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STUDIES IN GROUP IV ORGANOMETALLIC CHEMISTRY
XXXI*. ORGANOTIN HYDRIDE ADDUCTS WITH TIN ATOMS IN α,β- OR β,β-POSITIONS

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SUMMARY

The structure of several organotin hydride adducts which previously were assumed to contain tin atoms in β,α-positions (β-addition followed by α-addition) has been reinvestigated. As appeared from NMR spectroscopy the greater part of these linear molecules, polymers and heterocycles are in fact β,β-adducts. Mechanistic aspects of the formation of these compounds have been discussed.

INTRODUCTION

In 1956 and subsequent years a variety of reactions involving organotin hydrides were studied in our laboratory. In particular the thermal hydrostannation (*i.e.* addition reactions of the tin–hydrogen bond in the absence of catalysts) of unsaturated carbon–carbon double and triple bonds was investigated intensively[2-5]. Addition of the organotin group to the terminal carbon atom of terminal ethenes and ethynes seemed to be the rule (β-addition), as was evidenced by independent synthesis and by degradation of various 1/1 adducts[3-6]. In the hydrostannation of non-terminal carbon–carbon double bonds (for example ethyl crotonate) the organotin group became attached to the carbon atom bearing the smallest substituent[2-4,6]. From these facts the conclusion was drawn that the direction of the addition is governed by steric effects[4,6]. As a consequence the 2/1 adducts obtained from the reaction of two moles of triorganotin hydride with one mole of a terminal ethyne were formulated[4,5] as β,α-adducts, *i.e.* adducts in which the second organotin group is bound to the less sterically hindered α-carbon atom (α-addition):

$$\mathrm{H{-}\overset{\beta}{C}{\equiv}\overset{\alpha}{C}{-}R'} \xrightarrow{\mathrm{R_3SnH}} \underset{\beta\text{-adduct}}{\mathrm{R_3Sn{-}\overset{\beta}{C}H{=}\overset{\alpha}{C}H{-}R'}} \xrightarrow{\mathrm{R_3SnH}} \underset{\beta,\alpha\text{-adduct}}{\mathrm{R_3Sn{-}\overset{\beta}{C}H_2{-}\overset{\alpha}{C}H(SnR_3){-}R'}} \qquad (1)$$

Similarly, the cyclic 1/1 adducts [eqn. (2a)] and polymers [eqn. (2b)] derived from diorganotin dihydrides [or bis(organotin monohydrides)] and phenylethyne

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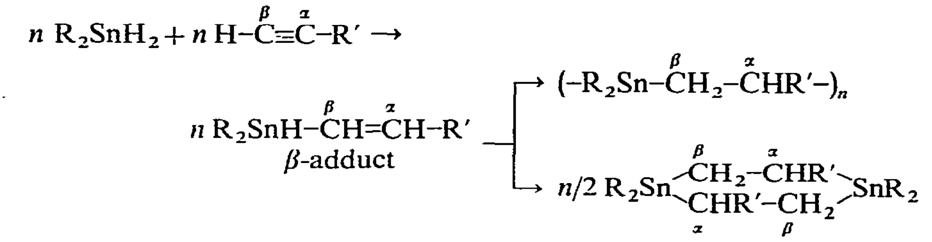
* For Part XXX see ref. 1.

were described by Noltes *et al.*[7-10] as β,α-adducts:



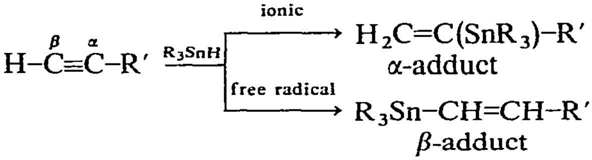
$$n\,R_2SnH_2 + n\,H\text{-}\overset{\beta}{C}\equiv\overset{\alpha}{C}\text{-}R' \rightarrow$$

$$n\,R_2SnH\text{-}\overset{\beta}{C}H=\overset{\alpha}{C}H\text{-}R' \;\; (\beta\text{-adduct}) \rightarrow (\text{-}R_2Sn\text{-}\overset{\beta}{C}H_2\text{-}\overset{\alpha}{C}HR'\text{-})_n \qquad (2a)$$

$$n\,R_2SnH\text{-}\overset{\beta}{C}H=\overset{\alpha}{C}H\text{-}R' \;\; (\beta\text{-adduct}) \rightarrow n/2\,R_2Sn\begin{smallmatrix}\overset{\beta}{C}H_2\text{-}\overset{\alpha}{C}HR'\\ \underset{\alpha}{C}HR'\text{-}\underset{\beta}{C}H_2\end{smallmatrix}SnR_2 \qquad (2b)$$

β,α-adducts

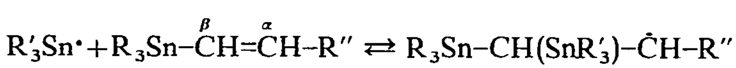
In 1964 Neumann[11,12] and Kuivila[13] proposed a free radical mechanism for both the free radical-catalyzed and the thermal hydrostannation of carbon–carbon unsaturated bonds. Such a mechanism will lead to β-addition upon formation of 1/1 adducts from terminal ethenes and ethynes. However, recently we have shown[14-19] that hydrostannation of carbon–carbon unsaturated bonds can proceed by an ionic as well as by a free radical mechanism. In the case of terminal ethenes and ethynes ionic addition leads to the formation of α-adducts, whereas free radical addition affords mainly or exclusively β-adducts[15,18,19], *i.e.*:



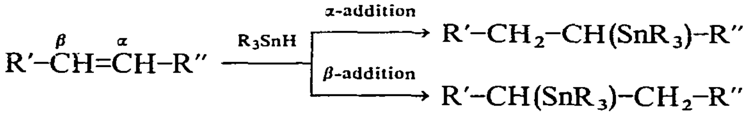
$$H\text{-}\overset{\beta}{C}\equiv\overset{\alpha}{C}\text{-}R' \xrightarrow[R_3SnH]{\text{ionic}} H_2C=C(SnR_3)\text{-}R' \;\; (\alpha\text{-adduct}) \qquad (3a)$$

$$H\text{-}\overset{\beta}{C}\equiv\overset{\alpha}{C}\text{-}R' \xrightarrow[\text{free radical}]{R_3SnH} R_3Sn\text{-}CH=CH\text{-}R' \;\; (\beta\text{-adduct}) \qquad (3b)$$

Moreover, we demonstrated[20] that the *cis–trans*-isomerization of the unsaturated 1/1 adducts obtained from ethynes proceeds by a reversible attack of an organotin radical on the β-carbon atom [eqn. (4)]. On the other hand both α- and β-addition may occur in the hydrostannation of internal carbon–carbon double and triple bonds[16,21-23] [eqns. (5) and (6)]. Consequently, α,β-, β,α- as well as β,β-

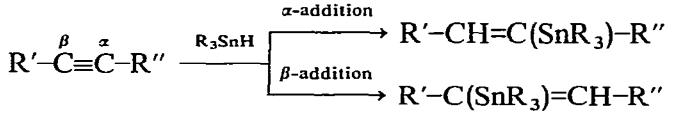


$$R'_3Sn^\bullet + R_3Sn\text{-}\overset{\beta}{C}H=\overset{\alpha}{C}H\text{-}R'' \rightleftarrows R_3Sn\text{-}CH(SnR'_3)\text{-}\dot{C}H\text{-}R'' \qquad (4)$$



$$R'\text{-}\overset{\beta}{C}H=\overset{\alpha}{C}H\text{-}R'' \xrightarrow[\alpha\text{-addition}]{R_3SnH} R'\text{-}CH_2\text{-}CH(SnR_3)\text{-}R'' \qquad (5a)$$

$$R'\text{-}\overset{\beta}{C}H=\overset{\alpha}{C}H\text{-}R'' \xrightarrow[\beta\text{-addition}]{R_3SnH} R'\text{-}CH(SnR_3)\text{-}CH_2\text{-}R'' \qquad (5b)$$



$$R'\text{-}\overset{\beta}{C}\equiv\overset{\alpha}{C}\text{-}R'' \xrightarrow[\alpha\text{-addition}]{R_3SnH} R'\text{-}CH=C(SnR_3)\text{-}R'' \qquad (6a)$$

$$R'\text{-}\overset{\beta}{C}\equiv\overset{\alpha}{C}\text{-}R'' \xrightarrow[\beta\text{-addition}]{R_3SnH} R'\text{-}C(SnR_3)=CH\text{-}R'' \qquad (6b)$$

(R'' = functional group)

addition seems to be possible in the formation of the 2/1 adducts, heterocycles and polymers mentioned above. This induced us to reinvestigate the structure of these hydrostannation adducts, which previously were assumed to be β,α-adducts.

RESULTS AND DISCUSSION*

Hydrostannation of ethyne

In the early work by van der Kerk and Noltes[4,5] the 2/1 adduct from triphenyltin hydride and ethyne was formulated as 1,2-bis(triphenylstannyl)ethane, (I). This structural assignment must be expected to be correct since in the formation of the 2/1 adduct the second organotin group adds in a free radical reaction to the terminal carbon atom of the 1/1 adduct [eqn. (8b)].

$$Ph_3SnH + H\text{-}C{\equiv}C\text{-}H \rightarrow Ph_3Sn\text{-}CH{=}CH_2 \qquad (7)$$

$$Ph_3Sn^{\bullet} + Ph_3Sn\text{-}CH{=}CH_2 \begin{cases} \nrightarrow (Ph_3Sn)_2CH\text{-}\dot{C}H_2 & (8a) \\ \rightarrow Ph_3Sn\text{-}\dot{C}H\text{-}CH_2\text{-}SnPh_3 & (8b) \end{cases}$$

$$\big\downarrow \, Ph_3SnH$$

$$\underset{(I)}{Ph_3Sn\text{-}CH_2\text{-}CH_2\text{-}SnPh_3} + Ph_3Sn^{\bullet} \qquad (9)$$

The NMR spectrum of a sample of the 2/1 adduct prepared in 1956 is in accord with the proposed structure (I) (singlet of the identical protons of the $-CH_2-CH_2-$ group at 1.87 ppm). Compound (I) was also obtained from the reaction of triphenyltin hydride and triphenylvinyltin[24]. Its NMR spectrum is identical to that of the 2/1 adduct obtained from ethyne.

Hydrostannation of methyl ethynecarboxylate

The 2/1 adducts obtained from the reaction of tripropyl- and triphenyltin hydride with this monosubstituted ethyne previously[4,5] were considered to be β,α-adducts. In general, reactions of trialkyltin hydrides with excess of alkyl ethynemonocarboxylates afford mixtures of products, among which the unsaturated α- and β-1/1 adducts are the principal components[16,17,25]. In the reaction of the α-adducts with trialkyltin hydrides the following conversions were observed[16]:

$$R'_3SnH + H_2C{=}C(SnR_3)\text{-}COOR'' \begin{cases} \rightarrow H_2C{=}C(SnR'_3)\text{-}COOR'' & (10a) \\ \rightarrow R'_3Sn\text{-}CH_2\text{-}CH_2\text{-}COOR'' & (10b) \\ \rightarrow R'_3Sn\text{-}CH_2\text{-}CH(SnR_3)\text{-}COOR'' & (10c) \end{cases}$$

In the absence of catalysts the reactions proceed very slowly, in particular the exchange reaction (10a). Addition of AIBN promotes the reactions considerably and thus a free radical mechanism is indicated. For R = R′ only reactions (10b) and (10c) can be observed; from these reactions (10c) is the principal one. For example, the reaction of trimethyltin hydride with a mixture of 82% of methyl α-(trimethylstannyl)acrylate, 8% of methyl *cis*-β-(trimethylstannyl)acrylate and 11% of methyl β-(trimethylstannyl)propionate (obtained under ionic conditions) afforded a mixture of 75% of α,β-adduct (II), 8% of β,β-adduct (IIIa) and 17% of methyl β-(trimethylstannyl)propionate (IVa):

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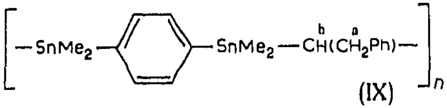
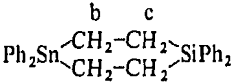
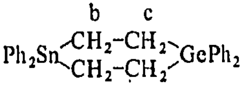
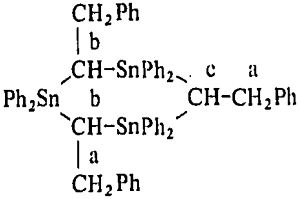
* NMR data of the compounds discussed have been collected in Table 1: chemical shifts are given in ppm downfield from TMS (internal).

TABLE 1

NMR DATA OF COMPOUNDS (I)–(XI)

Compounds		Chemical shifts[a] (ppm[b]) and coupling constants (Hz)					
		$\delta(H_a)$	$\delta(H_b)$	$\delta(H_c)$	$J(H_a\text{-}H_b)$	$J(H_a\text{-}H_c)$	$J(H_b\text{-}H_c)$
$Ph_3Sn\text{-}\overset{b}{CH_2}\text{-}\overset{b}{CH_2}\text{-}SnPh_3$	(I)		s 1.87				
$Me_3Sn\text{-}\overset{b,c}{CH_2}\text{-}\overset{a}{CH}(SnMe_3)\text{-}COOMe$	(II)	dd 2.50	dd 0.89	dd 1.32	4.5[c]	12.4[d]	12.9
$(Me_3Sn)_2\overset{b}{CH}\text{-}\overset{a}{CH_2}\text{-}COOMe$	(IIIa)	d 2.76	t 0.69		6.5		
$(Bu_3Sn)_2\overset{b}{CH}\text{-}\overset{a}{CH_2}\text{-}COOMe$	(IIIb)	d 2.76			7.0		
$(Ph_3Sn)_2\overset{b}{CH}\text{-}\overset{a}{CH_2}\text{-}COOMe$	(IIIc)	d 3.06	t 2.12		5.9		
$Me_3Sn\text{-}\overset{b}{CH_2}\text{-}\overset{a}{CH_2}\text{-}COOMe$	(IVa)	t 2.50	t 0.98		7.5		
$Ph_3Sn\text{-}\overset{b}{CH_2}\text{-}\overset{a}{CH_2}\text{-}COOMe$	(IVb)	t 2.60	t 1.60		7.6		
$Me_3Sn\text{-}\overset{b}{CH}(\overset{c}{CH_3})\text{-}\overset{a}{CH_2}\text{-}COOMe$	(V)	d 2.47		d 1.17	7.0		6.9
$(Ph_3Sn)_2\overset{b}{CH}\text{-}\overset{a}{CH_2}\text{-}Ph$	(VI)	d 3.38	t 2.29		7.8		

$Ph_3Sn\text{-}\overset{b}{C}H_2\text{-}\overset{a}{C}H_2\text{-}Ph$	(VII)	t 3.00	t 1.80		8.2	
$[\text{-}Pr_2Sn\text{-}\overset{b}{C}H(\overset{a}{C}H_2Ph)\text{-}]_n$	(VIIIa)	d 2.99			7.8	
$[\text{-}Bu_2Sn\text{-}\overset{b}{C}H(\overset{a}{C}H_2Ph)\text{-}]_n$	(VIIIb)	d 3.01			7.7	
	(IX)	d 3.19	t 1.49		8.5	
	(Xa)		s 1.63^e	s 1.63^e		
	(Xb)		m 1.71	m 1.83		
	(XI)	d 3.08	t 1.77	t 2.02	7.9	7.9

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[a] See also text for a discussion of the spectra; s: singlet; d: doublet; t: triplet; m: multiplet. [b] Downfield from tetramethylsilane internal. [c] $|J(H_a\text{-}H_b)|$. [d] $|J(H_a\text{-}H_c)|$. [e] Broad signal.

$$\left.\begin{array}{l} \mathrm{H_2C{=}CH(SnMe_3){-}COOMe\ (82\%)}\\ \mathrm{Me_3Sn{-}CH_2{-}CH_2{-}COOMe\ (10\%)}\\ \mathrm{Me_3Sn{-}CH{=}CH{-}COOMe\ (8\%)}\end{array}\right\} \xrightarrow{\mathrm{Me_3SnH}}$$

$$\left\{\begin{array}{ll} \mathrm{Me_3Sn{-}CH_2{-}CH(SnMe_3){-}COOMe} & [\mathrm{(II)}, 75\%]\\ \mathrm{Me_3Sn{-}CH_2{-}CH_2{-}COOMe} & [\mathrm{(IVa)}, 17\%]\\ \mathrm{(Me_3Sn)_2CH{-}CH_2{-}COOMe} & [\mathrm{(IIIa)}, 8\%]\end{array}\right. \qquad (11)$$

The structures of these compounds were established by means of NMR spectroscopy; (II): two $(CH_3)_3Sn$ signals at 0.11 and 0.19 ppm, ABC-pattern of $-CH-CH_2-$ protons; (IIIa): one $(CH_3)_3Sn$ signal at 0.14 ppm, A_2B-pattern of $-CH_2-CH-$ protons.

Obviously hydrostannation of the α-adduct affords the α,β-adduct (together with small amounts of the propionate), whereas hydrostannation of the β-adduct yields exclusively the β,β-adduct. The formation of the latter compound as the sole reaction product from the β-adduct was also demonstrated by the reaction of trimethyltin hydride with almost pure β-adduct (obtained under free radical conditions):

$$\mathrm{Me_3SnH + Me_3Sn{-}CH{=}CH{-}COOMe \rightarrow \underset{(IIIa)}{(Me_3Sn)_2CH{-}CH_2{-}COOMe}} \qquad (12)$$

Thus, in the formation of either of the 2/1 adducts the second organotin group becomes attached to the β-carbon atom. In the free radical addition to the α-adduct such an attack of the organotin radical must be expected[19]. In the hydrostannation of the β-adduct the formation of the β,α-adduct might be envisaged [eqn. (13a)]. Since this adduct is absent in the reaction mixture it is concluded that the free radical (B) is much more stable than the free radical (A). This is in accordance with the results obtained in the hydrostannation of methyl crotonate, which yields exclusively the β-adduct[16] [eqn. (14)].

$$\mathrm{Me_3Sn^{\bullet} + Me_3Sn{-}CH{=}CH{-}COOMe \rightarrow}$$

$$\begin{array}{lll} \not\rightarrow & \mathrm{Me_3Sn{-}\dot{C}H{-}CH(SnMe_3){-}COOMe} & (13a)\\ & \quad\mathrm{(A)} \qquad \hookrightarrow \beta,\alpha\text{-adduct} & \\ \rightarrow & \mathrm{(Me_3Sn)_2CH{-}\dot{C}H{-}COOMe} & (13b)\\ & \quad\mathrm{(B)} \qquad \hookrightarrow \beta,\beta\text{-adduct} & \end{array}$$

$$\mathrm{Me_3SnH + CH_3{-}CH{=}CH{-}COOMe \rightarrow \underset{(V)}{CH_3{-}CH(SnMe_3){-}CH_2{-}COOMe}} \qquad (14)$$

In the reaction of triphenyl-, tripropyl- and tributyltin hydride with the ethynecarboxylate mainly the β-1/1 adducts are formed as the primary products[17,25]. Consequently, the β,β-2/1 adducts will be obtained upon reaction with excess of the organotin hydrides. This was confirmed by NMR spectroscopy of a sample prepared in 1956 (R = Ph) and of reaction mixtures obtained upon repeating these additions (R = Bu, Ph). In the thermal addition the β,β-2/1 adducts and the β-(triorganostannyl)propionates are formed in a ratio of about 4/1. The purified products described previously[4,5] contain almost exclusively the β,β-adducts [(IIIb), R = Bu; (IIIc), R = Ph; compare Table 1].

Hydrostannation of phenylethyne

Hydrostannation of phenylethyne yields the β-1/1 adduct as the primary product[4,5,17]. As discussed some years ago[16] it must be expected that in the formation of the 2/1 adduct the second organotin group becomes attached to the β-carbon atom:

$$Ph_3Sn^{\bullet} + Ph_3Sn{-}CH{=}CH{-}Ph \nrightarrow Ph_3Sn{-}\dot{C}H{-}CH(SnPh_3){-}Ph \qquad (15a)$$

$$\rightarrow (Ph_3Sn)_2CH{-}\dot{C}H{-}Ph \qquad (15b)$$

$$\xrightarrow{Ph_3SnH} (Ph_3Sn)_2CH{-}CH_2{-}Ph + Ph_3Sn^{\bullet} \qquad (16)$$

(VI)

NMR spectra of a purified sample prepared[4,5] in 1956 (at that time described as the β,α-adduct) as well as of reaction mixtures obtained upon heating the reactants, revealed the presence of the β,β-2/1 adduct (VI) as the sole product (present in >90% yield in the reaction mixtures). The assignment of structure (VI) to the 2/1 adduct is based both on the pattern and on the chemical shifts of the $-CH_2-CH-$ protons in the NMR spectrum. In the spectrum the expected A_2B-pattern is observed. Upon comparing the spectra of compounds (IIIc) and (IVb) (see Table 1) it can be seen that introduction of a second Ph_3Sn-group at the β-carbon atom results in a downfield shift of the α- and β-protons of 0.4–0.5 ppm. In the spectrum of $Ph_3Sn-CH_2-CH_2-Ph$ [(VII), Table 1] these protons are found at 1.80 and 3.00 ppm. Thus, the corresponding protons of (VI) are expected to occur at 2.25 and 3.45 ppm, in fair agreement with the observed values of 2.29 and 3.38 ppm.

Polyaddition polymers from phenylethyne

Organotin dihydrides add to phenylethyne in a 1/1 ratio yielding primarily β-1/1 adducts[8,9]:

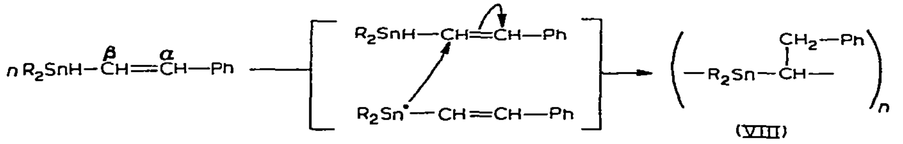
$$R_2SnH_2 + H{-}C{\equiv}C{-}Ph \rightarrow R_2SnH{-}CH{=}CH{-}Ph \qquad (17)$$

Further reaction of these ethylenic tin hydrides yield tin-containing polymers and heterocycles (see below). These polymers were considered[8,9] to have structure (C):

$$[-R_2Sn{-}CH_2{-}CH(Ph)-]_n$$

(C)

However, similar considerations as discussed above suggest that also in these cases the "second" tin atom will be bound to the β-carbon atom:

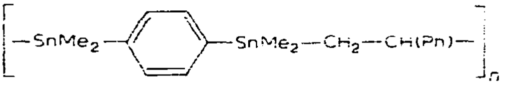


(VIII)

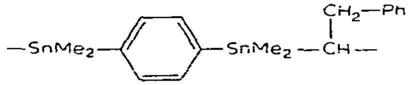
(18)

For R = Pr the NMR spectrum of the polymer showed the A-part of an A_2B-system at 2.99 ppm (J 7.8 Hz). The NMR data (pattern, δ, J and intensity) are completely in accord with structure (VIII), but not with the alternative one (C) mentioned above. A similar spectrum was observed for R = Bu (see also Table 1).

The polymer obtained from *p*-phenylenebis(dimethyltin hydride) and phenylethyne had been formulated[10] as:

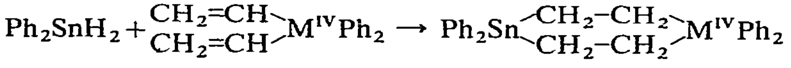


Also in this case the NMR spectrum revealed signals characteristic of the group $Sn_2CH{-}CH_2{-}Ph$. This implies that analogous to the findings above the polymer (IX) contains the structural unit:



Heterocycles from organotin dihydrides

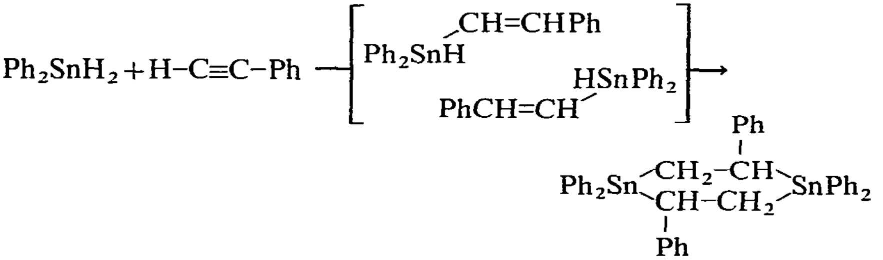
Tin-containing heterocycles can be obtained from the reaction of organotin hydrides with bifunctionally unsaturated compounds. For instance, bimetallic heterocycles were prepared from divinylmetal compounds and diphenyltin dihydride[7]:



$$Ph_2SnH_2 + \begin{matrix} CH_2{=}CH \\ CH_2{=}CH \end{matrix}\!\!>\! M^{IV}Ph_2 \rightarrow Ph_2Sn\!<\!\!\begin{matrix} CH_2{-}CH_2 \\ CH_2{-}CH_2 \end{matrix}\!\!>\! M^{IV}Ph_2 \tag{19}$$

(X)

The assignment of structure (X) to these heterocycles [(Xa), M^{IV} = Si and (Xb), M^{IV} = Ge] is correct, as appeared from NMR spectroscopy (see Table 1). It was thought[7,9] that a 1,4-distanna heterocycle could be obtained from the reaction of diphenyltin dihydride with phenylethyne according to:



$$Ph_2SnH_2 + H{-}C{\equiv}C{-}Ph \rightarrow \left[\begin{matrix} & CH{=}CHPh & \\ Ph_2SnH & & \\ & & HSnPh_2 \\ & PhCH{=}CH & \end{matrix}\right] \rightarrow Ph_2Sn\!<\!\!\begin{matrix} CH_2{-}CH(Ph) \\ CH(Ph){-}CH_2 \end{matrix}\!\!>\! SnPh_2 \tag{20}$$

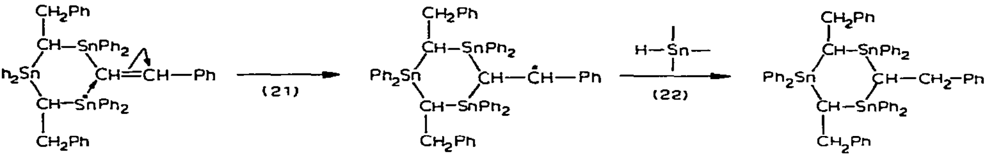
The two products melting at 70–72° (with sintering at 68°) and at 144–145° isolated in low yield from this reaction were believed to be *cis*- and *trans*-1,1,2,4,4,5-hexaphenyl-1,4-distannacyclohexane[7,9]. However, this implies that the heterocycle is formed by β,α-addition to phenylethyne. In analogy to the additions described in previous sections β,β-addition would be expected.

In the NMR spectrum of the high-melting product prepared in 1959 signals due to aliphatic protons were observed at 1.77 (triplet), 2.02 (triplet) and 3.08 (doublet) in a ratio of about 2/1/6. In the spectrum of the low-melting compound similar signals were found in this region together with a broad unresolved signal. Pattern, chemical shifts and ratio of the aliphatic protons of the high-melting product indicate that two types of CH–CH_2–Ph groups (formed by β,β-addition) are present in a ratio of 2/1. Consequently, this product has to be formulated as $[-Ph_2Sn-CH(CH_2Ph)-]_{3n}$ (as will be discussed below a mixture of products or conformers is less probable). Since such a formulation (mol. wt., 1131·n) is incompatible with the molecular weight found previously[7] by the Rast method (mol.wt., 817; $C_{40}H_{36}Sn_2$ calcd.: mol.wt., 754) the molecular weight determination was repeated. In benzene (Vapour Pressure Osmometer) the mol.wt. of the high-melting product was found to be 1118.

Essentially the same products were isolated upon repeating this addition reaction: a crystalline product melting at 139–141° (mol.wt., 1125) and a solid melting at 65–72°. However, the latter product consists of a mixture of compounds as appeared from the melting points and molecular weights of fractions obtained after repeated recrystallization. Both the melting behaviour (softening before melting, "m.p." in the range of 50–55° up to 100–105°) and the molecular weights of these fractions (between 1200 and 1800) suggest that this low-melting product in fact is a mixture of the high-melting heterocycle and low-molecular polymer. This is also in accord with the NMR spectrum.

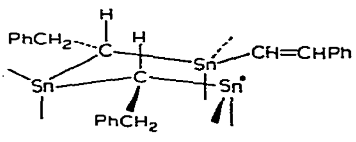
In conclusion, the reaction of diphenyltin dihydride with phenylethyne leads to the formation of polymeric species and a cyclic trimer instead of two isomeric dimers.

The two triplets observed in the NMR spectrum of the trimer apparently arise from axial and equatorial ring protons in a ratio of 2/1. Obviously the rigid heterocycle contains one benzyl group in the unfavourable axial position. The final reaction in the formation of the heterocycle is the ring closure according to:

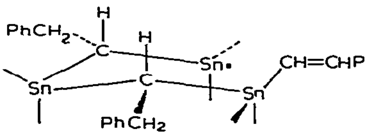


(D) (XI)

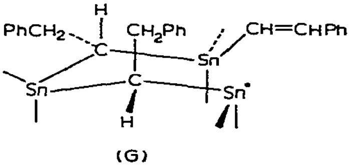
For the free radical (D) two pairs of enantiomers [(E), (F) and (G), (H)] must be envisaged, which need not to be present in equal amounts:



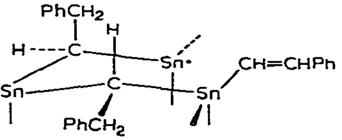
(E)



(F)

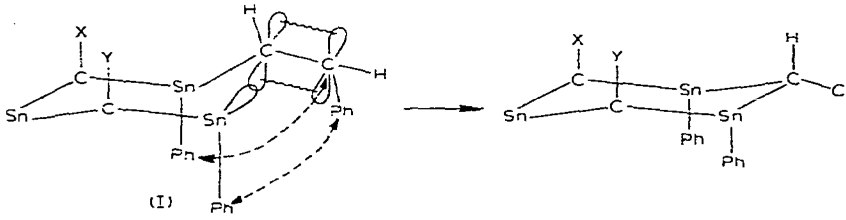


(G)

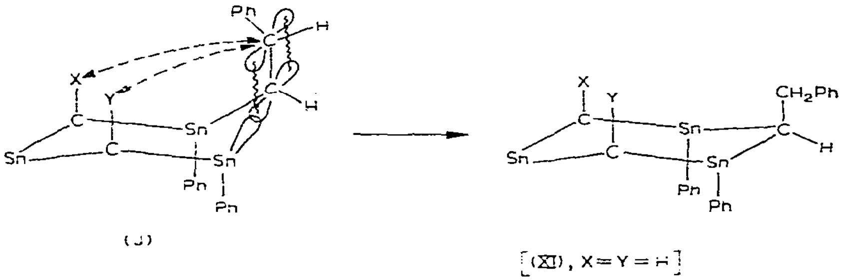


(H)

Ring closure of enantiomers (E) and (F) will occur in the favourable conformers shown above containing two axial hydrogen atoms at the pre-ring. Steric considerations strongly suggest that in this reaction the third hydrogen atom at the ring in the final product will become bound in equatorial position. In transition state (I) (X = Y = H) shown below a severe steric interaction is present between the phenyl groups attached to tin and the unsaturated group. In transition state (J) (X = Y = H) similar interactions are not present and consequently compound (XI) is formed preferentially from the enantiomeric pair (E) and (F).



(I) (23)



(J) (24)

[(XI), X = Y = H]

In the same way it can be shown that the formation of a heterocycle from the enantiomeric pair (G) and (H) is less probable. In this case 1,2-interaction [transition state (I), X or Y = CH_2Ph] or 1,3-interaction [transition state (J), X or Y = CH_2Ph] will retard or even prevent the formation of the heterocycle.

It thus seems that compound (XI) is the main or sole 1,3,5-tristanna-heterocycle as a result of stereochemical control of the ring-closure reaction.

NMR spectra

Relevant NMR data of the compounds discussed have been presented in Table 1. In this Table only the main spectra have been given, *i.e.* the spectra arising from those molecules containing tin atoms with $I = 0$* exclusively.

In general, satellite spectra arising from molecules containing ^{117}Sn ($I = \frac{1}{2}$) and ^{119}Sn ($I = \frac{1}{2}$) are similar to the main spectra. The satellite spectra of β,β-ditin compounds, however, may be quite different from the main spectra. For instance, at 60 MHz the main spectrum of $(Ph_3Sn)_2CHCH_2Ph$ [compound (VI)] consists of a normal A_2K-pattern: the 4 resonances of the A-part appear as two unresolved peaks

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* Natural abundance (%) of tin: $I = 0$ (83.46)[^{112}Sn (0.96), ^{114}Sn (0.66), ^{116}Sn (14.30), ^{118}Sn (24.03), ^{120}Sn (32.85), ^{122}Sn (4.92), ^{124}Sn (5.94)]; $I = \frac{1}{2}$ (16.54)[^{115}Sn (0.35), ^{117}Sn (7.61), ^{119}Sn (8.58)].

(in Table 1 indicated as doublet), the 4 resonances of the K-part appear as 4 peaks ("distorted triplet", in Table 1 indicated as triplet). At 100 MHz the spectrum approaches to an A_2X system. The satellite spectrum due to molecules containing for example one ^{118}Sn and either one ^{117}Sn or one ^{119}Sn atom is not an A_2KY or an A_2XY system as might be expected, but approaches to an AA'XY system [$\delta(H_A)=\delta(H_{A'})$, $J(H_A\text{–}H_X)=J(H_{A'}\text{–}H_X)$, $J(H_A\text{–}Y)\neq J(H_{A'}\text{–}Y)$]* .

EXPERIMENTAL**

Experimental techniques are identical to those described previously (see for example ref. 18).

NMR spectra (Varian Associates A-60*** and HR-100A NMR spectrometers) were run by Miss. L. Veldstra and Mr. J. W. Marsman. Molecular weight determinations (Mechrolab Vapour Pressure Osmometer) were carried out by Miss. H. Alberda. Gas chromatographic analyses (F&M Gas Chromatographs Models 500 and 810) were performed by Miss G. G. de Haan. IR spectra (Grubb Parsons Spectromaster) were run by Mrs. G. E. E. Snijders-Woldringh.

As an example of the procedure followed one experiment has been described below.

Reaction of trimethyltin hydride with methyl α-(trimethylstannyl)acrylate

A mixture of 3.83 g (23.2 mmoles) of trimethyltin hydride, 150 mg (0.9 mmole) of AIBN and 5.8 g of a hydrostannation product containing 82% (19.9 mmoles) of methyl α-(trimethylstannyl)acrylate, 8% (1.9 mmoles) of methyl *cis*-β-(trimethylstannyl)acrylate and 10% (2.3 mmoles) of methyl β-trimethylstannyl)propionate was heated at 55° for 17 h. After this heating period the reaction was complete as appeared from IR spectroscopy (only weak residual Sn–H absorption present). The NMR spectrum of the reaction mixture revealed the presence of methyl α,β-bis(trimethylstannyl)propionate (II), methyl β,β-bis(trimethylstannyl)propionate (IIIa) and of methyl β-(trimethylstannyl)propionate in a ratio of 75/8/17 (overall yield ~100%). Distillation of this product yielded a mixture containing 91% (14.5 mmoles) of (II) and 9% (1.4 mmoles) of (IIIa) as the main fraction (GLC and NMR analysis).

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* A full account of this spectroscopic work will be given elsewhere[26].

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