	methanol	0.9	71.9	30.7	22.5
(V)	acetone	0.5	75.9	33.6	25.0
(V)/$SnCl_2$	acetone	0.5	76.6	33.2	24.7
(V)	methanol	0.9	76.3	34.1	25.3
(V)/$SnCl_2$	methanol	0.9	76.2	33.9	25.1

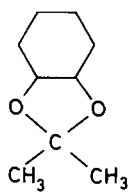
[a] In p.p.m. (±0.1) downfield from Me_4Si. [b] Spectrum also shows peaks at 108.0  , 28.7 (CH_3), and 26.4 (CH_3) p.p.m. [c] Spectrum also shows peaks at 108.0  , 28.8 (CH_3), and 26.6 (CH_3) p.p.m.

$SnCl_2 \cdot 2DMSO$ [11]), has been reported as −364 p.p.m. [12], and this is consistent with DMSO being a strong donor solvent.

The addition of an equimolar amount of $SnCl_4$ to (I) in acetone produces (II) in approximately 50% yield (as with $SnCl_2$), and, in this system, the ^{13}C chemical shift of (I) is −2.5 p.p.m. from that of the free diol. It is known that $SnCl_4$ is a strong Lewis acid [13], and this is reflected in a stronger coordinative interaction with the diol, resulting in a larger change in the ^{13}C chemical shift.

The ^{13}C NMR spectrum, in acetone, of *cis*-1,2-cyclohexanediol (III) in the presence of an equimolar amount of $SnCl_2$ (Table III), revealed, in addition to the three peaks expected for the ring carbon atoms, resonances at 108.0, 28.7 and 26.4 p.p.m., of which the former is characteristic of an  fragment, and the latter two peaks are shown by use of the INEPT pulse sequence [14] to be due to CH_3 groups.

These results again suggest the formation of a cyclic acetal, *cis*-1,2-isopropylidenedioxycyclohexane (IV):



(IV)

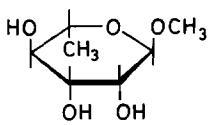
and this is confirmed by comparison with a ^{13}C spectrum of the pure acetal (IV) in acetone (Table III). It is of interest to note that, in this molecule, the methyl groups are inequivalent, due to the stereochemistry of the bicyclic ring system.

In the ^{13}C spectrum of $SnCl_2$/(III) in acetone, the diol (III) is not visible, suggesting that, if an equilibrium does exist, it lies substantially to the right:

$$(III) + (CH_3)_2CO \overset{SnCl_2}{\rightleftharpoons} (IV) + H_2O$$

In contrast to these results, the addition of an equimolar amount of $SnCl_2$ to an acetone solution of *trans*-1,2-cyclohexanediol (V), and a subsequent ^{13}C NMR spectrum, shows no evidence of acetal formation. This is not unexpected, however, since it is known that, with cyclic acetals, only the *cis*-isomers are stable [15]. The change in the ^{13}C chemical shifts (and, in particular, of C-1,2), (Table III), again suggests interaction of $SnCl_2$ with (V), as does the ^{119}Sn NMR spectrum, which shows a broad peak with a chemical shift of −279 p.p.m. (Table II). This is in contrast to the ^{119}Sn chemical shift of −243 p.p.m. shown by the $SnCl_2$/(III) solution in acetone, a value which corresponds to $SnCl_2$ alone in acetone, and, hence, is consistent with the absence of the diol (III).

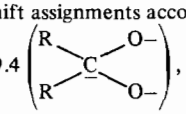
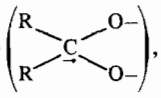
The effect of the addition of $SnCl_2$ to methyl α-*L*-rhamnopyranoside (VI), in acetone, was also investigated, since it has recently been reported [6] that $SnCl_2$ forms a 1:1 donor complex with (VI) in this solvent, in which the tin atom is coordinated to the *cis*-hydroxy groups.

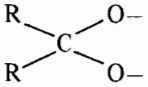


(VI)

TABLE IV. ^{13}C NMR Chemical Shifts for $SnCl_2$/(VI) Systems.

Solution	Solvent	Approximate Concentration (*M*)	^{13}C Chemical Shifts[a]						
			C-1	C-2	C-3	C-4	C-5	C-6	OCH_3
(VI)	acetone	0.4	102.2	72.5	71.8	73.8	68.9	18.1	54.7
(VI)[b]	acetone	0.4	101.8	72.9	72.0	73.9	68.9	17.9	54.7
(VI)/$SnCl_2$	acetone	0.4	101.3[c]	73.6[c]	72.4[c]	74.2[c]	68.6[c]	17.8[c]	55.0[c]
			98.8[d]	(79.6[d],	76.8[d],	75.1[d])	66.4[d]	17.8[d]	54.7[d]
(VII)[e]	acetone	0.4	98.9	(79.7,	76.8,	75.1)	66.4	17.8	54.7
(VI)	methanol	0.5	102.7	72.5	72.2	74.1	69.6	18.0	55.1
(VI)/$SnCl_2$	methanol	0.5	102.5	72.5	72.1	73.9	69.4	17.9	55.1

[a] In p.p.m. (±0.1) downfield from Me_4Si. [b] Chemical shift assignments according to ref. 16. [c] Lines due to unreacted (VI). [d] Lines due to (VII); spectrum also shows resonances at 109.4  , 28.4 (CH_3), and 26.6 (CH_3) p.p.m. [e] Spectrum also shows resonances at 109.3  , 28.4 (CH_3), and 26.5 (CH_3) p.p.m.

However, in view of our results with the vicinal diols (I) and (III), we anticipated that acetal formation would again occur in this system. Figure 1 and Table IV show the ^{13}C NMR spectrum and ^{13}C chemical shifts respectively, of an equimolar mixture of $SnCl_2$ and the sugar (VI) in acetone. The peak at 109.4 p.p.m. is indicative of the presence of a  fragment, and those at 28.4 and 26.6 p.p.m. are shown by the INEPT pulse sequence to be due to CH_3 groups.

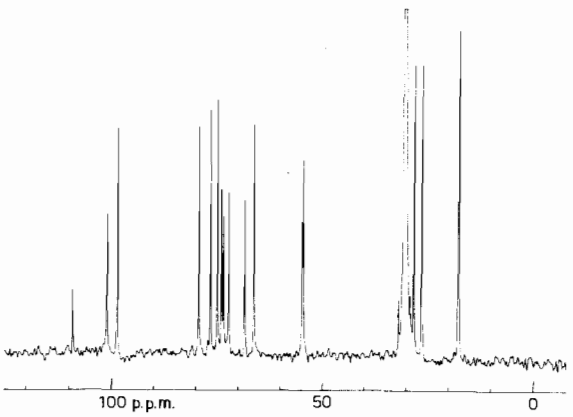
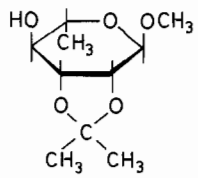


Fig. 1. ^{13}C NMR spectrum of the products of the reaction of equimolar amounts of $SnCl_2$ and (VI) in acetone.

Therefore, these results suggest that the major species present is not a donor complex, but is the cyclic acetal, methyl 2,3-O-isopropylidene-α-*L*-rhamnopyranoside (VII):



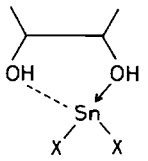
(VII)

This is confirmed by comparison with the ^{13}C NMR spectrum of an authentic solution of (VII) in acetone (Table IV), and, as in the acetal (IV), the methyl groups in (VII) are again inequivalent. The spectrum is in good agreement with the partial ^{13}C spectrum (*ca.* 46–108 p.p.m.), shown by Alföldi *et al.* [6], but we disagree with their assignment involving a $SnCl_2$/(VI) complex. The two methyl peaks which are assigned to the acetal (VII) are not mentioned by Alföldi *et al.* It may be seen in Fig. 1 that, as well as the peaks that have been assigned to the acetal (VII), resonances are present which are due to unreacted (VI). However, Table IV shows that the ^{13}C chemical shifts of these peaks are not identical to those of (VI) in the absence of $SnCl_2$. This is again likely to be due to an interaction of $SnCl_2$ with the sugar, resulting in shifts of –0.9 p.p.m. at C-1; 1.1 p.p.m. at C-2; 0.6 p.p.m. at C-3; 0.4 p.p.m. at C-4; and –0.3 p.p.m. at C-5. Thus, the largest effect occurs at C-2.

The $\delta(^{119}Sn)$ value for a 0.4 *M* solution of $SnCl_2$/(VI) in acetone is shifted to higher field by approximately 31 p.p.m. from $SnCl_2$ (0.4 *M* in acetone), consistent with weak complexation of the *cis*-hydroxyl groups with the tin atom, and the magnitude of the upfield shift is similar to that observed by Alföldi in the same system [6].

It has recently been suggested [3] that, in the selective monomethylation of vicinal diols using

methanol/diazomethane, with $SnCl_2$ as a catalyst, it is probable that only one of the hydroxyl groups is directly coordinated to the tin atom, and that the second OH.... Sn interaction is weaker:



The results obtained for $SnCl_2$/(VI) in acetone are fully consistent with this hypothesis, since, in the ^{13}C NMR spectrum, C-2 is shifted significantly to lower field than C-3. It is therefore expected that selective deactivation of the hydroxyl group on C-2 towards electrophilic attack will occur, and, in line with this, it has recently been shown that selective benzylation of (VI), with benzyl bromide, using $SnCl_2$ as a catalyst, occurs predominantly at C-3 [17].

As mentioned previously, the selective monomethylation reactions are usually, but not always, carried out in methanol solution. In the present study, the effect of adding $SnCl_2$ to solutions of (I), (III), (V) and (VI) in methanol {$\delta(^{13}C)CH_3OH$ = 50.0 p.p.m.}, has been investigated by ^{13}C NMR spectroscopy, but, as can be seen in Tables I, III and IV, within experimental error, the values of $\delta(^{13}C)$ are identical to those of the free diols, indicating that little or no interaction between $SnCl_2$ and the diol is occurring in this solvent, due to preferential coordination by CH_3OH to the tin. Hence, the donor ability towards the tin(II) atom presumably follows the order CH_3OH > diol > $(CH_3)_2CO$, and this is in accord with $\delta(^{119}Sn)$ NMR studies of solutions of $SnCl_2$ in methanol and acetone, which showed [10] that the former solvent invariably gave more negative δ values.

Further confirmation of these ideas was obtained when the ^{13}C NMR spectra of the $SnCl_2$/(I) system in the aprotic solvents, N,N-dimethylformamide (DMF) and dimethylsulphoxide (DMSO), were studied. The lack of change in the ^{13}C shifts of the diol on addition of $SnCl_2$ indicated preferential complexation with the strong donor solvents. In line with this observation, $SnCl_2$ is known to form strong donor complexes with DMF [18] and DMSO [11]. However, in the catalytic reaction involving a small quantity of $SnCl_2$ in methanol, the presence of diazomethane increases the pH of the solution drastically, and results in the formation of $Sn(OCH_3)_2$ [19], to which the diol presumably coordinates*. The possibility of studying the interaction of inorganic tin(II) salts with vicinal diols, by ^{13}C and ^{119}Sn NMR spectroscopy, under the same conditions encountered in the catalytic process, was considered, but this was not possible, due to the very low solubility of $Sn(OCH_3)_2$ in methanol.

Note added in proof: recent ^1H NMR and molecular weight studies [20] on the $[Sn(O^tBU)_2]_2/2\ ^tBuOH$ system, may be interpreted by the formation of an adduct, $Sn(O^tBu)_2 \cdot {}^tBuOH$.

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