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THE USE OF ^{119}Sn NMR FOR THE INVESTIGATION OF ORGANOTIN REACTIONS

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Abstract - Direct ^{119}Sn NMR has been employed as a very useful tool for the investigation of a variety of organotin reactions. The high sensitivity of tin chemical shifts to small structural changes has been used for discrimination between closely related isomers. Thus asymmetric hydrostannation of unsaturated chiral esters has been studied by means of the direct analysis of diastereoisomeric adducts in reaction mixtures. The three different configurational isomers of tetra-sec-butyltin have been distinguished and the results used for stereochemical study of electrophilic cleavage of the tin-carbon bond. Also other asymmetric induction processes have been evaluated. Alternatively ^{n}J(SnD) coupling constants, which are very easily observed after suitable deuterium labelling, have given access to very fruitful information. The Karplus-like angular dependence of ^{3}J(SnD) has been employed to determine the stereochemistry of several organotin Diels-Alder cycloadditions as well as the stereochemistry of alkene hydrostannations. For instance major *anti*-addition was found in the hydrostannation of phenylcyclohexene while *syn*-addition was dominant in the case of norbornene derivatives. The stereochemistry and the regioisomerism of alkyne hydrostannation has also been examined. Finally a complex analytical problem involving the regioselectivity and stereochemistry of the stannylation of allyl tosylates has been solved by the joint consideration of tin chemical shifts and coupling constants.

INTRODUCTION

The Nuclear Magnetic Resonance of tin is becoming an indispensable tool for organotin chemists. Commercially available multinuclear Fourier transform (FT) NMR instruments now easily allow the direct observation of nuclei such as ^{119}Sn (spin 1/2, natural abundance 8.68%).
The ^{119}Sn chemical shifts so far measured show a broad spread of values depending on the substituents or the coordination at the metal centre (1-3). Broad band proton decoupling usually gives narrow single lines and, due to its high sensitivity, the technique is likely to discriminate between closely related compounds or isomers. It must be emphasized that the short relaxation time T_1 of the tin nucleus (4,5) is of special interest for FT NMR because the use of gated decoupling techniques allows the suppression of the negative Overhauser effect of tin and hence permits quantitative determinations by integration.
However it may be difficult or impossible to assign structures on the basis of chemical shifts alone. This is especially true for instance in the case of configurational isomers, and other pieces of information are obviously necessary. In this situation ^{119}Sn NMR may again be of great help by consideration of coupling constants such as ^{n}J(SnH) and especially the expected angular dependence of ^{3}J(SnH). Unfortunately these constants rapidly become impossible to reach as soon as the organic groups bound to tin are complex or different.
We have been able to solve this problem in certain circumstances by performing selective deuterium labelling and observing ^{n}J(SnD) as typical 1:1:1 triplets, under broad band proton decoupling.
The present lecture is intended to illustrate the remarkable usefulness of ^{119}Sn NMR for rapid answers to problems which occurred during our investigation of some organotin reactions. In the first part we will focus mainly on the use of chemical shifts while the second will deal more specifically with coupling constants.

INVESTIGATION OF ORGANOTIN REACTIONS USING ^{119}Sn CHEMICAL SHIFTS

Asymmetric hydrostannation of unsaturated chiral esters

As part of a program devoted to the stereochemistry of cleavage of the non-activated tin-carbon bond, it was necessary to synthesize suitable models with tin linked to chiral carbon centres. Optically active sec-butyltrialkyltins were selected and were first obtained through the hydrostannation route (6) :

$$MeCH{=}CHCO_2(-)Men \xrightarrow[UV]{R_3SnH} MeCHCH_2CO_2(-)Men \xrightarrow[2)\ TsCl\ \ 3)\ LiAlH_4]{1)\ LiAlH_4} MeCHEt$$
$$\qquad\qquad\qquad\qquad\quad SnR_3 \qquad\qquad\qquad\qquad\qquad\qquad\quad SnR_3$$

The organotin hydrocarbons were found to be optically active as a consequence of the asymmetric induction occurring at the ester hydrostannation stage. The optical purities, around 20%, were determined with reasonable accuracy when R = Me from ^1H NMR spectra of the initial adducts : in the presence of a shift reagent, two distinct singlets of unequal intensities were observed and integrated for the trimethylstannyl groups in the diastereoisomeric adducts. The approach became difficult or impossible in the case of hydrostannations performed with tin hydrides in which R was not methyl and we were obliged to develop tedious correlation methods.

Subsequently the use of ^{119}Sn NMR (Note a) allowed fast and accurate determinations by analysis of the crude hydrostannation mixtures, without any shift reagent. For instance :

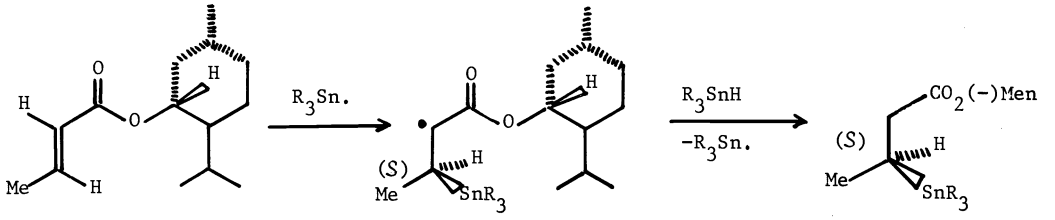
$$\overset{(R)}{R_3SnCHCH_2CO_2(-)Men}\ (Me) \quad \delta_{Sn}\begin{cases} R{=}Me & 10.12\ ppm \\ R{=}nBu & -8.40\ ppm \end{cases} \qquad \overset{(S)}{R_3SnCHCH_2CO_2(-)Men}\ (Me) \quad \delta_{Sn}\begin{cases} R{=}Me & 10.45\ ppm \\ R{=}nBu & -8.18\ ppm \end{cases}$$

We were prompted to use this simple and effective method to study in more detail the stereochemical course of the asymmetric induction process. Typical results obtained on *E* or *Z* isomers, with trimethyltin hydride without solvent, are presented below (7) :

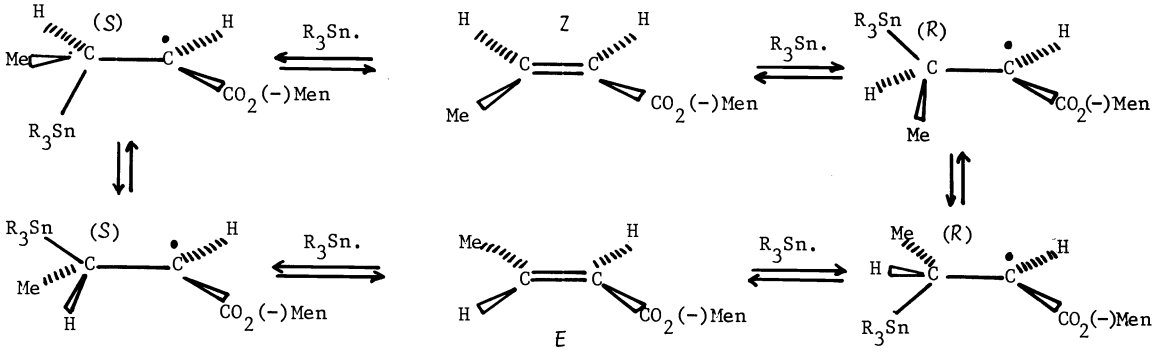
Experiment	Configuration of the substrate	Stoichiometry Me_3SnH/substrate	Temperature (°C)	Configuration at the new chiral centre (enantiomeric excess)
1	*E*	1	50	*R* (21%)
2	*Z*	1	50	*R* (18%)
3	*E*	3	-50	*R* (12%)
4	*Z*	10	-50	*S* (5%)

Prelog-type models for asymmetric induction allow good prediction for a large number of experiments and suffer only a few exceptions. In the case of α,β-unsaturated esters, the models involve *transoïd* conformations for the substrates and, according to the widely accepted mechanism for radical hydrostannation, an excess of the *S* configuration is to be expected from the *E*-crotonate :

Note a. All the determinations reported in the text have been recorded at 33.54 MHz on a Brucker WH 90 instrument, fitted with a Nicolet BNC 12 computer (4k program - 4k acquisition memory). Unless otherwise stated the solvent was deuterated benzene with concentrations in the range 30-80%. Chemical shifts are related to tetramethyltin.



It is clear that experiment 1 (as well as similar ones from nBu_3SnH and iBu_3SnH (6)) reveal anti-Prelog behavior. It is striking however that experiment 2 also led to a predominant *R* configuration and, at the same time, the unreacted ester showed almost complete isomerization to the *E* configuration. Geometrical isomerization accompanying hydrostannation is directly related to the reversibility of the addition of the organotin radical. Thus it was important to be able to slow down the isomerization process and accelerate the hydrogen transfer in order to avoid possible thermodynamic control (rapid interconversion of the diastereoisomeric radicals) :



Experiments were made at lower temperature and increased concentrations of tin hydride. At -20°C and especially at -50°C (exp. 3 and 4) it can be seen (Fig. 1) that *E* and *Z* isomers tend to give products with opposite configurations, in both cases the reverse of what would have been predicted on the basis of Prelog's models.

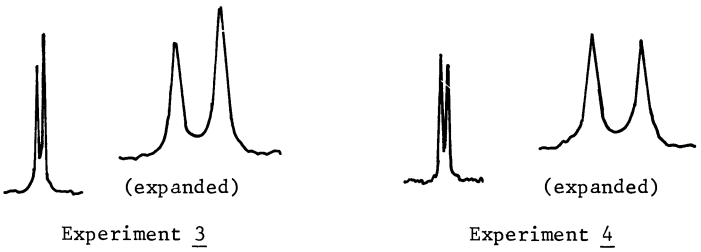
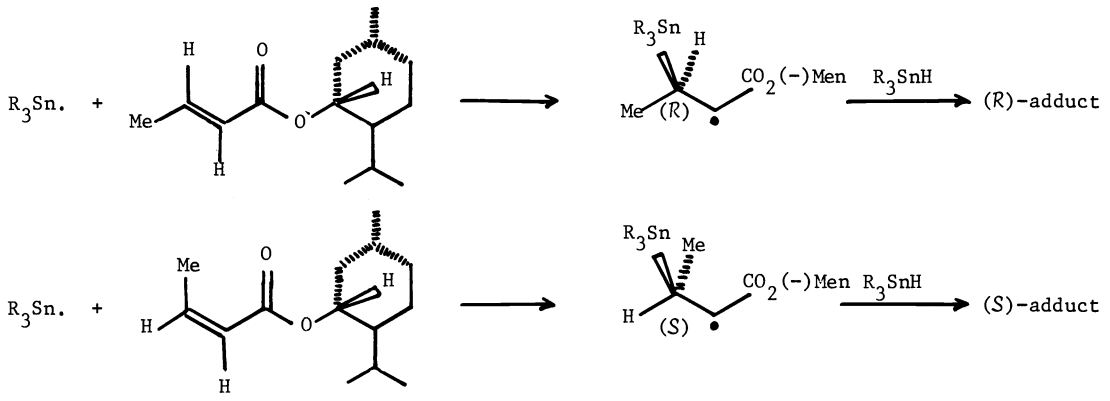
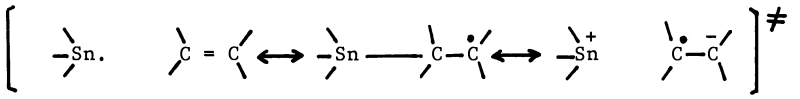


Fig.1. Asymmetric induction at -50°C. Experiment 3 : *E*-crotonate ; Me_3SnH/substrate : 3 - Experiment 4 : *Z*-crotonate ; Me_3SnH/substrate : 10.

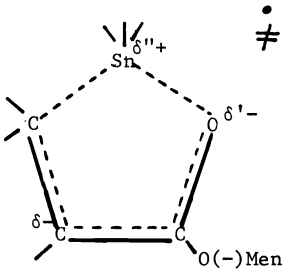
To rationalize these data we have suggested that the results could be ascribed to esters actually reacting in the *cisoïd* conformations :



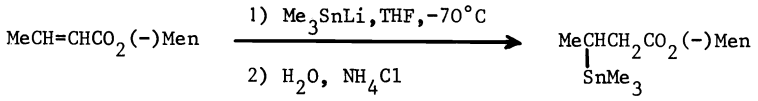
The proposal is based on the polar effects associated with radical hydrostannations. Trialkylstannyl radicals are nucleophilic and the transition states may be described by charge separated canonical forms :



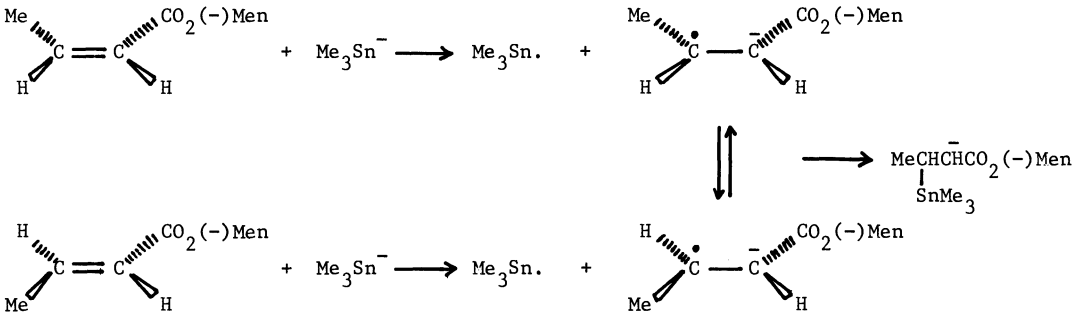
In the case of α,β-unsaturated esters the negative charges can be delocalized and the *cisoïd* conformations would allow stabilization of the transition states through electrostatic interaction :



A very different stereochemical outcome was observed when the same compounds were made by addition of a triorganostannylanion on menthyl crotonates (8). For instance, trimethylstannyllithium was added in high yields on either E or Z isomer :

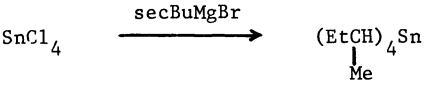


In both cases, ^{119}Sn NMR analysis revealed an excess of *ca* 13% in favor of the *S* configuration at the new chiral centre. In addition, the unreacted ester was recovered with almost no E-Z isomerization. A one electron transfer process, which appears to be a potential route for stannylanion reactions (9), could justify these data taking into account equilibrium between diastereoisomeric radical anions, in the same way as similar Grignard reagent additions (10) :



Synthesis and reactivity of tetra-sec-butyltin

Another illustration of the very high sensitivity of ^{119}Sn NMR was found during the synthesis of "tetra-sec-butyltin" (11) :



The sample could not reasonably be a single compound since there are four identical chiral centres around tin. Symbolizing by *R* or *S* the configurations of each centre, three diastereoisomeric compounds are expected :

$$(S_4Sn + R_4Sn) \quad , \quad (S_3RSn + R_3SSn) \quad \text{and} \quad S_2R_2Sn$$

Interestingly, S_2R_2Sn is intrinsically optically inactive due to the presence of an alternating fourfold axis. The amounts of isomers can be predicted with sufficient confidence as almost random introduction of *R* and *S* groups should occur (very slight asymmetric induction is to be expected from the first introduced sec-butyl group).

Analysis of the mixture by ^{13}C NMR did not lead to any discrimination of the isomers. On the other hand ^{119}Sn NMR ($CDCl_3$ + DMSO-d_6) showed three different signals (Fig. 2) and the quantitative determination was close to the expected theoretical values :

	S_2R_2Sn	$(R_3SSn + S_3RSn)$	$(R_4Sn + S_4Sn)$
δ_{Sn} ppm	-45.20	-45.34	-45.76
found %	35.8	49	15.2
theoretical % (random substitution)	37.5	50	12.5

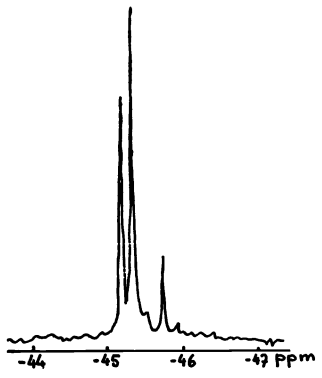


Fig. 2. ^{119}Sn NMR spectrum of "tetra-sec-butyltin".

This observation, only possible through the use of ^{119}Sn NMR, also gave access to the stereochemistry of bromine cleavage of a sec-butyl group in tetra-sec-butyltin (in addition to similar results for the cleavage of other sec-butyltrialkyltin compounds (12)) :

$$(EtCH(Me))_4Sn \xrightarrow[MeOH,\ C_6H_{12}]{Br_2} (EtCH(Me))_3SnBr + EtCHBr(Me)$$

A sample of dextrorotatory material was made from (S)-(+)-2-triphenylstannylbutane according to :

$$Ph_3SnCHEt(Me) \xrightarrow{Br_2} Br_3SnCHEt(Me) \xrightarrow{secBuMgBr} (EtCH(Me))_4Sn$$

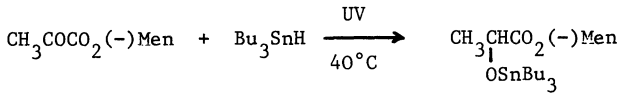
Its ^{119}Sn NMR spectrum was, as expected, identical to that obtained previously from the Grignard reaction of tin tetrachloride indicating, if the starting material had been optically pure, the following approximate composition :

$$S_4Sn\ 12.5\% \quad S_3RSn\ 37.5\% \quad S_2R_2Sn\ 37.5\% \quad R_3SSn\ 12.5\%$$

A brominolysis experiment, monitored by ^{119}Sn NMR, showed that the three diastereoisomeric compounds presented essentially the same reactivity towards the electrophile. With the reasonable assumption that S_3RSn (or R_3SSn) would show very similar rates for R or S group abstraction (random cleavage), a complete stereospecific cleavage of one group, with retention of configuration, would give sec-butyl bromide as a 5/8 S + 3/8 R mixture (25% enantiomeric excess). The actual cleavage gave an overall retention of configuration (7.5% enantiomeric excess) meaning roughly 35% stereospecificity (the sec-butyltriphenyltin used was only 86% optically pure). It is worth mentioning that tri-sec-butyltin bromide should be present as a 1:3 mixture (S_3SnBr + R_3SnBr : 25% ; S_2RSnBr + R_2SSnBr : 75%). However only a broad band was observed in the ^{119}Sn NMR ($CDCl_3$ + DMSO-d_6), possibly due to intermolecular associations.

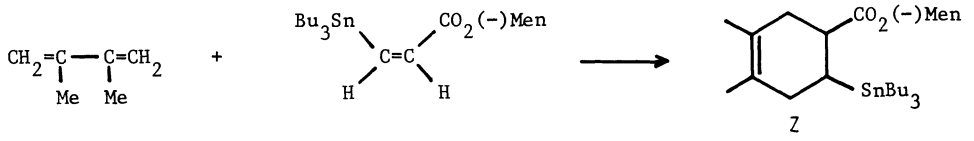
Evaluation of other asymmetric induction processes

Reduction of (-)menthyl acetylformate with tributyltin hydride (13).



Two diastereoisomeric adducts were observed as two sharp singlets at 70.7 and 71.3 ppm ($CDCl_3$), but within experimental error, in the same quantities. Since there is practically no asymmetric synthesis, it is obviously impossible to assign to each signal its corresponding configuration. The related (-)menthyl benzoylformate reacted asymmetrically however with tributyltin hydride with optical purities in the range 5-17% depending on the experimental conditions.

Diels-Alder reaction of 2,3-dimethylbutadiene with (-)menthyl β-tributylstannylacrylate (8).



We will see later how ^{119}Sn NMR was used to determine the stereochemistry of related cycloadditions. Experiments run in different conditions (140°C in sealed tube or 7°C under 10 kbars) led in high yields to the same mixture with two different signals for tin (-12.84 and -14.82 ppm) in relative intensities close to 56:44. It is again impossible, from this limited information, to assign the configurations.

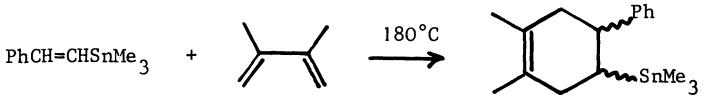
INVESTIGATION OF ORGANOTIN REACTIONS USING ^{119}Sn COUPLING CONSTANTS

As already mentionned $^{n}J(SnH)$ coupling constants might be highly informative but difficult or impossible to determine. They have been obtained indirectly through the immediate observation of $^{n}J(SnD)$ after appropriate deuterium labelling. Several stereo- and regio-isomeric problems were solved in this way (14).

Stereochemistry of organotin Diels-Alder reactions

In an effort to synthesize suitable models for further stereochemical studies, we have examined a series of thermal Diels-Alder cycloadditions and tried to determine their stereochemistry.

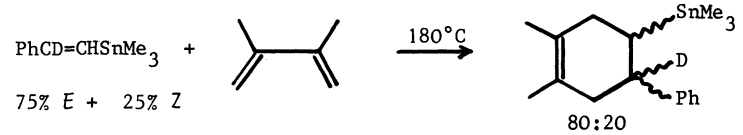
Cycloaddition of 2,3-dimethylbutadiene with styryltrimethyltins (8,14). Two different mixtures of isomeric styryltins were caused to react at 180°C in a sealed tube with 2,3-dimethylbutadiene and led to a similar mixture of diastereoisomeric adducts :



85% E + 15% Z — 89 : 11

30% E + 70% Z — 81 : 19

The non-stereospecificity of the process was found to be associated with an extensive $Z \rightleftharpoons E$ isomerization of the organotin reagent at the temperature of the reaction. The stereochemistry of the more abundant isomer was assigned as E (8) with the help of ^{13}C NMR and chiefly the Karplus-type dependence of $^{3}J(^{117-119}Sn-^{13}C)$ (15). However such a determination requires first the assignment of certain specific carbons and then the search for $^{117-119}Sn$ satellites. A much more convenient determination was made through the use of direct ^{119}Sn NMR and the consideration of $^{3}J(SnD)$. Thus, a mixture of deuterated styryltrimethyltins (easily obtained by deuterostannation of phenylacetylene (16)) was reacted in the same way with the diene :



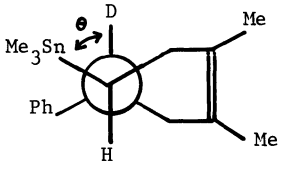
75% E + 25% Z — 80:20

The NMR spectrum of the crude reaction mixture showed two triplets :

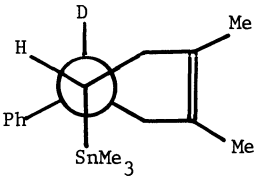
δ_{Sn} : - 3.39 ppm ; $^{3}J(SnD)$: 2.1 Hz for the more abundant isomer

δ_{Sn} : - 5.18 ppm ; $^{3}J(SnD)$: 18.4 Hz for the less abundant isomer

Considering that cyclohexene derivatives tend to adopt half-chair conformations and taking into account the conformational energies of the substituents (3.0 Kcal/mole for phenyl (17) and 0.9 Kcal/mole for trimethylstannyl (18)), the more stable conformations are the following :



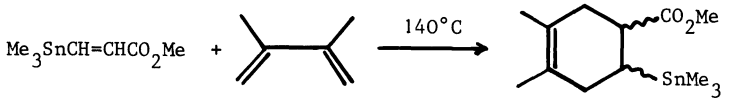
E-isomer



Z-isomer

In agreement with ^{13}C NMR findings (15), $^{3}J(SnD)$ coupling constants can be assigned : 2.1 Hz to the E-adduct (θ = 60°) and 18.4 Hz to the Z-adduct (θ = 180°). These data correspond to the reasonably expected Karplus-like behavior for the angular dependence of $^{3}J(SnD)$.

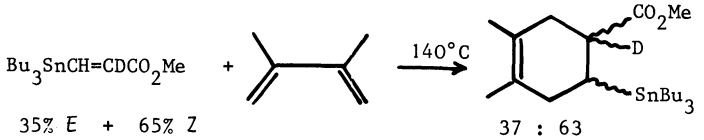
Cycloaddition of 2,3-dimethylbutadiene with β-tributylstannylacrylates (8). Two different experiments have shown cycloadditions with higher degrees of stereospecificity :



92% E + 8% Z — 94 : 6

25% E + 75% Z — 17 : 83

Due to overlapping of signals in the ^{13}C NMR spectra it was not possible to assign the configuration of the major isomer. In order to solve the problem a similar experiment was run with deuterated stannylacrylate (deuterostannation of methyl propiolate (19)):



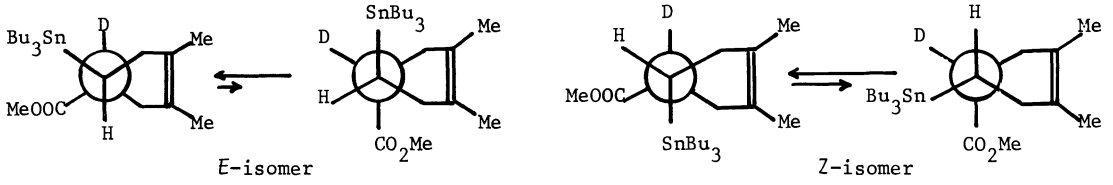
35% E + 65% Z — 37 : 63

The NMR of the crude reaction product showed a triplet and an apparent singlet :

δ_{Sn} : -13.02 ppm ; $^{3}J(SnD)$: 15.2 Hz for the more abundant isomer

δ_{Sn} : -15.55 ppm ; $^{3}J(SnD)$: $<$ 2 Hz for the less abundant isomer

Since the conformational energy of a carbomethoxy group is close to 1.27 Kcal/mole (17), the assignment of the isomers is the following :



θ = 60° θ = 60° θ = 180° θ = 60°

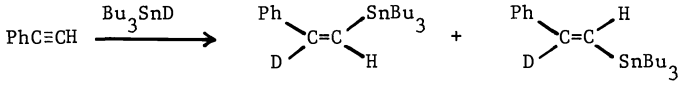
$^3J(SnD)$: < 2 Hz $^3J(SnD)$: 15.2 Hz

The conclusion is that the cycloadditions occured mainly as a stereospecific $\pi_s^2 + \pi_s^4$ process.

It is important to note that the chemical shifts of the E and Z isomers are reversed in comparison with those of the adducts obtained from styryltrimethyltins : in the absence of other information, such as coupling constants, it would be unwise to assign configurations solely on the basis of chemical shifts.

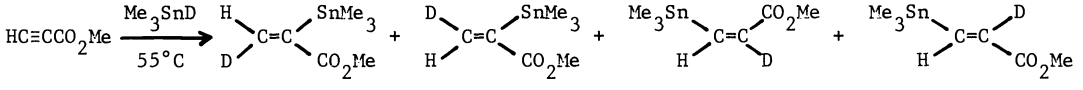
Stereoisomerism and regioisomerism of alkyne hydrostannation

The reaction of tin hydrides (or tin deuterides) with alkynes is known to give usually mixtures of stereo- and regio-isomers. We have found that fast and direct product analysis can be performed by ^{119}Sn NMR. For instance, in the case of phenylacetylene, already studied by ^1H NMR, $^3J(SnD)$ were found to be in agreement with published values for $^3J(SnH)$ (16,19) :



δ_{Sn} ppm	-56.0	-43.2
$^3J(SnD)$ Hz	20.5	9.8

The deuterostannation of methyl propiolate constitutes a more complex case in which the distribution of the adducts was determinedvery rapidly without prior separation of the mixture (other organotin compounds were also present) (19) :



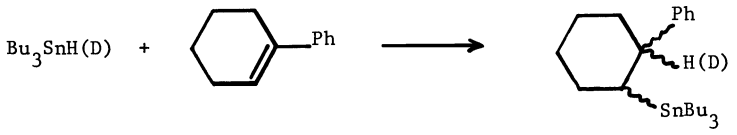
	~60%	~10%	~25%	~5%
δ_{Sn} ppm	-27.8	-27.8	-51.2	-32.5
$^3J(SnD)$ Hz	19.5	9.2	19.5	9.9

It is anticipated that even less favorable cases could be studied as well. For instance the deuterostannation of disubstituted alkynes would give informative ^{119}Sn NMR spectra though in the case of hydrostannation the observation of $^3J(SnH)$ would certainly require excellent signal/noise ratio and ^1H chemical shifts compatible with the observation of tin satellites (19).

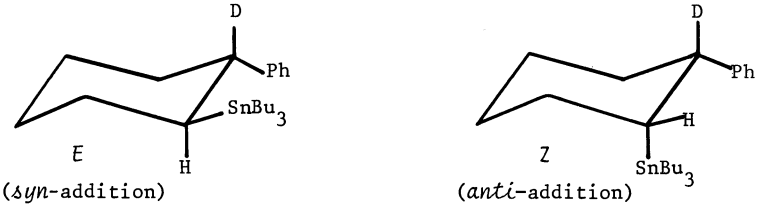
Stereochemistry of alkene hydrostannation

The stereochemistry of alkene hydrostannation has only been studied in a very limited number of cases (20,21). ^{119}Sn NMR has now given direct access to the stereochemistry in the case of cyclohexene and norbornene derivatives (8,14).

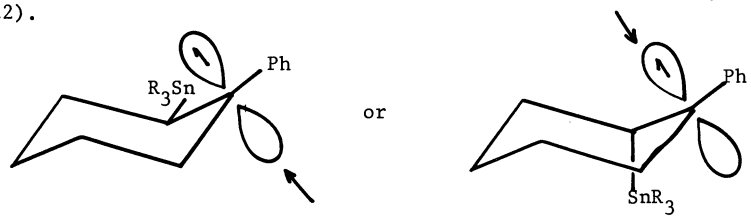
Phenylcyclohexene was reacted with tributyltin hydride at 180°C and gave an adduct in moderate yield, which was increased to over 90% at 50°C under high pressure (10 kbars). Similar results were obtained from tributyltin deuteride :



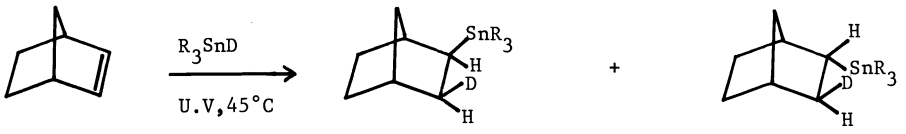
The regioselectivity of the addition was easily demonstrated by the use of ^{13}C NMR (8) but ^{119}Sn NMR allowed direct elucidation of the stereochemistry. Two isomers, shown in their more stable conformations, are expected :



The spectrum showed for the major component an intense triplet at -21.3 ppm with $^3J(SnD)$: 20.5 Hz. Such a value is consistent with a dihedral angle of 180° (*anti*-addition). A similar result was obtained for the addition of trimethyltin deuteride. However, in both deuterostannation experiments a minor signal (~5%) was observed at chemical shifts compatible with *E* isomers, as apparent singlets ($^3J(SnD)$ expected : ~ 2 Hz). The dominant *anti*-addition mechanism can be accounted for by the usual free radical mechanism. After addition of the bulky stannyl group, the deuterium transfer is likely to occur mainly from the less hindered side (22).

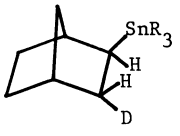


In the case of norbornene, the precise stereochemistry of deuterostannation was also easily determined using ^{119}Sn NMR and the expected angular dependence of $^3J(SnD)$ for 0 and 120°C :

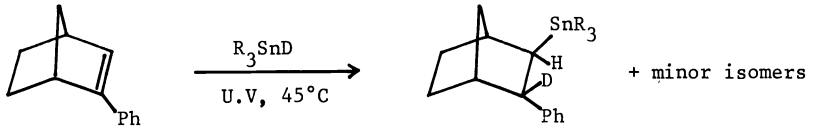


Me_3SnD	~ 90% ; δ_{Sn} : 3.3 ppm	~ 10% ; δ_{Sn} : -0,5 ppm
	$^3J(SnD)$: 16.8 Hz	$^3J(SnD)$: 5.6 Hz
Bu_3SnD	~ 80% ; δ_{Sn} : -13.5 ppm	~ 20% ; δ_{Sn} : -12.4 ppm
	$^3J(SnD)$: 15 Hz	$^3J(SnD)$: 4.8 Hz

In both experiments, a small amount of a third isomer is also slightly apparent under the triplet corresponding to the major adduct : its chemical shift and small coupling constant (5 to 6 Hz) agrees with the following structure :



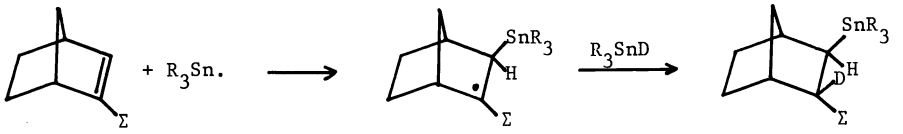
A substituted derivative like 1-phenylnorbornene gave similar data showing more than 80% *syn* addition :



R = Me $^3J(SnD)$: 15.6 Hz (δ_{Sn} : 4.9 ppm)

R = Bu $^3J(SnD)$: 14 Hz (δ_{Sn} : -11.1 ppm)

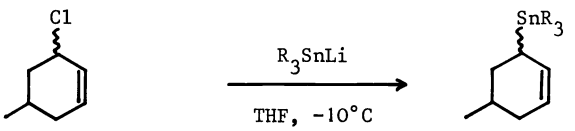
The overall results are consistent with a mechanism in agreement with preferential *exo* entries as usual in the norbornene series (23) :



While the coupling constant approach is very helpful, it must be emphasized that chemical shifts alone cannot be used for the identification of configurations : see for instance the inversion of chemical shifts corresponding to the adducts obtained from norbornene when R = Me or Bu.

Regioisomerism and stereochemistry of the stannylation of allyl tosylates

In this last illustration, consideration of both chemical shifts and coupling constants have led to the resolution of an organotin analytical problem. Allyltin compounds have been extensively studied in the last few years as reagents for organic synthesis. In view of broader applications, it appeared necessary to obtain further insight into the mechanistic and stereochemical aspects of tin-allyl bond cleavage and as a consequence there was a need for the synthesis of suitable stereomodels. We had already shown that direct metallation of isomeric 5-methyl-2-cyclohexenyl chlorides with stannylanions occurred with clean inversion of configuration (24) :

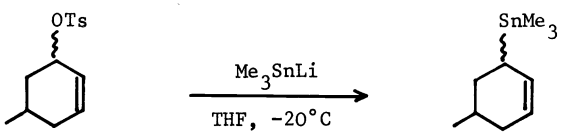


R = Me, Bu

Z → E

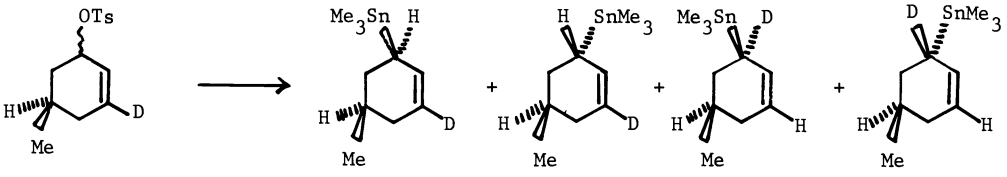
E → Z

Identification of the configurations was made unambiguously with the help of ^{13}C NMR ($^3J(SnC)$). Starting now from the corresponding tosylates we found again tributylstannyllithium giving substitutions with clean inversion of configuration but trimethylstannyllithium, for unclear reasons, much less specific (14,25) :



Z/E : 94/6 E/Z : 28/72

A control experiment, using a deuterated substrate and ^{119}Sn NMR analysis showed indeed that we were not dealing with a clean S_N2-like substitution (Fig. 3) :



Z/E : 94/6	~ 13%	~ 36%	~ 17%	~ 34%
δ_{Sn}	-0.29	-2.72	-0.37	-2.82
$^{n}J(SnD)$	2.6	3.5	12.7	12.9
	(I)	(II)	(III)	(IV)

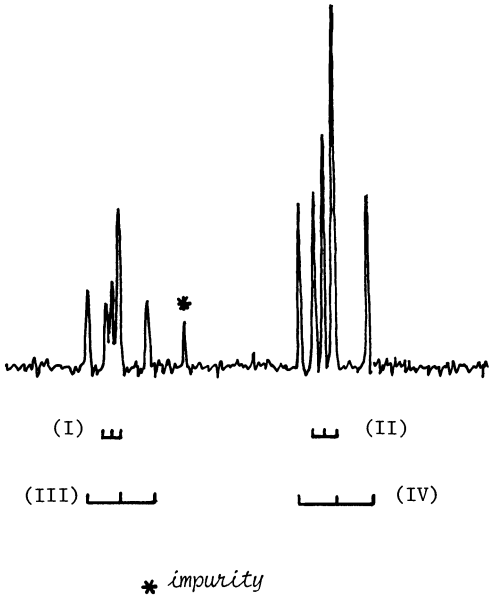


Fig.3. ^{119}Sn NMR spectrum of the mixture obtained from trimethylstannyllithium and deuterated 5-methyl-2-cyclohexenyl tosylate (94% Z + 6% E)

The qualitative and quantitative analysis of this complex mixture was made from a single ^{119}Sn spectrum using the already known chemical shifts and considering $^{2}J(SnD)$ to be larger than $^{4}J(SnD)$ (26). Under suitable experimental conditions the deuterated substrate reacted with tributylstannyllithium with the expected clean inversion of configuration and without deuterium scrambling (8).

CONCLUSION

The examples which have been discussed in this text show how useful ^{119}Sn NMR can be for the investigation of organotin reactions. The high sensitivity of chemical shifts to small structural changes around tin can be very helpful for discrimination and quantitative analysis of closely related isomers. However in many typical cases it can be difficult and it may sometimes be unsafe to assign structures and configurations on this basis only. The coupling constants $^{n}J(SnD)$ which are very easily observed constitute a fruitful complement to chemical shifts. Of course the method applies only whenever a suitable deuterium atom can be introduced at selected places, but this is often possible using accessible reagents like organotin deuterides. In this aspect $^{3}J(SnD)$ promises to be of major value for stereochemical studies since its angular dependence appears to follow the usual Karplus-like behavior. This statement is backed up by independent determinationsusing more conventionnal NMR techniques and already well established results.

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