Tetravinyl Disubstituted Distannoxanes. Disproportionation Reactions to Trivinyltin Derivatives

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The reactions of divinyldiallyltin and carboxylic acids R'COOH (R', = H, CH$_3$, CH$_2$Cl, CHCl$_2$, CCl$_3$, CF$_3$) in water–acetone at room temperature afford the following products: trivinyltin carboxylate for R' = H, CH$_3$; trivinyltin monochloroacetate together with tetravinyl-1-monochloroacetoxy-3-hydroxy-distannoxane (type B) and tetravinyl-1,3-bis(mono-chloroacetoxy)-distannoxane (type A) for R' = CH$_2$Cl; both distannoxanes of type A and B for R' = CHCl$_2$ and CCl$_3$; only that of type A for R' = CF$_3$.

The trivinyltin derivatives having R' = H, CH$_3$, CH$_2$Cl seem to be produced by a disproportionation reaction of the appropriate distannoxanes. This process has been experimentally established for R' = CH$_2$Cl and is favoured by protic media (H$_2$O–(CH$_3$)$_2$-CO, CH$_3$OH) in comparison with aprotic solvents (CH$_3$CN, CHCl$_3$).

Introduction

It is known that tin–allyl bonds in unsymmetric tetraorganotin derivatives are easily and preferentially cleaved by both electrophilic and nucleophilic reagents [1–3].

Previous work has shown that the reactions between R$_2$Sn(CH$_2$–CH=CH$_2$)$_2$ substrates (R = allyl [4], butyl [5] and vinyl [6]) with haloacetic acids R'COOH in protic media have been successfully employed to prepare distannoxanes of type A, (R$_2$-SnOOCR')$_2$O, and/or B, (HO)R$_2$Sn–O–SnR$_2$-(OOCR'). As a part of these studies, we wish to report the results of the divinyldiallyltin reaction with formic, acetic and monochloroacetic acids. In the case of the non-halogenated acids trivinyltin formate or acetate are the main products, whereas both distannoxanes and trivinyltin derivatives are isolated when monochloroacetic acid is employed. The redistribution of the vinyl groups involved in this process has been investigated.

Experimental

Divinyldiallyltin (b.p. 72–74 °C at 17 mm Hg) has been prepared by reacting divinyltin dichloride and allylmagnesium chloride in ethyl ether [6]. All the chemicals and solvents used were of reagent grade. Characterization of the compounds was made by elemental analysis, melting point determination and IR spectra. These were recorded on a Perkin Elmer Model 457 spectrophotometer with KBr optics, using nujol mulls.

Reaction of Divinyldiallyltin and R'COOH Acids in Aqueous Acetone. General Procedure

Equimolar amounts (typically 15 mmol) of the reagents in 50 cm^3 of water–acetone (50/50, v/v) were mixed and kept under stirring at room temperature. The reaction products were isolated at different times. In the cases of the halogenated acid (R' = CH$_2$-Cl, CHCl$_2$, CCl$_3$) precipitates, which were found to be distannoxanes of type B (very slightly soluble in the medium used), were separated by filtration. The other products were recovered from the solutions as solid residues by pumping off the solvent. The various components were separated by fractional crystallization from chloroform–n-hexane mixture.

Reaction of divinyldiallyltin

With formic acid. The main product was trivinyltin formate (m.p. 79–80 °C, lit. [7], 80–81 °C). In addition a poorly defined polymeric product*, which is presumably vinylstannoic acid, was formed.

The yield of the trivinyltin formate attained a maximum of about 50% after 6 days and then decreased. At longer reaction time, the amount of the polymeric product was increased.

With acetic acid. Trivinyltin acetate (m.p. 159–160 °C, lit. [8], 159–160°, 161–162 °C) together with a polymeric substance were the products.

In this case also the yield of the trivinyltin derivative increased with time (up to about 50% after 7 days) and decreased at longer reaction time. It was found that the yields were not affected by changing

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*The mass spectrum of this product showed fragments with mass higher than 800.
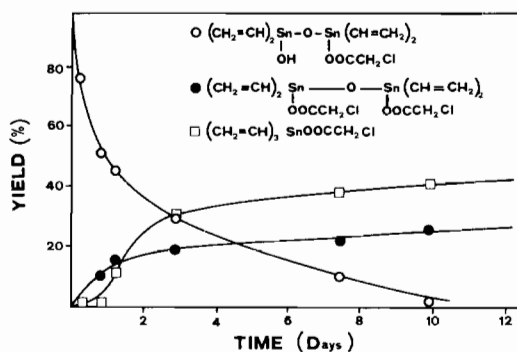
Figure 1. Distributions of the products in the reaction of divinyl diallyltin and monochloroacetic acid at room temperature.

the reactant ratios (CH_3COOH/R_2SnR_2') from 0.5 to 10.

With monochloroacetic acid. As shown in Fig. 1 several products were obtained from this reaction. At the initial stage of the reaction only tetravinyl-1-monochloroacetoxy-3-hydroxydistannoxane was found as precipitate (m.p.: dec. over 240 °C. Found: C, 25.68; H, 3.13; Cl, 7.61. $C_{10}H_{15}O_4ClSn_2$ calcd.: C, 25.44; H, 3.20; Cl, 7.51%). It subsequently disappeared: trivinyltin monochloroacetate (m.p. 129–130 °C, lit. [8], 127–128 °C), tetravinyl-1,3-monochloroacetoxydistannoxane (m.p. at 175 °C, found: C, 26.51; H, 3.05; Cl, 13.06. $C_{12}H_{16}O_5Cl_2Sn_2$ calcd.: C, 26.27; H, 2.94; Cl, 12.9%) together with a polymeric product were obtained.

With dichloro-, trichloro-, trifluoro-acetic acids These previously published reactions [6] have been reexamined in order to check the yields of the products at different times. Distannoxanes A, in solution, and B, as precipitate, were formed with

dichloro- and trichloro-acetic acids. After few hours the amounts of the two products were about the same. At longer reaction time the distannoxane B disappeared and the yield of distannoxane A increased up to about 80%. Only tetravinyl-1,3-trifluoroacetoxydistannoxane (90% after 32 h) was obtained, in solution, with trifluoroacetic acid.

Disproportionation of Tetravinyl-1-monochloroacetoxy-3-hydroxydistannoxane (type B) in Water–Acetone
The reaction has been performed by stirring, under heterogeneous conditions, distannoxane of type B (10 mmol) in water–acetone (50 cm³). Trivinyltin monochloroacetate (yield up to 90% after 10 days) was obtained together with a polymeric product.
The formation of trivinyltin monochloroacetate also has been established in methanol, acetonitrile and chloroform with low yield (10 ~ 20% after 10 days).

Disproportionation of Tetravinyl-1,3-haloacetoxydistannoxane (type A)
Similar reaction as above has been performed by using the distannoxane of type A. For example, a yield of 75% of the trivinyltin derivative was obtained after 10 days with the monochloro derivative. However, the dichloro-, trichloro- and trifluoroacetoxy derivatives did not undergo analogous disproportionation but were recovered unchanged.

Discussion

The results obtained in the reactions of the $(CH_2=CH)_2Sn(CH_2-CH=CH_2)_2$ substrate with $R'COOH$ acids are summarized in the following scheme,
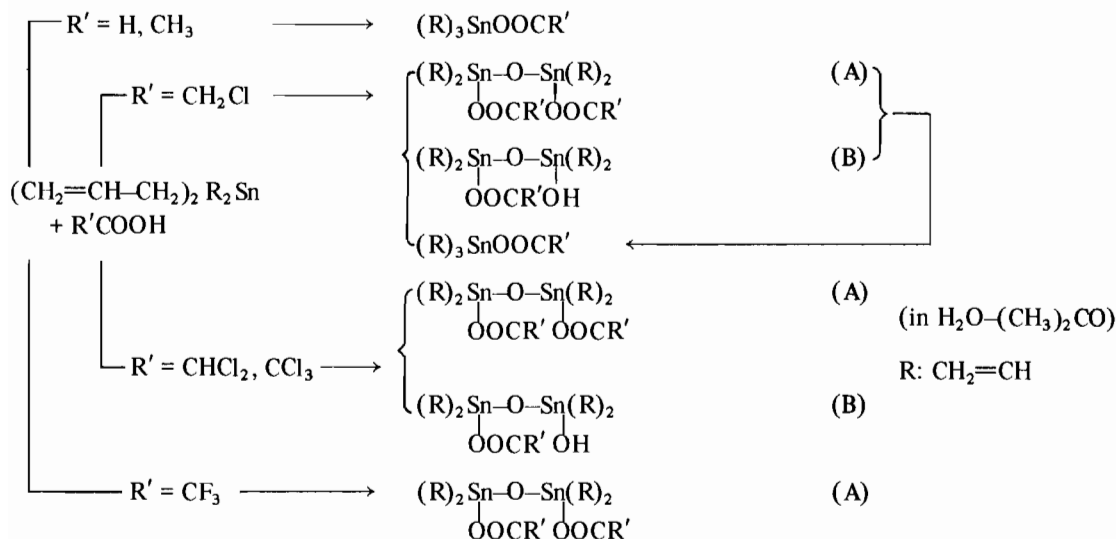
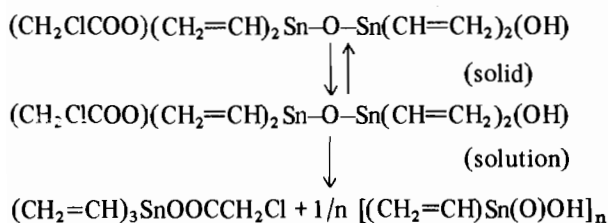TABLE 1. Products Arising from the Reactions of Mixed Allyltin with Carboxylic Acids at Room Temperature.

R'COOH R'	Substrate		
	$(CH_2=CH)_2 Sn(CH_2-CH=CH_2)_2$ [b] (this work and ref. 6)	$(n-C_4H_9)_2 Sn(CH_2-CH=CH_2)_2$ (ref. 5)	$(CH_2=CH-CH_2)_4 Sn$ [a] (ref. 4)
H	Trivinyltin formate[c]	$Bu_2(CH_2=CH-CH_2)SnOOCH$ [a] Distannoxane B[a]	$(CH_2=CH-CH_2)_3SnOOCH$
CH_3	Trivinyltin acetate[c]	$Bu_2(CH_2=CH-CH_2)SnOOCCH_3$ [a] Distannoxane B[a]	$(CH_2=CH-CH_2)_3SnOOCCH_3$
CH_2Cl	Trivinyltin haloacetate Distannoxane A[d] Distannoxane B	Distannoxane A[a] Distannoxane B[b]	Distannoxane A
$CHCl_2$	Distannoxane A Distannoxane B	Distannoxane A[a,b]	Distannoxane A
CCl_3	Distannoxane A Distannoxane B	Distannoxane A[a] Distannoxane B[b]	Distannoxane A
CF_3	Distannoxane A	Distannoxane B[a,b]	

[a]Medium used: wet methanol. [b]Medium used: water–acetone mixture. [c]Together with vinylstannoic acid. [d]Yields dependent on time (see Fig. 1).

The main points are: (i) trivinyltin carboxylates are recovered when R' = H, CH₃ and CH₂Cl; (ii) in some cases (R' = CH₂Cl, CHCl₂ and CCl₃) both distannoxanes are prepared in a ratio which is dependent on time; (iii) the distannoxane of type A is isolated with R' = CF₃.

These findings emphasize that the vinyl system works differently from those previously reported [4–5], as can be seen from Table I.

It is noteworthy that both tetravinyl-monochloroacetate distannoxanes of type A and B disproportionate to give trivinyltin carboxylate and a polymeric product:

$(CH_2ClCOO)(CH_2=CH)_2 Sn-O-Sn(CH=CH_2)_2(OH)$

$\downarrow\uparrow$ (solid)

$(CH_2ClCOO)(CH_2=CH)_2 Sn-O-Sn(CH=CH_2)_2(OH)$

$\downarrow$ (solution)

$(CH_2=CH)_3SnOOCCH_2Cl + 1/n\ [(CH_2=CH)Sn(O)OH]_n$

It may be inferred that this is the reaction route also to trivinyltin formate and acetate for which the corresponding distannoxanes were not isolated. It appears qualitatively that the disproportionation reaction of compound of type B is faster than that of compound of type A, and with respect to the media used the following velocity trend is indicated:

$$(H_2O-(CH_3)_2CO) \gg CH_3OH > CHCl_3 = CH_3CN.$$
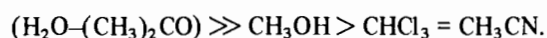
It is known [4, 5, 9, 10] that in chloroform solution a dimer ⇄ monomer equilibrium is established with distannoxanes so that in such a solvent the disproportion reaction must involve these species. By taking into account the structures of distannoxanes of type A (I) and B (II) in solution as previously discussed [11, 12].


(I)   (II)
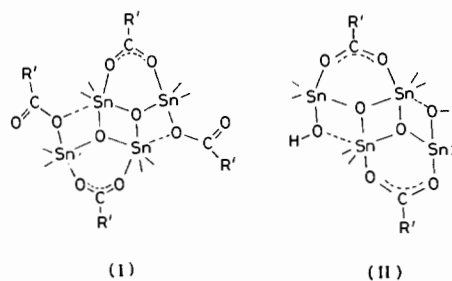
an internal rearrangement, promoted by the presence of the π-electron of the vinyl group [13], may be considered as, for example:
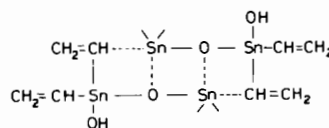

The reaction may be thought of as an electrophilic intramolecular attack by the tin centre on the vinyl group. Examples of disproportionation by a electrophilic attack under mild conditions in polar protic as

well as non protic solvents are common for organotin systems [14–16]. But this would be the first case of disproportionation dealing with disubstituted distannoxanes. These are fairly stable compounds both in solid and in solution. The disproportionation probably is attributable to the particular tendency of the vinyl group to undergo electrophilic attack. Strong electronwithdrawing groups attached to the –COO give more ionic character to the Sn–OCO bond. This may induce a comparable reinforcement of the tin–vinyl and Sn–O–Sn bonds, thus accounting for the stability of haloacetoxydistannoxanes.

In protic media such as methanol and water–acetone a much broader pattern of equilibria will be present, concerning neutral, charged, mononuclear and polynuclear species [17, 18]. Charged species typically arise from equilibria such as:

$$Y(CH_2{=}CH)_2 SnOOCR' + nH_2O \rightleftarrows$$

$$Y(CH_2{=}CH)_2 Sn(OH_2)_n^+ + \bar{O}OCR$$
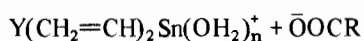
[$Y = (OH)(CH_2{=}CH)_2 Sn{-}O{-}$]. These equilibria favour the products when the base ($R'COO^-$) is weak. Conversely if $R'COO^-$ is a base of significant strength an equilibrium such as

$$Y(CH_2{=}CH)_2 SnOOCR' + nH_2O \rightleftarrows$$

$$Y(CH_2{=}CH)_2 SnOH(H_2O)_{n-1} + HOOCR'$$
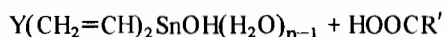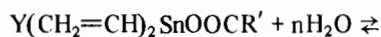
would be predominant, with practically no formation of charged species. In charged species the tin–vinyl bond should be strengthened by the resonance so that in protic solvent the trifluoro- and trichloro-acetoxy derivatives are stabilized over acetoxy- and formoxy- ones.

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