

## 2,2-Functionally disubstituted organotin compounds: synthesis and reactivity

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### Abstract

A series of 2,2-difunctional organotin compounds of the general type  $\text{Me}_3\text{SnCH}_2\text{CHXY}$  ( $\text{X}, \text{Y} = \text{P}(\text{O})\text{R}_2$  or  $\text{C}(\text{O})\text{R}$ ;  $\text{R} = \text{O}^i\text{Pr}$ ,  $\text{OEt}$  or  $\text{Ph}$ ) has been synthesized by stannylmethylation of the appropriate 2,2-difunctional methanides  $\text{Na}[\text{CHXY}]$  with iodomethyl trimethylstannane. Derivatives with phenyl groups on tin cannot be made by this method.

The reactions of the title compounds at the tin atom and at the acidic CH group of the bridging carbon atom and modifications of the functional  $\text{P}(\text{O})\text{R}_2$  and  $\text{C}(\text{O})\text{R}$  groups are described.

*Key words:* Tin; Phosphoryl

### 1. Introduction

Diphosphorylmethanes \*  $\text{H}_2\text{C}[\text{P}(\text{O})\text{X}]_2$  ( $\text{X} = \text{OR}$ ,  $\text{R}$ ) and their derivatives in which the  $\text{CH}_2$  group bears substituents have a variety of applications. Methylene bisphosphonates are of particular interest from the medical point of view [1,2].

In continuation of our investigations on organophosphorus substituted tin compounds [3] we became interested in introducing organotin substituents at the central carbon atom of diphosphoryl methanes. Such derivatives should be of interest in respect of their potential biological activity, and furthermore the presence of two donor groups in the molecule, the Lewis acidity of the tin centre and the presence of the acidic CH function at the bridging carbon atom imply a rich chemistry and interesting structural possibilities. We include in our investigations derivatives bearing  $\text{C}(\text{O})\text{OR}$  and  $\text{C}(\text{O})\text{R}$  groups as substituents at the central carbon atom.

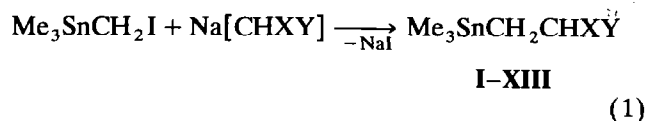
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\* We use the term "phosphoryl" to include all species containing the  $\text{P}=\text{O}$  group (phosphonates, phosphinates and phosphine oxides).

Recently, we presented the first examples of the title compounds [4], and Hutchinson and Fuchs [5] have described the synthesis of  $\text{Me}_3\text{SnCH}_2\text{CH}(\text{PO}_3^i\text{Pr}_2)\text{COO}^i\text{Bu}$ . Below we report the synthesis and reactivity of 2,2-functionally disubstituted organotin compounds of the general type  $\text{Me}_3\text{SnCH}_2\text{CHXY}$  ( $\text{X}, \text{Y} = \text{P}(\text{O})\text{R}_2$  or  $\text{C}(\text{O})\text{R}$ ;  $\text{R} = \text{O}^i\text{Pr}$ ,  $\text{OEt}$  or  $\text{Ph}$ ).

### 2. Results and discussion

A series of the title compounds (Table 1)  $\text{Me}_3\text{SnCH}_2\text{CHXY}$  with (i)  $\text{X} = \text{Y} = \text{P}(\text{O})\text{R}_2$  ( $\text{R} = \text{O}^i\text{Pr}$  or  $\text{Ph}$ ), (ii)  $\text{X} = \text{P}(\text{O})\text{R}_2$ ,  $\text{Y} = \text{C}(\text{O})\text{R}$  ( $\text{R} = \text{O}^i\text{Pr}$  or  $\text{Ph}$ ) and (iii)  $\text{X} = \text{Y} = \text{C}(\text{O})\text{R}$  ( $\text{R} = \text{OEt}$  or  $\text{Ph}$ ) was obtained by the addition of a solution of the corresponding sodium methanide  $\text{Na}[\text{CHXY}]$  to iodomethyl trimethylstannane at 80–100°C; the reaction is depicted as follows:



The related compound  $^i\text{BuMe}_2\text{SnCH}_2\text{CH}(\text{PO}_3^i\text{Pr}_2)_2$  (XIV) was prepared analogously.

Before isolating **II**–**X** and **XIV** by distillation or recrystallization, careful removal of the sodium iodide is necessary because otherwise dealkylation of the phosphonate and phosphinate groups by NaI takes place. The yields of **I**–**XIV** are about 60–75%. Replacement of  $O^iPr$  by OEt in the phosphonate- and phosphinate-substituted methanides results in a drastic fall in the yield.

The identities of **I**–**XIV** were established by NMR and IR data (Table 1), microanalyses and mass spectroscopy.

The presence of two asymmetric centres in the phosphinates **II** and **V**–**VII** gives rise to the appearance of two sets of signals in the  $^{31}P$  and  $^{119}Sn$  NMR spectra due to the existence of the two pairs of diastereomeric enantiomers:  $P(R)C(R)$  and  $P(S)C(S)$ ;  $P(R)C(S)$  and  $P(S)C(R)$ . In addition to the two chiral phosphorus atoms, in compound **IV** the bridging carbon atom is also a centre of pseudoasymmetry [6]. Consequently, the compound exists as two diastereomeric enantiomers ( $P(R)CP(R)$  and  $P(S)CP(S)$ ), which form a racemate, and two *meso* compounds  $P(R)C(r)P(S)$  and

TABLE 1. Physical constants,  $^{31}P$ ,  $^{119}Sn$  NMR and IR data for  $Me_3SnCH_2CHXY$  (**I**–**XIII**) and  $tBuMe_2SnCH_2CH(PO_3^iPr)_2$  (**XIV**)

Compound	X Y	M.p. (b.p. at $10^{-2}$ Torr) (°C)	$\delta^{31}P(X)$ $\delta^{31}P(Y)$ (ppm)	$\delta^{119}Sn$ (ppm)	$^3J(^{119}Sn, ^{31}P(X))$ $^3J(^{119}Sn, ^{31}P(Y))$ (Hz)	Solvent	$\nu(P(X)O)^a$ $\nu(P(Y)O)$ ( $cm^{-1}$ )	$\nu(C(X)O)^a$ $\nu(C(Y)O)$ ( $cm^{-1}$ )
<b>I</b>	$P(O)Ph_2$ $P(O)Ph_2$	148–150	32.0	4.8 (t)	69.0	Dimethyl- formamide	1196	
<b>II</b>	$P(O)Ph_2$ $P(O)(O^iPr)Ph$	65– 72 83– 88	31.0, 31.2 (d) <sup>b</sup> 38.6, 39.4 (d) <sup>b</sup>	2.5 (d/d) –3.5 (d/d)	61.5, 73.8 125.0, 126.6	$CH_2Cl_2$	1197 1216	
<b>III</b>	$P(O)Ph_2$ $P(O)(O^iPr)_2$	45– 50	30.0 23.3	13.0 (d/d)	124.1 71.3	$CH_2Cl_2$	1200 1230	
<b>IV</b>	$P(O)(O^iPr)Ph$ $P(O)(O^iPr)Ph$	78– 88 <sup>c</sup>	38.5 <sup>c</sup> 37–41 (m)	11.5 (t) <sup>c</sup> 15.0 (d/d) 16.0 (t)	96 <sup>c</sup> $\Sigma J = 170$ 80	$CHCl_3$	1212 <sup>c</sup>	
<b>V</b>	$P(O)(O^iPr)Ph$ $P(O)(O^iPr)_2$	(140–150) <sup>d</sup>	37.2 23.0	8.2 (d/d) 9.2 (d/d)	75.2, 86.4 121.0, 139.8	$CH_3OH$	1230	
<b>VI</b>	$P(O)(O^iPr)Ph$ $C(O)Ph$	92– 97	38.6, 36.9	5.9 (d) 8.1 (d)	195.4 221.1	Toluene	1227	1670
<b>VII</b>	$P(O)(O^iPr)Ph$ $C(O)O^iPr$	(150–160)	37.2, 37.6	3.1 (d) 4.0 (d)	207.1 206.3	$CH_2Cl_2$	1219	1723
<b>VIII</b>	$P(O)(O^iPr)_2$ $P(O)(O^iPr)_2$	(90–100) <sup>d</sup>	24.0	3.7 (t)	111.7	Toluene	1241	
<b>IX</b>	$P(O)(O^iPr)_2$ $C(O)Ph$	(120–125)	21.4	6.5 (d)	263.0	$CHCl_3$	1247	1681
<b>X</b>	$P(O)(O^iPr)_2$ $C(O)O^iPr$	(90– 93)	22.2	2.0 (d)	182.0	Neat	1254	1730
<b>XI</b>	$C(O)Ph$ $C(O)Ph$	80– 85		3.6		$CH_3OH$		1668
<b>XII</b>	$C(O)Ph$ $C(O)OEt$	(90– 95)		4.2		Neat		1670 1718
<b>XIII</b>	$C(O)OEt$ $C(O)OEt$	(60)		3.6		$CH_2Cl_2$		1732
<b>XIV</b>	$P(O)(O^iPr)_2$ $P(O)(O^iPr)_2$	(120–140) <sup>d</sup>	23.0	15.0 (t)	106.0	$CHCl_3$	1240	

<sup>a</sup> IR: 2% in  $CCl_4$ .

<sup>b</sup>  $^2J(^{31}P-^{31}P) = 4.5$  Hz.

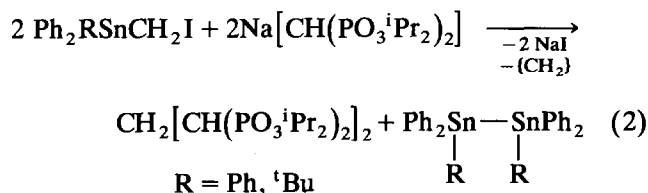
<sup>c</sup> Enriched *meso* compound.

<sup>d</sup> Kugelrohr distillation at  $5 \times 10^{-5}$  Torr; bath temperature in parentheses.

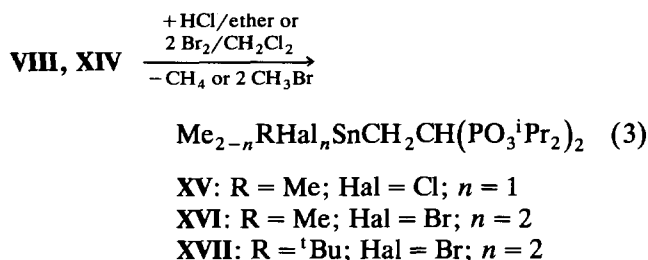
$P(R)C(s)P(S)$ . The phosphorus atoms in the racemate are not equivalent and give rise to the formation of an ABX spin system (A, B =  $^{31}\text{P}$ ; X =  $^{119}\text{Sn}$ ). Each of the two *meso* compounds appears as an  $A_2X$  spin system because in these the phosphorus atoms are equivalent [6c]. By repeated recrystallization from hexane, one of the *meso* compounds of IV was obtained in a highly enriched state. The mixture of the remaining stereoisomers was a waxy solid.

In the EI mass spectra of I–XIV the peak of the molecular ion is weak or not detectable, but all the compounds show an intense peak for the  $[M-\text{CH}_3]^+$  ion. The enhanced stability of this triorganotin cation obviously arises from intramolecular interactions between the donor groups and tin.

When the reaction shown in eqn. (1) is carried out with phenyl- instead of alkyl-substituted iodomethylstannanes, no stannylmethylation of the difunctional methanes occurs. Instead, cleavage of the  $\text{ICH}_2\text{-Sn}$  bond is observed [7]; thus in the reaction of  $\text{Ph}_2\text{RSnCH}_2\text{I}$  (R = Ph,  $^t\text{Bu}$ ) with  $\text{Na}[\text{CH}(\text{PO}_3^i\text{Pr}_2)_2]$  the corresponding distannanes and 1,1,3,3-tetrakis(diisopropoxyphosphonyl)propane were isolated (eqn. (2)):



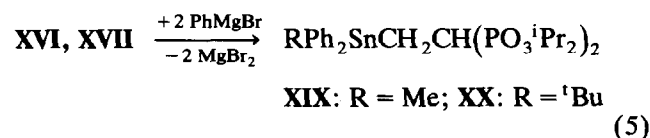
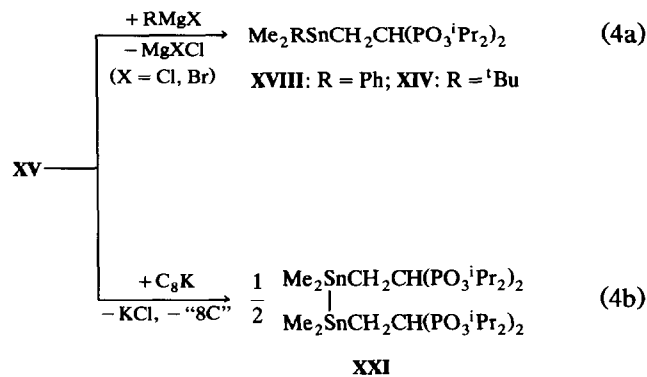
As a consequence of the intramolecular interaction between the functional groups and the tin atom in the transition state [8], treatment of I–XIV with HCl in ether or with bromine in  $\text{CHCl}_3$  results in a regioselective halodealkylation of the methyl groups at tin, as shown for VIII and XIV in eqn. (3):



The monochlorides are formed with HCl in ether, even when an excess of the halogenating agent is used. These compounds can also be prepared by a redistribution reaction of I–XIV with dimethyltin dichloride. The corresponding monobromides can be made by reaction with bromine in a 1 : 1 molar ratio. The dibromides XVI and XVII are formed with an excess of bromine (eqn. (3)).

The halides of I–XIV exhibit intramolecular donor–acceptor interactions and dynamic behaviour in solution, as will be described elsewhere.

We carried out some representative reactions of the tin–halogen bond of XV–XVII with strong nucleophiles. With Grignard reagents both the monohalides and dihalides are alkylated at tin (eqns. (4a) and (5)).



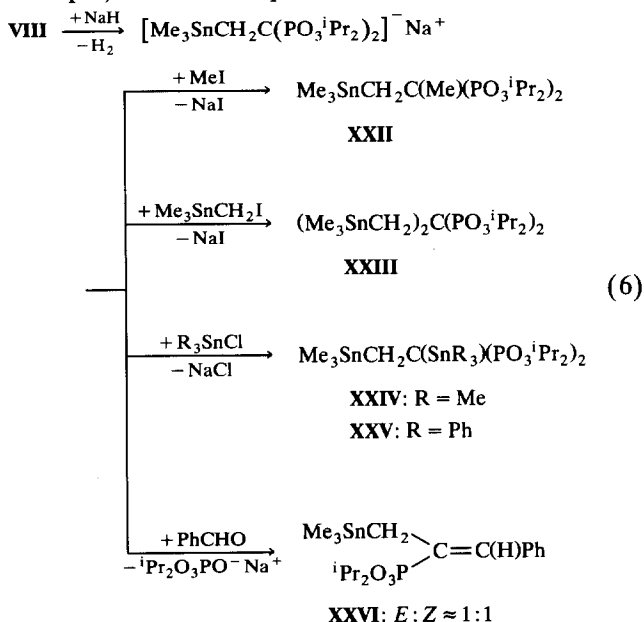
In the case of XV the reaction with  $^t\text{BuMgCl}$  (eqn. (4a)) to XIV is accompanied by a reduction to give the distannane  $[\text{Me}_2\text{SnCH}_2\text{CH}(\text{PO}_3^i\text{Pr}_2)_2]_2$  (XXI) with about 40% yield. Compound XXI can be made with a better yield and higher purity by reduction of XV with one equivalent of potassium graphite ( $\text{C}_8\text{K}$ ) (eqn. (4b)). The presence of a tin–tin bond in XXI is revealed unambiguously by the upfield shift and the triplet–triplet splitting of the  $^{119}\text{Sn}$  NMR signal due to the  $^3J(\text{SnCCP})$  and the  $^4J(\text{SnSnCCP})$  couplings.

The addition of a further equivalent of  $\text{C}_8\text{K}$  to XXI does not give the expected functional potassium stannide as is usually the case with simple hexaorganodistannanes [9]. Instead, there is deprotonation at the central carbon atom to give  $[\text{K}]_2[\text{Me}_2\text{SnCH}_2\text{C}(\text{PO}_3^i\text{Pr}_2)_2]_2$ , as indicated by a broadened  $^{31}\text{P}$  NMR signal, which is situated at  $\delta = 39$  ppm, within the shift range observed for carbanions of methylene bisphosphonates [10]. Addition of further  $\text{C}_8\text{K}$  causes decomposition of XXI.

The successful high yield synthesis of the phenyl-substituted 2,2-bis(diisopropoxyphosphonyl)ethylstannanes XVIII–XX according to eqns. (4a) and (5) shows that the difference in the behaviour of the reaction of  $\text{Na}[\text{CHXY}]$  with  $\text{Me}_3\text{SnCH}_2\text{I}$  (eqn. (1)) and that with phenyl-substituted iodomethylstannanes (eqn. (2)) is not the result of instability of the 2,2-difunctionally

substituted phenylstannanes but of the availability of an alternative reaction path.

The acidic hydrogen atom on the bridging carbon atom, which provides a further reactive centre in the title compounds, can be deprotonated with sodium hydride. The resulting functional carbanions undergo the expected reactions with electrophiles as shown, for example, for **VIII** in eqn. (6):



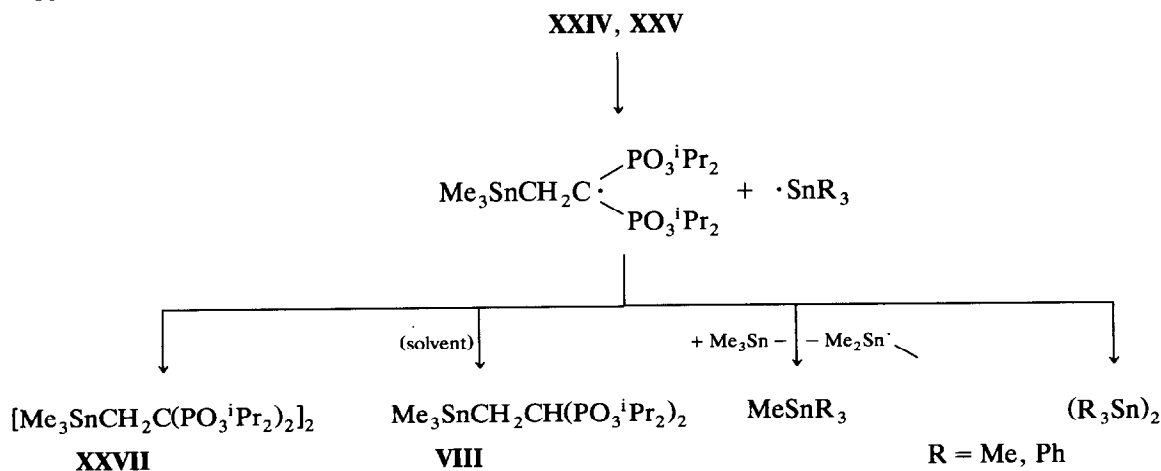
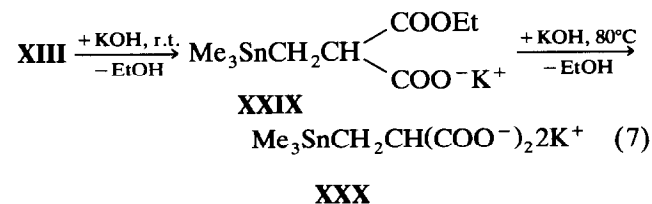
Compounds **XXII** and **XXIII** were isolated with a good yield. The doubled intensity of the tin satellites in the  $^{31}\text{P}$  NMR spectrum of **XXIII** compared with that for **VIII** indicates the presence of two tin atoms in the molecule. The existence of **XXIV** and **XXV** in freshly prepared reaction solutions was established by  $^{31}\text{P}$  and  $^{119}\text{Sn}$  NMR spectroscopy (Section 3), but these compounds decompose rapidly if the reaction mixtures are kept. The mode of decomposition of **XXIV** and **XXV** suggested in Scheme 1 is based on the NMR studies

and the isolation of the products  $\text{MeSnPh}_3$  and  $\text{Ph}_6\text{Sn}_2$ .

After homolytic cleavage of the functionally substituted Sn–C bond the resulting radicals dimerize to give **XXVII** and  $(\text{R}_3\text{Sn})_2$  ( $\text{R} = \text{Me}$  or  $\text{Ph}$ ). The formation of the other stable final products **VIII** and  $\text{MeSnR}_3$  probably results from hydrogen abstraction from the solvent (**VIII**) and methyl group transfer from any of the  $\text{Me}_3\text{Sn}$ -containing species to the  $\text{R}_3\text{Sn}\cdot$  radical respectively.

The Horner reaction of **VIII** with benzaldehyde (eqn. (6)) yields **XXVI** as an equimolar mixture of the *E* and *Z* isomer. This behaviour is in contrast with that of the unsubstituted  $\text{CH}_2(\text{PO}_3\text{Et}_2)_2$  which is converted exclusively into the *E* isomer [10]. Obviously, because of the presence of the  $\text{Me}_3\text{SnCH}_2$  substituent, in the intermediate addition product formed from **VIII** with benzaldehyde neither of the possible conformations that determine the pathway for the phosphate elimination is favoured [10]. The Horner reaction of **X** with benzaldehyde proceeds stereoselectively. Unfortunately, the  $^3J(^{13}\text{C}-\text{C}-^1\text{H})$  coupling in  $\text{Me}_3\text{SnCH}_2(\text{CO}_2^i\text{Pr})_2\text{C}=\text{C}(\text{H})\text{Ph}$  (**XXVIII**), the most useful criterion for distinguishing between the *E* and *Z* isomer [11], is at 8 Hz, in between the limiting values expected for the two isomers.

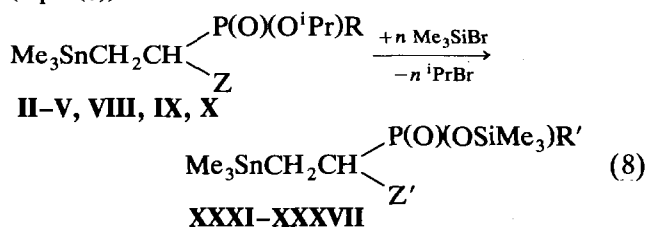
We describe now the derivatization of the functional ester groups in **I–XIV**. The stannylmethylated malonic ester **XIII** can be transformed into its monopotassium and dipotassium salt by stepwise addition of one or two equivalents of potassium hydroxide in alcoholic solution (eqn. (7)):



Scheme 1. Proposed decomposition pathway of  $\text{Me}_3\text{SnCH}_2\text{C}(\text{SnR}_3)(\text{PO}_3^i\text{Pr}_2)_2$  ( $\text{R} = \text{Me}$  (**XXIV**),  $\text{R} = \text{Ph}$  (**XXV**)).

Compounds **XXIX** and **XXX** are soluble in methanol, ethanol and water.

The transformation of the stannylmethylated phosphonates and phosphinates into their free acids was carried out via the silylphosphonates and phosphinates, which can be made by the bromosilane method [12] (eqn. (8)):



	<i>n</i>	R	R'	Z	Z'
XXXI	1	Ph	Ph	P(O)Ph <sub>2</sub>	P(O)Ph <sub>2</sub>
XXXII	2	O <sup>i</sup> Pr	OSiMe <sub>3</sub>	P(O)Ph <sub>2</sub>	P(O)Ph <sub>2</sub>
XXXIII	2	Ph	Ph	P(O)(O <sup>i</sup> Pr)Ph	P(O)(OSiMe <sub>3</sub> )Ph
XXXIV	3	Ph	Ph	P(O)(O <sup>i</sup> Pr) <sub>2</sub>	P(O)(OSiMe <sub>3</sub> ) <sub>2</sub>
XXXV	4	O <sup>i</sup> Pr	OSiMe <sub>3</sub>	P(O)(O <sup>i</sup> Pr) <sub>2</sub>	P(O)(OSiMe <sub>3</sub> ) <sub>2</sub>
XXXVI	2	O <sup>i</sup> Pr	OSiMe <sub>3</sub>	C(O)Ph	C(O)Ph
XXXVII	2	O <sup>i</sup> Pr	OSiMe <sub>3</sub>	C(O)O <sup>i</sup> Pr	C(O)O <sup>i</sup> Pr

At a low reaction temperature and with an excess of Me<sub>3</sub>SiBr, compounds **XXXI-XXXVII** can be isolated with a high purity (<sup>1</sup>H and <sup>31</sup>P NMR) from the reaction mixture after evaporation of the solvent. However, at higher reaction temperatures the formation of the silyl esters **XXXI-XXXVII** is accompanied by a redistribution between bromosilane and the trimethyltin group of the starting compounds to give a very complex mixture.

The <sup>31</sup>P and <sup>119</sup>Sn NMR spectra show that **XXXI**, **XXXIII** and **XXXIV** (in contrast with their precursors **II**, **IV** and **V**) do not exist as stereoisomers despite the presence of two chiral centres in the molecules. This is because of intramolecular 1,3-migration of the trimethylsilyl group between the two oxygen atoms of the silylated phenylphosphinate groups, as described for other chiral silylphosphinates [13].

Hydrolysis of **XXXI-XXXVII** results in the intermediate formation of the corresponding stannylmethylated phosphonic and phosphinic acids, which are unstable and undergo a cyclization by intramolecular attack of an acid group on a tin-bonded methyl group [3a]. The isolated reaction products are 1,2,5-

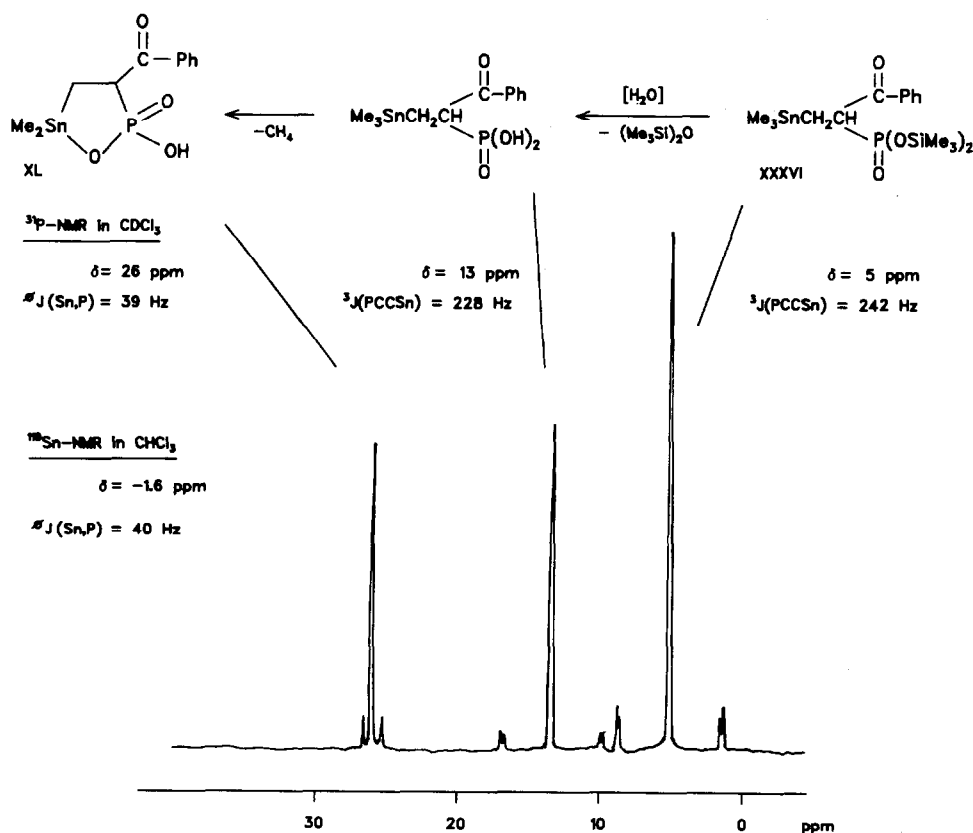
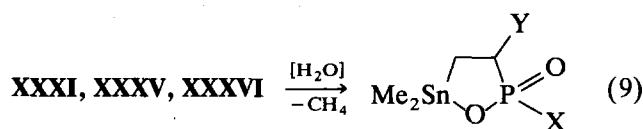


Fig. 1. <sup>31</sup>P NMR spectrum of the partial hydrolysis of Me<sub>3</sub>SnCH<sub>2</sub>CH[P(O)OSiMe<sub>3</sub>]<sub>2</sub>C(O)Ph (**XXXVI**).

oxaphosphastannolanes, as shown for examples in eqn. (9):



XXXVIII: X = Ph; Y = P(O)Ph<sub>2</sub>

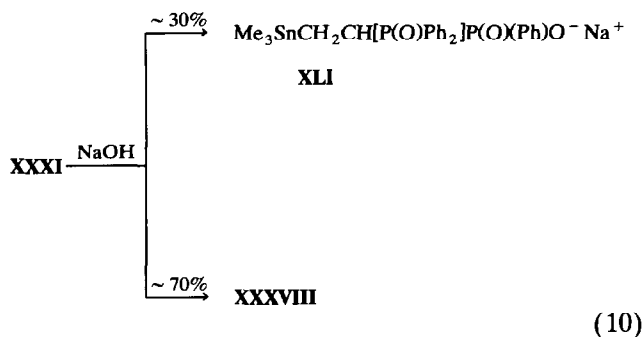
XXXIX: X = OH; Y = PO<sub>3</sub>H<sub>2</sub>

XL: X = OH; Y = C(O)Ph

In the case of XXXVI the stepwise course of the hydrolysis was detected by <sup>31</sup>P NMR studies on a sample which had been exposed to air moisture. Besides the signals for XXXVI and XL, the spectrum shows also a signal for the intermediately formed free phosphonic acid (Fig. 1).

The cyclic structure of XXXVIII–XL is revealed by the small value of the coupling constant between the tin and the ring phosphorus atom which represents the sum of <sup>3</sup>J(<sup>119</sup>SnCC<sup>31</sup>P) and <sup>2</sup>J(<sup>119</sup>SnO<sup>31</sup>P) (see ref. 3c). The heterocycles XXXVIII–XL undergo dynamic processes in solution. This is revealed by their NMR data, which show no indication of the existence of stereoisomers even though the compounds contain two chiral centres. Furthermore, the <sup>119</sup>Sn NMR spectrum of XXXIX shows only a triplet, as a consequence of a fast exchange process of the two phosphonic acid groups on the tin atom.

In order to suppress the cyclization process and to trap the free acids as their sodium salts, the hydrolysis of the silyl esters was performed with an excess of sodium hydroxide. However, only in the case of XXXI the desired sodium salt was not the sole product (eqn. (10)):



The identity of XLI was indicated by the NMR spectroscopy evidence for the presence of the trimethyltin group and the appearance of an [M + H]<sup>-1</sup> ion at *m/e* = 557 in the Ar-FAB mass spectrum.

In all other cases, with XXXI–XXXVII in alkaline medium cyclization takes place exclusively. For silyl esters with more than one Me<sub>3</sub>SiO group in the

molecule the cyclic products are isolated as sodium salts, e.g. the trisodium salt of XXXIX (XLII). Compound XLII undergoes the same exchange of the two phosphonate groups at the tin atom as found for XXXIX.

### 3. Experimental details

#### 3.1. General comments

All reactions with air- or moisture-sensitive compounds were carried out under dry argon with purified and dried solvents.

The NMR spectra were recorded on Bruker WP 200 and Bruker AC 80 spectrometers with TMS (<sup>1</sup>H and <sup>13</sup>C), 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) or Me<sub>4</sub>Sn (<sup>119</sup>Sn) as reference.

IR spectra were recorded on a Carl Zeiss Specord 75 IR instrument. Mass spectra were obtained with a Finnigan MAT 212 spectrometer by EI at 70 eV and 500 K.

Microanalyses of all compounds were carried out with a Carlo Erba elemental analyser (C, ±0.4%; H, ±0.2%; Hal ±0.5%).

#### 3.2. Iodomethylstannanes

##### 3.2.1. Me<sub>3</sub>SnCH<sub>2</sub>I

This was by the method of Seyferth and Andrews [14]. To obtain a better yield of Me<sub>3</sub>SnCH<sub>2</sub>I the iodomethylzinc reagent should be added to trimethyltin chloride immediately after its preparation. In order to ensure completion of the reaction a 2:1 molar ratio of the reactants and a prolonged reaction time (12–14 h at 40°C) are required. The reaction mixture was worked up as described previously [14]: yield, 90–95%; b.p. 62–64°C at 11 Torr; *n*<sub>D</sub><sup>20</sup> = 1.5550 ([14]: yield, 86%; b.p., 54–55°C at 5.5 Torr; *n*<sub>D</sub><sup>25</sup> = 1.5511).

##### 3.2.2. <sup>t</sup>BuPh<sub>2</sub>SnCH<sub>2</sub>I

This was made in the way described for Me<sub>3</sub>SnCH<sub>2</sub>I but from IZnCH<sub>2</sub>I and <sup>t</sup>BuPh<sub>2</sub>SnCl in a 4:1 molar ratio (yield, 70%; b.p., 125–135°C (Kugelrohr distillation at 5 × 10<sup>-5</sup> Torr); *n*<sub>D</sub><sup>25</sup> = 1.6176). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.57 (s, 9H, SnCCH<sub>3</sub>, <sup>3</sup>J(SnCCH) = 76.5 Hz); 2.49 (s, 2H, SnCH<sub>2</sub>, <sup>2</sup>J(SnCH) = 23.3 Hz) ppm <sup>119</sup>Sn NMR (CDCl<sub>3</sub>): δ -102 ppm.

##### 3.2.3. <sup>t</sup>BuMe<sub>2</sub>SnCH<sub>2</sub>I

This was made in the way as described for <sup>t</sup>BuPh<sub>2</sub>SnCH<sub>2</sub>I but from IZnCH<sub>2</sub>I and <sup>t</sup>BuMe<sub>2</sub>SnCl (molar ratio, 2.5:1) (yield 85%; b.p., 83–85°C at 5 Torr; *n*<sub>D</sub><sup>20</sup> = 1.5358). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.05 (s, 6H, SnCH<sub>3</sub>, <sup>2</sup>J(SnCH) = 50.3 Hz); 1.01 (s, 9H, SnCCH<sub>3</sub>, <sup>3</sup>J(SnCCH) = 70.6 Hz); 1.65 (s, 2H, SnCH<sub>2</sub>, <sup>2</sup>J(SnCH) = 18.3 Hz) ppm. <sup>119</sup>Sn NMR (neat): δ 22.0 ppm.

### 3.3. Difunctional methanes

These were prepared by the published methods:  $\text{CH}_2[\text{C}(\text{O})\text{Ph}]_2$  and  $[\text{Ph}(\text{O})\text{C}]\text{CH}_2(\text{CO}_2\text{Et})$  [15],  $(^i\text{Pr}_2\text{O}_3\text{P})\text{CH}_2(\text{CO}_2^i\text{Pr})$  [16],  $(^i\text{Pr}_2\text{O}_3\text{P})\text{CH}_2[\text{C}(\text{O})\text{Ph}]$ ,  $[\text{Ph}(^i\text{PrO})(\text{O})\text{P}]\text{CH}_2(\text{CO}_2^i\text{Pr})$  and  $[\text{Ph}(^i\text{PrO})(\text{O})\text{P}]\text{CH}_2[\text{C}(\text{O})\text{Ph}]$  [17],  $\text{CH}_2(\text{PO}_3^i\text{Pr}_2)_2$  [18],  $\text{CH}_2[\text{P}(\text{O})(\text{O}^i\text{Pr})\text{Ph}]_2$  [6c,19],  $\text{CH}_2[\text{P}(\text{O})\text{Ph}_2]_2$  [20],  $[\text{Ph}_2(\text{O})\text{P}]\text{CH}_2[\text{P}(\text{O})(\text{O}^i\text{Pr})\text{Ph}]$ ,  $[\text{Ph}_2(\text{O})\text{P}]\text{CH}_2(\text{PO}_3^i\text{Pr}_2)$  and  $[\text{Ph}(^i\text{PrO})(\text{O})\text{P}]\text{CH}_2(\text{PO}_3^i\text{Pr}_2)$  [6c].

### 3.4. 2,2-Bis(diisopropoxyphosphonyl)ethyl dimethyltin chloride (XV)

Compound XV was prepared according to ref. 4.

### 3.5. Synthesis of the title compounds I–XIV

A solution of 0.1–1 mol  $\text{Na}[(\text{CHXY})]$  in 50–500 ml of toluene (I–VII, XII–XIV) or n-heptane (VIII–XI) respectively (prepared from  $\text{CH}_2\text{XY}$  and excess of NaH (77%; Merck) at room temperature) was filtered and then added dropwise to a pre-heated (80–110°C) solution of the iodomethylstannane (10% excess) in 50–500 ml of the same solvent. The heating was continued and, when the pH value of the mixture had reached 7, the reaction was judged to be complete. In the cases of I and XI–XIII the final products were isolated after filtration of the reaction mixture, removal of the solvent and purification by distillation or recrystallization.

Before II–X and XIV were isolated, NaI and other water-soluble byproducts were removed from the product solution by aqueous extraction. After extraction of the aqueous solution with  $5 \times 100$  ml portions of diethyl ether the combined organic extracts were dried over  $\text{Na}_2\text{SO}_4$ , the solvent removed, and II–X and XIV purified by recrystallization or distillation. The yields of I–XIV were 60–75%.

### 3.6. Reaction of $\text{Ph}_2\text{R}\text{SnCH}_2\text{I}$ ( $\text{R} = \text{Ph}, ^i\text{Bu}$ ) with $\text{Na}[\text{HC}(\text{PO}_3^i\text{Pr})_2]_2$

The reaction was performed as described for I–XIV. The distannanes were isolated as pure compounds. 1,1,3,3-Tetrakis(diisopropoxyphosphonyl)propane containing some starting material and distannane was identified spectroscopically.

$(\text{Ph}_3\text{Sn})_2$ : m.p., 230°C ([21] 231–232°C).  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -143.0 ( $^1J(^{119}\text{Sn}^{117}\text{Sn}) = 4275$  Hz) ppm ([22]:  $\delta$  -143.6 ( $^1J(^{119}\text{Sn}^{117}\text{Sn}) = 4470$  Hz) ppm).

$(^i\text{BuPh}_2\text{Sn})_2$ : m.p. 123–129°C.  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -99 ppm. ( $^1J(^{119}\text{Sn}^{117}\text{Sn})$  is not resolved.)

$\text{CH}_2[\text{CH}(\text{PO}_3^i\text{Pr}_2)_2]_2$ :  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  21.4 ppm.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  36.4 (t/t,  $\text{CH}_2\text{CH}$ ,  $^1J(\text{CP}) = 133$  Hz,  $^3J(\text{CCCP}) = 7$  Hz (the  $\text{CH}_2$  signal overlaps with the multiplet of the ester  $\text{CH}_3$  groups) ppm. (For comparison for  $\text{CH}_2[\text{CH}(\text{PO}_3\text{Et}_2)_2]_2$  [23]:  $^{31}\text{P}$  NMR

( $\text{CCl}_4$ ):  $\delta$  22.5 ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  34.1 (t/t,  $\text{CH}_2\text{CH}$ ,  $^1J(\text{CP}) = 131.6$  Hz,  $^3J(\text{CCCP}) = 6.9$  Hz); 22.0 (qui,  $\text{CH}_2\text{CH}$ ,  $^2J(\text{CCP}) = 4.0$  Hz) ppm.)

### 3.7. 2,2-Bis(diisopropoxyphosphonyl)ethyl organotin dibromides (XVI and XVII)

A solution of bromine (0.02–0.04 mol) in 10–50 ml of  $\text{CH}_2\text{Cl}_2$  was added dropwise at  $-75^\circ\text{C}$  to a solution of 0.01–0.02 mol of VIII or XIV in 20–100 ml of dry  $\text{CH}_2\text{Cl}_2$ . The reaction of the first equivalent of bromine was indicated by its immediate decolourization. The second bromodemethylation step required overnight stirring at room temperature. After removal of the  $\text{CH}_2\text{Cl}_2$ , XVI and XVII were recrystallized from  $\text{CH}_2\text{Cl}_2$ -hexane with a yield of 90%.

XVI: m.p., 135–136°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.4 (s, 3H,  $\text{SnCH}_3$ ,  $^2J(\text{SnCH}) = 90.0$  Hz) ppm.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  25 ( $J(\text{Sn}, \text{P}) = 205$  Hz) ppm.  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -100 ppm (very broad) (all data are concentration dependent and reported for 10% solutions).

XVII: m.p., 103–105°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.7 (s, 9H,  $\text{SnCCH}_3$ ,  $^3J(\text{SnCCH}) = 160.6$  Hz) ppm.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  25 ( $J(\text{Sn}, \text{P}) = 174$  Hz) ppm.  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -114 (t,  $J(\text{Sn}, \text{p}) = 174$  Hz) ppm.

### 3.8. 2,2-Bis(diisopropoxyphosphonyl)ethyl triorganostannanes (XIV and XVIII–XX)

A onefold to twofold excess of  $\text{PhMgBr}$  or  $^i\text{BuMgCl}$  in ether was added at room temperature to a stirred solution of 0.01–0.05 mol of XV, XVI or XVII in 50–250 ml of dry ether. When addition of the Grignard reagent was complete, the mixtures were refluxed for 2 h, treated with a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  and worked up in the usual manner.

The reaction of XV with  $^i\text{BuMgCl}$  gave a mixture of XIV and the distannane XXI. The former was isolated by Kugelrohr distillation at  $5 \times 10^{-5}$  Torr and a bath temperature of 120–140°C (yield, 65%;  $n_D^{20} = 1.4666$ ; for spectroscopic data see Table 1). During this procedure, XXI decomposed.

XVIII–XX remain after evaporation of the solvent with yields of about 90% as colourless oils which cannot be distilled.

XVIII:  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  23 ( $^3J(\text{SnCCP}) = 126$  Hz) ppm.  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -35 (t) ppm.

XIX:  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  23 ( $^3J(\text{SnCCP}) = 132$  Hz) ppm.  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -72 (t) ppm.

XX:  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  23 ( $^3J(\text{SnCCP}) = 106$  Hz) ppm.  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -77 (t) ppm.

### 3.9. 1,2-Bis[2,2-bis(diisopropoxyphosphonyl)ethyl]-1,1,2,2-tetramethyldistannane (XXI)

A solution of 12.4 g (23 mmol) of XV in 30 ml THF was added to a cooled ( $-78^\circ\text{C}$ ) suspension of 3.1 g (23

mmol) of  $C_8K$  (prepared as described in ref. 24) by heating a magnetically stirred mixture of 0.9 g of potassium and 2.2 g of dry graphite to 100–150°C until it became homogeneous in 20 ml of THF. After overnight stirring the solution was filtered to remove the graphite and KCl, and the solvent was removed, to leave 10.3 g (89%) of **XXI** as a colourless oil.  $^{13}C$  NMR (neat):  $\delta$  -7.5 (SnCH<sub>3</sub>,  $^1J(SnC) = 230$  Hz,  $^2J(SnSnC) = 67$  Hz) ppm.  $^{31}P$  NMR (THF-*d*<sub>8</sub>):  $\delta$  24 ( $^3J(SnCCP) = 115$  Hz,  $^4J(SnSnCCP)$  is not detectable) ppm.  $^{119}Sn$  NMR (neat):  $\delta$  -76 (t/t,  $^3J(SnCCP) = 115$  Hz,  $^4J(SnSnCCP) = 17$  Hz) ppm.

### 3.10. 1-Trimethylstannylmethyl-1,1-bis(diisopropoxyphosphonyl) ethane (**XXII**)

A solution of 19.5 g (37.4 mmol) of **VIII** in 20 ml of toluene was added at room temperature to a stirred suspension of an excess of sodium hydride (2.6 g, 83.4 mmol; 77%; Merck) in 20 ml of toluene. When  $H_2$  evolution was complete, the mixture was stirred for 30 min at 40°C and then filtered and added slowly with stirring to a heated (80°C) solution of 10.6 g (75 mmol) of methyl iodide in 30 ml of toluene. Work-up of the mixture as described for **II–X** gave 14.8 g (74%) of **XXII** (b.p., 110–120°C at 0.02 Torr;  $n_D^{20} = 1.4666$ ).  $^1H$  NMR (CDCl<sub>3</sub>):  $\delta$  0.12 (s, 9H, SnCH<sub>3</sub>,  $^2J(SnCH) = 54.2$  Hz) ppm.  $^{13}C$  NMR (CDCl<sub>3</sub>):  $\delta$  -6.9 (s, SnCH<sub>3</sub>,  $^1J(SnC) = 342$  Hz); 16.7 (t, SnCH<sub>2</sub>,  $^2J(CCP) = 5.6$  Hz); 19.8 (t, SnCH<sub>2</sub>CCH<sub>3</sub>,  $^2J(CCP) = 4.8$  Hz); 39.2 (t, SnCH<sub>2</sub>C,  $^1J(CP) = 136.3$  Hz) ppm.  $^{31}P$  NMR (CDCl<sub>3</sub>):  $\delta$  27 ( $^3J(PCCSn) = 136$  Hz) ppm.  $^{119}Sn$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -11 ppm (t,  $^3J(SnCCP) = 136$  Hz) ppm.

### 3.11. Bis(trimethylstannylmethyl)-bis(diisopropoxyphosphonyl) methane (**XXIII**)

In the way described for **XXII**, a solution of the sodium methanide of **VIII** was treated with a 10% excess of Me<sub>3</sub>SnCH<sub>2</sub>I. After recrystallization of the crude product, **XXIII** was isolated as colourless air-stable crystals (yield, 65%; m.p., 133–135°C).  $^1H$  NMR (CDCl<sub>3</sub>):  $\delta$  0.11 (s, 18H, SnCH<sub>3</sub>,  $^2J(SnCH) = 53.8$  Hz) ppm.  $^{13}C$  NMR (CDCl<sub>3</sub>):  $\delta$  -6.3 (s, SnCH<sub>3</sub>,  $^1J(SnC) = 342$  Hz); 17 (t, SnCH<sub>2</sub>,  $^1J(SnC) = 357$  Hz,  $^2J(CCP) = 5.2$  Hz); 42.5 (t, SnCH<sub>2</sub>C,  $^1J(CP) = 135$  Hz) ppm.

### 3.12. Bis(diisopropoxyphosphonyl)-trimethylstannylmethyl-triorganostannylmethanes (**XXIV** and **XXV**)

A sodium methanide solution of **VIII** in toluene (see above) was added at room temperature to a stirred solution of the equivalent amount of Me<sub>3</sub>SnCl or Ph<sub>3</sub>SnCl in *n*-heptane or THF respectively. After stirring of the mixture at 40°C and filtration, the  $^{31}P$  and  $^{119}Sn$  NMR spectra of the solutions showed only the signals of the stannylated products.

**XXIV**:  $^{31}P$  NMR (*n*-heptane):  $\delta$  29 ( $^2J(SnCP) = 46$  Hz,  $^3J(SnCCP) = 102$  Hz) ppm.  $^{119}Sn$  NMR:  $\delta$  47 (t, Me<sub>3</sub>SnCP,  $^2J(SnCP) = 46$  Hz); -40 (t, Me<sub>3</sub>SnCH<sub>2</sub>,  $^3J(SnCCP) = 102$  Hz) ppm.

**XXV**:  $^{31}P$  NMR (THF):  $\delta$  27 ( $^2J(SnCP) = 50$  Hz,  $^3J(SnCCP) = 63$  Hz) ppm.  $^{119}Sn$  NMR:  $\delta$  -126 (t, Ph<sub>3</sub>Sn,  $^2J(SnCP) = 50$  Hz); -13 (t, Me<sub>3</sub>Sn,  $^3J(SnCCP) = 63$  Hz) ppm.

After storage of the reaction solutions for several days at room temperature the signal pattern of the NMR spectra had changed markedly. On the basis of  $^{31}P$  and  $^{119}Sn$  NMR spectroscopic data the decomposition was judged to follow the pathway shown in Scheme 1.

**XXVII**:  $^{31}P$  NMR (*n*-heptane): 36 ( $^3J(SnCCP) = 170$  Hz) ppm.  $^{119}Sn$  NMR: -31 (t) ppm.

**VIII**: see Table 1.

Me<sub>4</sub>Sn:  $^{119}Sn$  NMR (*n*-heptane):  $\delta$  0 ( $^1J(SnC) = 335$  Hz) ppm. ([25] (neat): ( $^1J(SnC) = 337.8$  Hz).)

Ph<sub>3</sub>SnMe: m.p., 59–61°C ([26]: 61°C).  $^{119}Sn$  NMR (THF): -93 ppm ([27] (CCl<sub>4</sub>): -98 ppm).

Ph<sub>6</sub>Sn<sub>2</sub>: m.p., 230°C ([21]: 231–232°C).  $^{119}Sn$  NMR (THF):  $\delta$  -143 ( $^1J(^{119}Sn^{117}Sn) = 4280$  Hz) ppm. ([22] (CDCl<sub>3</sub>):  $\delta$  -143.6 ( $^1J(^{119}Sn^{117}Sn) = 4470$  Hz) ppm.)

### 3.13. 1-Trimethylstannylmethyl-1-diisopropoxyphosphonyl-2-phenylethene (**XXVI**)

A solution of Na[Me<sub>3</sub>SnCH<sub>2</sub>C(PO<sub>3</sub><sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>], prepared as described above from 5 g (9.6 mmol) of **VIII** in toluene, was added to 1.2 g (11 mmol) of benzaldehyde in toluene. The slightly exothermic reaction was completed by stirring for 1 h at 40°C. After filtration of the solution and distillation of the solvents 3.6 g (84%) of **XXVI** were left as a colourless oil (b.p., 125–130°C at 0.07 Torr;  $n_D^{20} = 1.5195$ ).  $^{31}P$  NMR (neat,  $^1H$  coupled):  $\delta$  (*trans*) 19.8 ( $^3J(PCCH) = 24$  Hz);  $\delta$  (*cis*), 15.8 ( $^3J(PCCH) = 47.2$  Hz) ppm. (For assignment of vicinal PH couplings in vinylphosphonates see ref. 10 and the references cited therein).  $^{119}Sn$  NMR (neat):  $\delta$  (*trans*) 3.5 (d,  $^3J(SnCCP) = 34$  Hz);  $\delta$  (*cis*) 7.5 (d,  $^3J(SnCCP) = 29$  Hz) ppm.

### 3.14. Isopropyl 2-trimethylstannyl-2-phenylacrylate (**XXVIII**)

As described for **XXVI**, a solution of sodium methanide, prepared from 4.4 g (10 mmol) of **X** in toluene, was treated with 1.2 g (11 mmol) of benzaldehyde in the same solvent to give 3.1 g (84%) of **XXVIII** as a colourless liquid (b.p., 115°C at 0.07 Torr;  $n_D^{20} = 1.5322$ ).  $^1H$  NMR (CDCl<sub>3</sub>):  $\delta$  0.1 (s, 9H, SnCH<sub>3</sub>,  $^2J(SnCH) = 54.9$  Hz); 2.28 (s, 2H, SnCH<sub>2</sub>,  $^2J(SnCH) = 66.8$  Hz (the signal from the vinyl proton is superimposed on those from the phenyl group) ppm.  $^{13}C$  NMR (CDCl<sub>3</sub>):  $\delta$  -9.0 (SnCH<sub>3</sub>,  $^1J(SnC) = 330$  Hz); 13.9



TABLE 2.  $^{31}\text{P}$  and  $^{119}\text{Sn}$  NMR data for the silyl esters  $\text{Me}_3\text{SnCH}_2\text{CHXY}$  (XXXI–XXXVII) <sup>a,b</sup>

	XXXI	XXXII	XXXIII	XXXIV	XXXV	XXXVI	XXXVII
	X = P(O)Ph <sub>2</sub> Y = P(OXOSiMe <sub>3</sub> )Ph	X = P(O)Ph <sub>2</sub> Y = P(OXOSiMe <sub>3</sub> ) <sub>2</sub>	X = P(OXOSiMe <sub>3</sub> )Ph Y = P(OXOSiMe <sub>3</sub> ) <sub>2</sub>	X = P(OXOSiMe <sub>3</sub> )Ph Y = P(OXOSiMe <sub>3</sub> ) <sub>2</sub>	X = P(OXOSiMe <sub>3</sub> ) <sub>2</sub> Y = P(OXOSiMe <sub>3</sub> )Ph	X = C(O)Ph Y = P(OXOSiMe <sub>3</sub> ) <sub>2</sub>	X = C(O)O <sup>i</sup> Pr Y = P(OXOSiMe <sub>3</sub> ) <sub>2</sub>
$\delta_{31\text{P}}(\text{X})$ (ppm)	31	31	31	29	8	5	6
$\delta_{31\text{P}}(\text{Y})$ (ppm)	31	7	36 (broad)	-1 (d/d)	2 (t)	-1 (d)	+3 (d)
$\delta_{119\text{Sn}}$ (ppm)	6 (d/d)	3 (d/d)	-27 (t, broad)	147	128	-	-
$^3J(\text{SnCCP}(\text{X}))$ (Hz)	52	68	160	85	-	-	-
$^3J(\text{SnCCP}(\text{Y}))$ (Hz)	133	141	-	-	242	-	174

<sup>a</sup> Solvent,  $\text{CDCl}_3$ <sup>b</sup> The  $^1\text{H}$  NMR chemical shifts of the  $\text{Me}_3\text{Sn}$  and  $\text{Me}_3\text{Si}$  groups in XXXI–XXXVII range from  $-0.06$  to  $0.03$  ppm ( $^2J(\text{SnCH}) = 54$  Hz) and from  $0.1$  to  $0.3$  ppm respectively.

( $\text{SnCH}_2$ ,  $^1J(\text{SnC}) = 275$  Hz,  $^3J(\text{CCCH}) = 8$  Hz (taken from a gated spectrum)).  $^{119}\text{Sn}$  NMR (neat):  $\delta$  4.8 ppm.

### 3.15. Potassium salts of the trimethylstannylmethylmalonate XIII (XXIX and XXX)

**XXIX:** a solution of 0.41 g (7.3 mmol) of KOH in ethanol was added to a solution of 2.5 g (7.4 mmol) of XIII in ethanol. The solvent was evaporated off to leave XXIX as a white, very hygroscopic powder (yield, 2.1 g (81%); m.p., 80–90°C).  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  0.37 (s, 9H,  $\text{SnCH}_3$ ,  $^2J(\text{SnCH}) = 54.5$  Hz); 1.51 (d, 2H,  $\text{SnCH}_2$ ,  $^2J(\text{SnCH})$  not resolved); 1.58 (t, 3H,  $\text{COOCH}_2\text{CH}_3$ ,  $^3J(\text{HCCH}) = 7.1$  Hz); 3.76 (t, 1H,  $\text{SnCH}_2\text{CH}$ ,  $^3J(\text{HCCH}) = 8.1$  Hz); 4.49 (qua, 2H,  $\text{COOCH}_2\text{CH}_3$ ) ppm.

**XXX:** an ethanolic solution of 0.82 g (14.6 mmol) of KOH was added to 2.5 g (7.4 mmol) of XIII and the mixture was refluxed for several hours. XXX separated out as a powder (m.p., above 260°C).

### 3.16. Silyl-esters of II–V, VIII, IX and X (XXXI–XXVII)

A solution of 10 mmol of  $\text{Me}_3\text{SiBr}$  in 10 ml of dry methylene chloride was added dropwise at –30°C to a stirred solution of about 10 mmol of the isopropyl-esters in the same solvent. The mixture was kept overnight and the volatile compounds were then removed *in vacuo* (0.1 Torr) at room temperature. The colourless oils of XXXI–XXXVII then obtained were of high purity and were used for further reactions without distillation (the NMR data are given in Table 2).

### 3.17. 2-Oxo-2-hydroxy-3-benzoyl-5,5-dimethyl-1,2,5-oxaphosphastannolane (XL)

Freshly prepared XXXVI (1.96 g, 4 mmol), obtained by the method described above, was dissolved in dry  $\text{CDCl}_3$ . To allow monitoring of the hydrolysis reaction by NMR spectroscopy the solution was exposed to air for some hours (see Fig. 1). Finally, the addition of water led to the precipitation of 1.1 g (83%) of XL (m.p., 85°C).

### 3.18. Sodium-[(2-trimethylstannyl-1-diphenylphosphinyl)ethyl]phenylphosphinate (XLI) and 2-oxo-2-phenyl-3-diphenylphosphinyl-5,5-dimethyl-1,2,5-oxaphosphastannolane (XXXVIII)

A solution of 3 g (5 mmol) of XXXI in 10 ml of methylene chloride was added dropwise to an excess of 1.5 g (37.5 mmol) of NaOH in 10 ml of water. The organic layer, which contained XXXVIII and XLI as a fine dispersion, was separated and washed twice with a small amount of cold water. After evaporation of the solvent the residue was digested several times with small amounts of hot methanol. Concentration of the

methanolic solution gave 1 g (36%) of XLI as a white non-melting powder.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  –0.1 (s, 9H,  $\text{SnCH}_3$ ,  $^2J(\text{SnCH}) = 54.0$  Hz) ppm.  $^{31}\text{P}$  NMR:  $\delta$  24.0 (d,  $P^1(\text{O})\text{Ph}_2$ ); 37 (d,  $P^2(\text{O})(\text{Ph})\text{O}^-$ ),  $^2J(\text{P}, \text{P}) = 6$  Hz) ppm.  $^{119}\text{Sn}$  NMR:  $\delta$  –9 (d/d,  $^3J(\text{Sn}, P^1) = 31$  Hz,  $^3J(\text{Sn}, P^2) = 145$  Hz) ppm. EI-MS (matrix: triethylene glycol,  $^{120}\text{Sn}$ , *m/e* (%): 579 (62,  $\text{M} + 23$ ), 557 (10,  $\text{M} + \text{H}$ ), 541 (26,  $\text{M} - \text{CH}_3$ ).

The white solid which remained after digestion of the crude product mixture with hot methanol was nearly pure XXXVIII. It was also obtained as the sole product when XXXI was treated with water. It had a m.p. of about 180°C (the melt decomposes at about 230°C with gas evolution).  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  0.7 (s, 6H,  $\text{SnCH}_3$ ,  $^2J(\text{SnCH}) = 69.8$  Hz) ppm.  $^{31}\text{P}$  NMR:  $\delta$  34 (broad,  $P^1(\text{O})\text{Ph}_2$  and  $P^2(\text{O})\text{Ph}(\text{ring})$ ) ppm.  $^{119}\text{Sn}$  NMR:  $\delta$  –34 (d/d,  $^3J(\text{Sn}, P^1) = 324$  Hz,  $J(\text{Sn}, P^2) = 22$  Hz) ppm. Ar FAB MS (matrix: triethylene glycol,  $^{120}\text{Sn}$ , *m/e* (%): 519 (14,  $\text{M} + \text{H}$ ).

### 3.19. 2-Oxo-2-hydroxy-5,5-dimethyl-1,2,5-oxaphosphastannol-3-yl-phosphonic acid (XXXIX) and trisodium 2-oxo-2-hydroxy-5,5-dimethyl-1,2,5-oxaphosphastannol-3-yl-phosphonate (XLII)

An excess of water was added dropwise to a solution of 3.2 g (5.5 mmol) of XXXV in 10 ml of dry methylene chloride. When gas evolution ceased,  $\text{CH}_2\text{Cl}_2$  and water were removed to leave XXXIX in quantitative yield (1.5 g) as a microcrystalline powder (m.p., above 350°C).

Addition of three equivalents of 0.1 M aqueous NaOH transformed XXXIX into its trisodium salt XLII (m.p., above 360°C).

**XXXIX:**  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  0.58 (s, 6H,  $\text{SnCH}_3$ ,  $^2J(\text{SnCH}) = 70.5$  Hz) ppm.  $^{31}\text{P}$  NMR:  $\delta$  17 (broad,  $P^1(\text{O})(\text{OH})_2$ ,  $J(\text{Sn}, P^1) = 183$  Hz); 34 (broad,  $P^2(\text{OH})\text{OH}(\text{ring})$ ,  $^3J(\text{SnCCP}^2) = 210$  Hz) ppm.  $^{119}\text{Sn}$  NMR:  $\delta$  –34 (t (broad),  $J(\text{Sn}, P^1)$  and  $^3J(\text{SnCCP}^2) = 198$  Hz) ppm.

**XLII:**  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  0.7 (s, 6H,  $\text{SnCH}_3$ ,  $^2J(\text{SnCH}) = 68.5$  Hz) ppm.  $^{31}\text{P}$  NMR:  $\delta$  23 ( $P^1(\text{O})\text{O}^{2-}$  and  $P^2(\text{O})\text{O}^-$  (ring)) ppm.  $^{119}\text{Sn}$  NMR:  $\delta$  –63 ( $^3J(\text{SnCCP}^1)$  and  $J(\text{Sn}, P^2(\text{ring})) = 215$  Hz) ppm.

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