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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 Me_3SnCH_2CHXY (X, Y = $P(O)R_2$ or C(O)R; R = O^iPr, OEt or Ph) has been synthesized by stannylmethylation of the appropriate 2,2-difunctional methanides Na[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 $P(O)R_2$ and C(O)R groups are described.

Key words: Tin; Phosphoryl

1. Introduction

Diphosphorylmethanes * $H_2C[P(O)X]_2$ (X = OR, R) and their derivatives in which the 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 C(O)OR and C(O)R groups as substituents at the central carbon atom.

Recently, we presented the first examples of the title compounds [4], and Hutchinson and Fuchs [5] have described the synthesis of $Me_3SnCH_2CH(PO_3{}^iPr_2)COO^tBu$. Below we report the synthesis and reactivity of 2,2-functionally disubstituted organotin compounds of the general type Me_3SnCH_2CHXY (X, Y = $P(O)R_2$ or C(O)R; R = O^iPr, OEt or Ph).

2. Results and discussion

A series of the title compounds (Table 1) Me_3SnCH_2CHXY with (i) X = Y = $P(O)R_2$ (R = O^iPr or Ph), (ii) X = $P(O)R_2$, Y = C(O)R (R = O^iPr or Ph) and (iii) X = Y = C(O)R (R = OEt or Ph) was obtained by the addition of a solution of the corresponding sodium methanide Na[CHXY] to iodomethyl trimethylstannane at 80–100°C; the reaction is depicted as follows:

$$Me_3SnCH_2I + Na[CHXY] \xrightarrow[-NaI]{} \underset{\textbf{I–XIII}}{Me_3SnCH_2CHXY} \qquad (1)$$

The related compound $^tBuMe_2SnCH_2CH(PO_3{}^iPr_2)_2$ (**XIV**) was prepared analogously.

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

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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^{i}Pr 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 $^tBuMe_2SnCH_2CH(PO_3{}^iPr_2)_2$ (**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	ν(P(X)O) [a] ν(P(Y)O) (cm^{-1})	ν(C(X)O) [a] ν(C(Y)O) (cm^{-1})
I	$P(O)Ph_2$	148–150	32.0	4.8 (t)	69.0	Dimethylformamide	1196	
	$P(O)Ph_2$							
II	$P(O)Ph_2$	65– 72	31.0, 31.2 (d) [b]	2.5 (d/d)	61.5, 73.8	CH_2Cl_2	1197	
	$P(O)(O^iPr)Ph$	83– 88	38.6, 39.4 (d) [b]	−3.5 (d/d)	125.0, 126.6		1216	
III	$P(O)Ph_2$	45– 50	30.0	13.0 (d/d)	124.1	CH_2Cl_2	1200	
	$P(O)(O^iPr)_2$		23.3		71.3		1230	
IV	$P(O)(O^iPr)Ph$	78– 88 [c]	38.5 [c]	11.5 (t) [c]	96 [c]	$CHCl_3$	1212 [c]	
	$P(O)(O^iPr)Ph$		37–41 (m)	15.0 (d/d)	$\Sigma J = 170$			
				16.0 (t)	80			
V	$P(O)(O^iPr)Ph$	(140–150) [d]	37.2	8.2 (d/d)	75.2, 86.4	CH_3OH	1230	
	$P(O)(O^iPr)_2$		23.0	9.2 (d/d)	121.0, 139.8			
VI	$P(O)(O^iPr)Ph$	92– 97	38.6, 36.9	5.9 (d)	195.4	Toluene	1227	
	C(O)Ph			8.1 (d)	221.1			1670
VII	$P(O)(O^iPr)Ph$	(150–160)	37.2, 37.6	3.1 (d)	207.1	CH_2Cl_2	1219	
	$C(O)O^iPr$			4.0 (d)	206.3			1723
VIII	$P(O)(O^iPr)_2$	(90–100) [d]	24.0	3.7 (t)	111.7	Toluene	1241	
	$P(O)(O^iPr)_2$							
IX	$P(O)(O^iPr)_2$	(120–125)	21.4	6.5 (d)	263.0	$CHCl_3$	1247	
	C(O)Ph							1681
X	$P(O)(O^iPr)_2$	(90– 93)	22.2	2.0 (d)	182.0	Neat	1254	
	$C(O)O^iPr$							1730
XI	C(O)Ph	80– 85		3.6		CH_3OH		1668
	C(O)Ph							
XII	C(O)Ph	(90– 95)		4.2		Neat		1670
	C(O)OEt							1718
XIII	C(O)OEt	(60)		3.6		CH_2Cl_2		1732
	C(O)OEt							
XIV	$P(O)(O^iPr)_2$	(120–140) [d]	23.0	15.0 (t)	106.0	$CHCl_3$	1240	
	$P(O)(O^iPr)_2$							

[a] IR: 2% in CCl_4.

[b] $^2J(^{31}PC^{31}P) = 4.5$ Hz.

[c] Enriched meso compound.

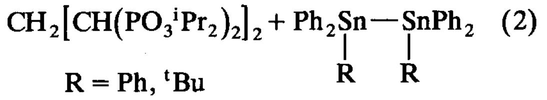
[d] Kugelrohr distillation at 5×10^{-5} Torr; bath temperature in parentheses.

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}P; X = ^{119}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 $[M-CH_3]^+$ 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 ICH_2–Sn bond is observed [7]; thus in the reaction of Ph_2RSnCH_2I (R = Ph, ^tBu) with $Na[CH(PO_3{}^iPr_2)_2]$ the corresponding distannanes and 1,1,3,3-tetrakis(diisopropoxyphosphonyl)propane were isolated (eqn. (2)):

$$2\,Ph_2RSnCH_2I + 2Na\left[CH(PO_3{}^iPr_2)_2\right] \xrightarrow[\substack{-2\,NaI\\ -\{CH_2\}}]{}$$



$$CH_2\left[CH(PO_3{}^iPr_2)_2\right]_2 + \underset{R}{\underset{|}{Ph_2Sn}}-\underset{R}{\underset{|}{SnPh_2}} \qquad (2)$$

R = Ph, ^tBu

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 $CHCl_3$ results in a regioselective halodealkylation of the methyl groups at tin, as shown for **VIII** and **XIV** in eqn. (3):

$$\textbf{VIII, XIV} \xrightarrow[-CH_4\text{ or }2\,CH_3Br]{\substack{+HCl/\text{ether or}\\ 2\,Br_2/CH_2Cl_2}}$$

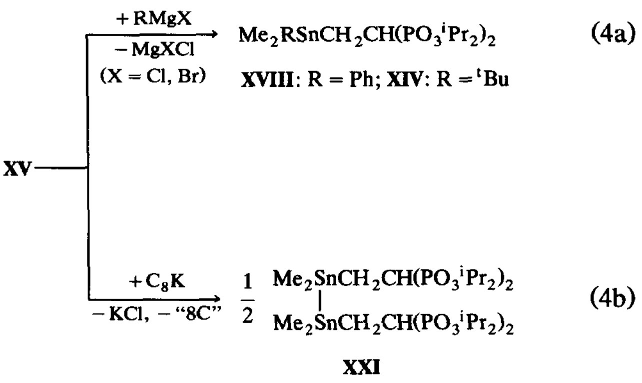
$$Me_{2-n}RHal_nSnCH_2CH(PO_3{}^iPr_2)_2 \qquad (3)$$

XV: R = Me; Hal = Cl; $n = 1$
XVI: R = Me; Hal = Br; $n = 2$
XVII: R = ^tBu; Hal = Br; $n = 2$

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)).



$$\textbf{XV} \xrightarrow[\substack{-MgXCl\\ (X = Cl, Br)}]{+RMgX} Me_2RSnCH_2CH(PO_3{}^iPr_2)_2 \qquad (4a)$$

XVIII: R = Ph; **XIV**: R = ^tBu

$$\textbf{XV} \xrightarrow[-KCl,\ -\text{“8C”}]{+C_8K} \frac{1}{2}\ \begin{array}{c} Me_2SnCH_2CH(PO_3{}^iPr_2)_2 \\ | \\ Me_2SnCH_2CH(PO_3{}^iPr_2)_2 \end{array} \qquad (4b)$$

XXI

$$\textbf{XVI, XVII} \xrightarrow[-2\,MgBr_2]{+2\,PhMgBr} RPh_2SnCH_2CH(PO_3{}^iPr_2)_2 \qquad (5)$$

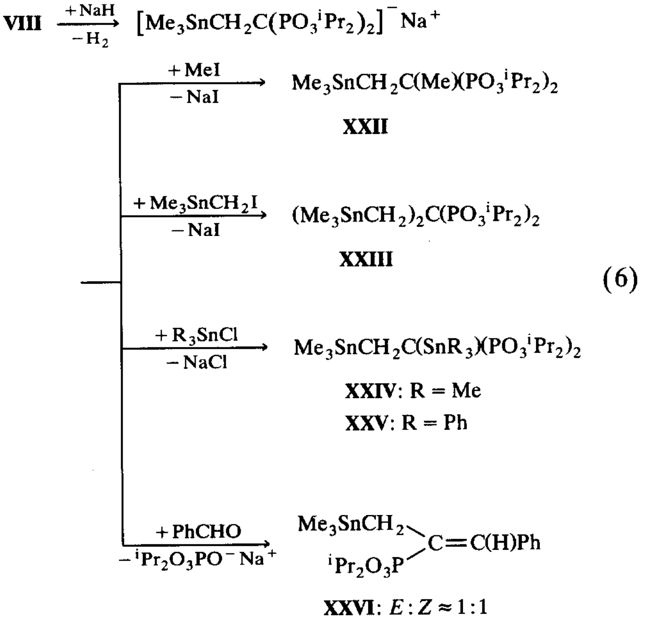
XIX: R = Me; **XX**: R = ^tBu

In the case of **XV** the reaction with ^tBuMgCl (eqn. (4a)) to **XIV** is accompanied by a reduction to give the distannane $[Me_2SnCH_2CH(PO_3{}^iPr_2)_2]_2$ (**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 (C_8K) (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}Sn NMR signal due to the ^3J(SnCCP) and the ^4J(*Sn*SnCCP) couplings.

The addition of a further equivalent of C_8K 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 $[K]_2[Me_2SnCH_2C(PO_3{}^iPr)_2]_2$, as indicated by a broadened ^{31}P NMR signal, which is situated at $\delta = 39$ ppm, within the shift range observed for carbanions of methylene bisphosphonates [10]. Addition of further C_8K 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 Na[CHXY] with Me_3SnCH_2I (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):



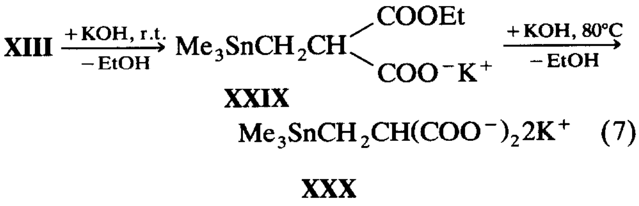
(6)

Compounds **XXII** and **XXIII** were isolated with a good yield. The doubled intensity of the tin satellites in the ^{31}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}P and ^{119}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 $MeSnPh_3$ and Ph_6Sn_2.

After homolytic cleavage of the functionally substituted Sn–C bond the resulting radicals dimerize to give **XXVII** and $(R_3Sn)_2$ (R = Me or Ph). The formation of the other stable final products **VIII** and $MeSnR_3$ probably results from hydrogen abstraction from the solvent (**VIII**) and methyl group transfer from any of the Me_3Sn-containing species to the $R_3Sn\cdot$ radical respectively.

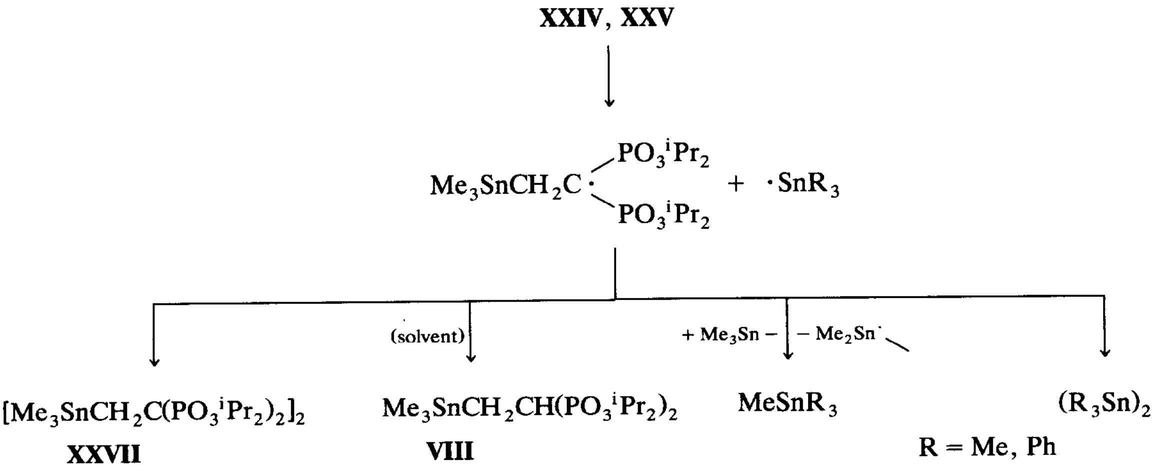
The Horner reaction of **VIII** with benzaldehyde (eqn. (6)) yields **XXVI** as an equimolar mixture of the *E* and *Z* isomer. This behaviour is in contrast with that of the unsubstituted $CH_2(PO_3Et_2)_2$ which is converted exclusively into the *E* isomer [10]. Obviously, because of the presence of the Me_3SnCH_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 $^3J(^{13}CCC^1H)$ coupling in $Me_3SnCH_2(CO_2{}^iPr)_2C{=}C(H)Ph$ (**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)):



$$\mathbf{XIII} \xrightarrow[-EtOH]{+KOH,\ r.t.} Me_3SnCH_2CH\begin{cases}COOEt\\ COO^-K^+\end{cases} \xrightarrow[-EtOH]{+KOH,\ 80^\circ C} Me_3SnCH_2CH(COO^-)_2 2K^+ \quad (7)$$

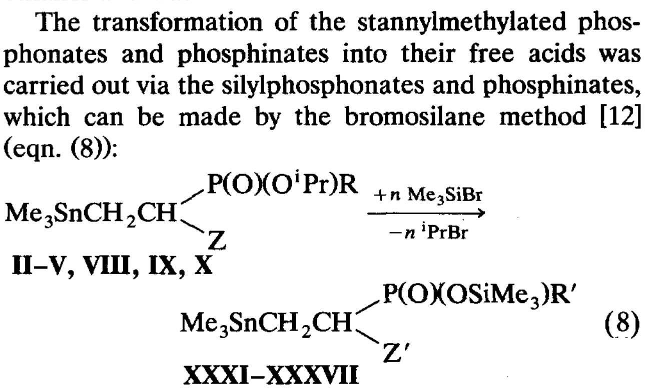
XXIX **XXX**



Scheme 1. Proposed decomposition pathway of $Me_3SnCH_2C(SnR_3)(PO_3{}^iPr_2)_2$ (R = Me (**XXIV**), R = 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)):



$$\underset{\textbf{II–V, VIII, IX, X}}{Me_3SnCH_2CH\begin{cases}P(O)(O^iPr)R\\ Z\end{cases}} \xrightarrow[-n\ ^iPrBr]{+n\ Me_3SiBr} \underset{\textbf{XXXI–XXXVII}}{Me_3SnCH_2CH\begin{cases}P(O)(OSiMe_3)R'\\ Z'\end{cases}} \quad (8)$$

	n	R	R′	Z	Z′
XXXI	1	Ph	Ph	$P(O)Ph_2$	$P(O)Ph_2$
XXXII	2	O^iPr	$OSiMe_3$	$P(O)Ph_2$	$P(O)Ph_2$
XXXIII	2	Ph	Ph	$P(O)(O^iPr)Ph$	$P(O)(OSiMe_3)Ph$
XXXIV	3	Ph	Ph	$P(O)(O^iPr)_2$	$P(O)(OSiMe_3)_2$
XXXV	4	O^iPr	$OSiMe_3$	$P(O)(O^iPr)_2$	$P(O)(OSiMe_3)_2$
XXXVI	2	O^iPr	$OSiMe_3$	C(O)Ph	C(O)Ph
XXXVII	2	O^iPr	$OSiMe_3$	$C(O)O^iPr$	$C(O)O^iPr$

At a low reaction temperature and with an excess of Me_3SiBr, compounds **XXXI–XXXVII** can be isolated with a high purity (^1H and ^{31}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 ^{31}P and ^{119}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 ch~~iral 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-

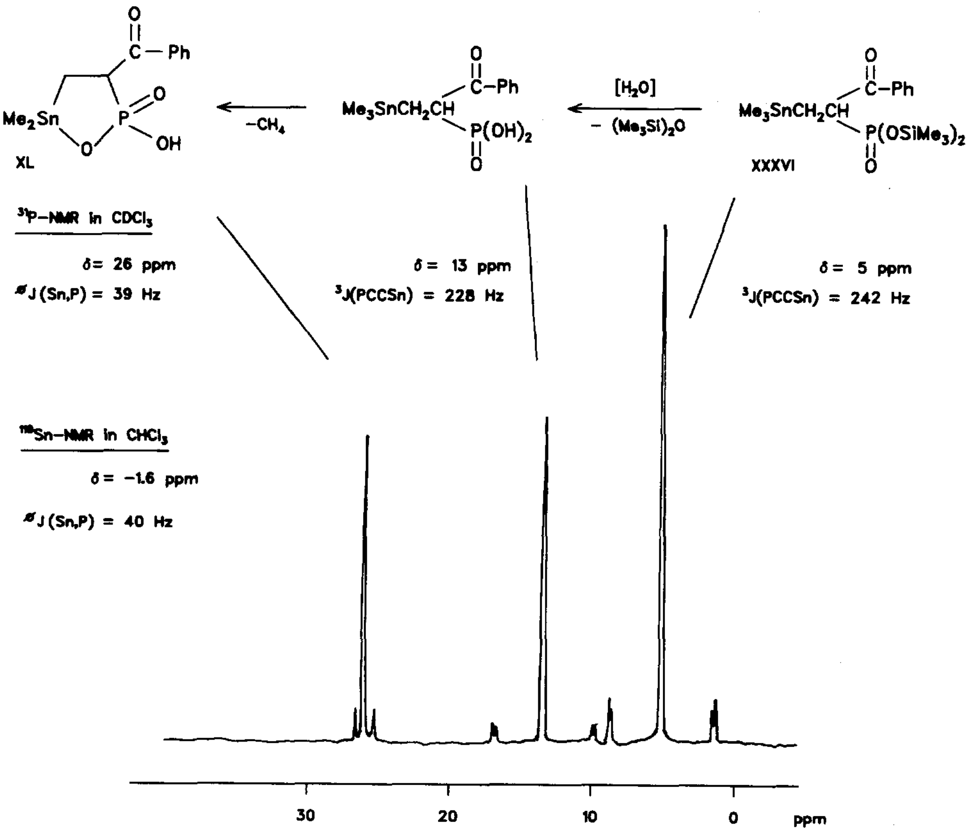
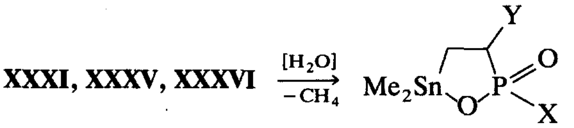


Fig. 1. ^{31}P NMR spectrum of the partial hydrolysis of $Me_3SnCH_2CH[P(O)(OSiMe_3)_2]C(O)Ph$ (**XXXVI**).

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



(9)

XXXVIII: $X = Ph$; $Y = P(O)Ph_2$

XXXIX: $X = OH$; $Y = PO_3H_2$

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

In the case of **XXXVI** the stepwise course of the hydrolysis was detected by ^{31}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 $^3J(^{119}SnCC^{31}P)$ and $^2J(^{119}SnO^{31}P)$ (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 ^{119}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)):

(10)

The identity of **XLI** was indicated by the NMR spectroscopy evidence for the presence of the trimethyltin group and the appearance of an $[M + H]^{-1}$ 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_3SiO 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 (^1H and ^{13}C), 85% H_3PO_4 (^{31}P) or Me_4Sn (^{119}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_3SnCH_2I

This was by the method of Seyferth and Andrews [14]. To obtain a better yield of Me_3SnCH_2I 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; $n_D^{20} = 1.5550$ ([14]: yield, 86%; b.p., 54–55°C at 5.5 Torr; $n_D^{25} = 1.5511$).

3.2.2. $^tBuPh_2SnCH_2I$

This was made in the way described for Me_3SnCH_2I but from $IZnCH_2I$ and $^tBuPh_2SnCl$ in a 4:1 molar ratio (yield, 70%; b.p., 125–135°C (Kugelrohr distillation at 5×10^{-5} Torr); $n_D^{25} = 1.6176$). ^1H NMR ($CDCl_3$): δ 1.57 (s, 9H, $SnCCH_3$, $^3J(SnCCH) = 76.5$ Hz); 2.49 (s, 2H, $SnCH_2$, $^2J(SnCH) = 23.3$ Hz) ppm ^{119}Sn NMR ($CDCl_3$): δ −102 ppm.

3.2.3. $^tBuMe_2SnCH_2I$

This was made in the way as described for $^tBuPh_2SnCH_2I$ but from $IZnCH_2I$ and $^tBuMe_2SnCl$ (molar ratio, 2.5:1) (yield 85%; b.p., 83–85°C at 5 Torr; $n_D^{20} = 1.5358$). ^1H NMR (C_6D_6): δ 0.05 (s, 6H, $SnCH_3$, $^2J(SnCH) = 50.3$ Hz); 1.01 (s, 9H, $SnCCH_3$, $^3J(SnCCH) = 70.6$ Hz); 1.65 (s, 2H, $SnCH_2$, $^2J(SnCH) = 18.3$ Hz) ppm. ^{119}Sn NMR (neat): δ 22.0 ppm.

3.3. Difunctional methanes

These were prepared by the published methods: $CH_2[C(O)Ph]_2$ and $[Ph(O)C]CH_2(CO_2Et)$ [15], $({}^iPr_2O_3P)CH_2(CO_2{}^iPr)$ [16], $({}^iPr_2O_3P)CH_2[C(O)Ph]$, $[Ph({}^iPrO)(O)P]CH_2(CO_2{}^iPr)$ and $[Ph({}^iPrO)(O)P]CH_2$-$[C(O)Ph]$ [17], $CH_2(PO_3{}^iPr_2)_2$ [18], $CH_2[P(O)(O{}^iPr)$-$Ph]_2$ [6c,19], $CH_2[P(O)Ph_2]_2$ [20], $[Ph_2(O)P]CH_2[P(O)$-$(O{}^iPr)Ph]$, $[Ph_2(O)P]CH_2(PO_3{}^iPr_2)$ and $[Ph({}^iPrO)(O)$-$P]CH_2(PO_3{}^iPr_2)$ [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 Na[(CHXY)] in 50–500 ml of toluene (**I–VII**, **XII–XIV**) or n-heptane (**VIII–XI**) respectively (prepared from CH_2XY 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 × 100 ml portions of diethyl ether the combined organic extracts were dried over Na_2SO_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 Ph_2RSnCH_2I ($R = Ph$, ${}^tBu$) with $Na[HC(PO_3{}^iPr)_2]_2$

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.

$(Ph_3Sn)_2$: m.p., 230°C ([21] 231–232°C). ^{119}Sn NMR ($CDCl_3$): δ −143.0 ($^1J(^{119}Sn^{117}Sn) = 4275$ Hz) ppm ([22]: δ −143.6 ($^1J(^{119}Sn^{117}Sn) = 4470$ Hz) ppm).

$({}^tBuPh_2Sn)_2$: m.p. 123–129°C. ^{119}Sn NMR ($CDCl_3$): δ −99 ppm. ($^1J(^{119}Sn^{117}Sn)$ is not resolved.)

$CH_2[CH(PO_3{}^iPr_2)_2]_2$: ^{31}P NMR ($CDCl_3$): δ 21.4 ppm. ^{13}C NMR (C_6D_6): δ 36.4 (t/t, $CH_2\mathit{C}H$, $^1J(CP) =$ 133 Hz, $^3J(CCCP) = 7$ Hz (the $\mathit{C}H_2$ signal overlaps with the multiplet of the ester CH_3 groups) ppm. (For comparison for $CH_2[CH(PO_3Et_2)_2]_2$ [23]: ^{31}P NMR (CCl_4): δ 22.5 ppm. ^{13}C NMR ($CDCl_3$): δ 34.1 (t/t, $CH_2\mathit{C}H$, $^1J(CP) = 131.6$ Hz, $^3J(CCCP) = 6.9$ Hz); 22.0 (qui, $\mathit{C}H_2CH$, $^2J(CCP) = 4.0$ 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 CH_2Cl_2 was added dropwise at −75°C to a solution of 0.01–0.02 mol of **VIII** or **XIV** in 20–100 ml of dry CH_2Cl_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 CH_2Cl_2, **XVI** and **XVII** were recrystallized from CH_2Cl_2–hexane with a yield of 90%.

XVI: m.p., 135–136°C. ^1H NMR ($CDCl_3$): δ 1.4 (s, 3H, $SnCH_3$, $^2J(SnCH) = 90.0$ Hz) ppm. ^{31}P NMR ($CDCl_3$): δ 25 ($J(Sn, P) = 205$ Hz) ppm. ^{119}Sn NMR ($CDCl_3$): δ −100 ppm (very broad) (all data are concentration dependent and reported for 10% solutions).

XVII: m.p., 103–105°C. ^1H NMR ($CDCl_3$): δ 1.7 (s, 9H, $SnCCH_3$, $^3J(SnCCH) = 160.6$ Hz) ppm. ^{31}P NMR ($CDCl_3$): δ 25 ($J(Sn, P) = 174$ Hz) ppm. ^{119}Sn NMR ($CDCl_3$): δ −114 (t, $J(Sn, p) = 174$ Hz) ppm.

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

A onefold to twofold excess of PhMgBr or ${}^tBuMgCl$ 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 NH_4Cl and worked up in the usual manner.

The reaction of **XV** with ${}^tBuMgCl$ gave a mixture of **XIV** and the distannane **XXI**. The former was isolated by Kugelrohr distillation at 5×10^{-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}P NMR ($CDCl_3$): δ 23 ($^3J(SnCCP) = 126$ Hz) ppm. ^{119}Sn NMR ($CDCl_3$) δ −35 (t) ppm.

XIX: ^{31}P NMR ($CDCl_3$): δ 23 ($^3J(SnCCP) = 132$ Hz) ppm. ^{119}Sn NMR ($CDCl_3$): δ −72 (t) ppm.

XX: ^{31}P NMR ($CDCl_3$): δ 23 ($^3J(SnCCP) = 106$ Hz) ppm. ^{119} Sn NMR ($CDCl_3$): δ −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°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): δ -7.5 (SnCH_3, ^{1}J(SnC) = 230 Hz, ^{2}J(SnSnC) = 67 Hz) ppm. ^{31}P NMR (THF-d_8): δ 24 (^{3}J(SnCCP) = 115 Hz, ^{4}J(SnSnCCP) is not detectable) ppm. ^{119}Sn NMR (neat): δ -76 (t/t, ^{3}J(SnCCP) = 115 Hz, ^{4}J(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; $n_D^{20} = 1.4666$). ^{1}H NMR ($CDCl_3$): δ 0.12 (s, 9H, SnCH_3, ^{2}J(SnCH) = 54.2 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ -6.9 (s, SnCH_3, ^{1}J(SnC) = 342 Hz); 16.7 (t, SnCH_2, ^{2}J(CCP) = 5.6 Hz); 19.8 (t, $SnCH_2CCH_3$, ^{2}J(CCP) = 4.8 Hz); 39.2 (t, $SnCH_2C$, ^{1}J(CP) = 136.3 Hz) ppm. ^{31}P NMR ($CDCl_3$): δ 27 (^{3}J(PCCSn) = 136 Hz) ppm. ^{119}Sn NMR (CD_2Cl_2): δ -11 ppm (t, ^{3}J(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_3SnCH_2I. After recrystallization of the crude product, **XXIII** was isolated as colourless air-stable crystals (yield, 65%; m.p., 133–135°C). ^{1}H NMR ($CDCl_3$): δ 0.11 (s, 18H, SnCH_3, ^{2}J(SnCH) = 53.8 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ -6.3 (s, SnCH_3, ^{1}J(SnC) = 342 Hz); 17 (t, SnCH_2, ^{1}J(SnC) = 357 Hz, ^{2}J(CCP) = 5.2 Hz); 42.5 (t, $SnCH_2C$, ^{1}J(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_3SnCl or Ph_3SnCl 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): δ 29 (^{2}J(SnCP) = 46 Hz, ^{3}J(SnCCP) = 102 Hz) ppm. ^{119}Sn NMR: δ 47 (t, Me_3SnCP, ^{2}J(SnCP) = 46 Hz); -40 (t, Me_3SnCH_2, ^{3}J(SnCCP) = 102 Hz) ppm.

XXV: ^{31}P NMR (THF): δ 27 (^{2}J(SnCP) = 50 Hz, ^{3}J(SnCCP) = 63 Hz) ppm. ^{119} Sn NMR: δ -126 (t, Ph_3Sn, ^{2}J(SnCP) = 50 Hz); -13 (t, Me_3Sn, ^{3}J(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 (^{3}J(SnCCP) = 170 Hz) ppm. ^{119}Sn NMR: -31 (t) ppm.

VIII: see Table 1.

Me_4Sn: ^{119}Sn NMR (n-heptane): δ 0 (^{1}J(SnC) = 335 Hz) ppm. ([25] (neat): (^{1}J(SnC) = 337.8 Hz).)

Ph_3SnMe: m.p., 59–61°C ([26]: 61°C). ^{119}Sn NMR (THF): -93 ppm ([27] (CCl_4): -98 ppm).

Ph_6Sn_2: m.p., 230°C ([21]: 231–232°C). ^{119}Sn NMR (THF): δ -143 ($^{1}J(^{119}Sn^{117}Sn) = 4280$ Hz) ppm. ([22] ($CDCl_3$): δ -143.6 ($^{1}J(^{119}Sn^{117}Sn) = 4470$ Hz) ppm.)

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

A solution of $Na[Me_3SnCH_2C(PO_3{}^{i}Pr_2)_2]$, 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, ^{1}H coupled): δ (*trans*) 19.8 (^{3}J(PCCH) = 24 Hz); δ (*cis*), 15.8 (^{3}J(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): δ (*trans*) 3.5 (d, ^{3}J(SnCCP) = 34 Hz); δ (*cis*) 7.5 (d, ^{3}J(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; $n_D^{20} = 1.5322$). ^{1}H NMR ($CDCl_3$): δ 0.1 (s, 9H, SnCH_3, ^{2}J(SnCH) = 54.9 Hz); 2.28 (s, 2H, SnCH_2, ^{2}J(SnCH) = 66.8 Hz (the signal from the vinyl proton is superimposed on those from the phenyl group) ppm. ^{13}C NMR ($CDCl_3$): δ -9.0 (SnCH_3, ^{1}J(SnC) = 330 Hz); 13.9

TABLE 2. ^{31}P and ^{119}Sn NMR data for the silyl esters Me_3SnCH_2CHXY (**XXXI–XXXVII**) [a,b]

	XXXI X = $P(O)Ph_2$ Y = $P(O)(OSiMe_3)Ph$	**XXXII** X = $P(O)Ph_2$ Y = $P(O)(OSiMe_3)_2$	**XXXIII** X = $P(O)(OSiMe_3)Ph$ Y = $P(O)(OSiMe_3)Ph$	**XXXIV** X = $P(O)(OSiMe_3)_2$ Y = $P(O)(OSiMe_3)Ph$	**XXXV** X = $P(O)(OSiMe_3)_2$ Y = $P(O)(OSiMe_3)_2$	**XXXVI** X = C(O)Ph Y = $P(O)(OSiMe_3)_2$	**XXXVII** X = $C(O)O^iPr$ Y = $P(O)(OSiMe_3)_2$
$\delta_{^{31}P}(X)$ (ppm)	31	31		8	8	–	–
$\delta_{^{31}P}(Y)$ (ppm)	31	7	36 (broad)	29		5	6
$\delta_{^{119}Sn}$ (ppm)	6 (d/d)	3 (d/d)	−27 (t, broad)	−1 (d/d)	2 (t)	−1 (d)	+3 (d)
$^3J(SnCCP(X))$ (Hz)	52	68	160	147	128	–	–
$^3J(SnCCP(Y))$ (Hz)	133	141		85		242	174

[a] Solvent, $CDCl_3$

[b] The ^1H NMR chemical shifts of the Me_3Sn and Me_3Si groups in **XXXI–XXXVII** range from −0.06 to 0.03 ppm ($^2J(SnCH) \approx 54$ Hz) and from 0.1 to 0.3 ppm respectively.

(SnCH_2, ^1J(SnC) = 275 Hz, ^3J(CCCH) = 8 Hz (taken from a gated spectrum)). ^{119}Sn NMR (neat): δ 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}H NMR (D_2O): δ 0.37 (s, 9H, SnCH_3, ^2J(SnCH) = 54.5 Hz); 1.51 (d, 2H, SnCH_2, ^2J(SnCH) not resolved); 1.58 (t, 3H, $COOCH_2CH_3$, ^3J(HCCH) = 7.1 Hz); 3.76 (t, 1H, $SnCH_2CH$, ^3J(HCCH) = 8.1 Hz); 4.49 (qua, 2H, $COOCH_2CH_3$) 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–XXXVII)*

A solution of 10 mmol of Me_3SiBr in 10 ml of dry methylene chloride was added dropwise at −30°C to a stirred solution of about 10 mmol of the isopropylesters 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 $CDCl_3$. 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}H NMR (CD_3OD): δ −0.1 (s, 9H, $SnCH_3$, ^2J(SnCH) = 54.0 Hz) ppm. ^{31}P NMR: δ 24.0 (d, $P^1(O)Ph_2$); 37 (d, P^2(O)(Ph)O$^-$), ^2J(P, P) = 6 Hz) ppm. ^{119}Sn NMR: δ −9 (d/d, ^3J(Sn, P^1) = 31 Hz, ^3J(Sn, P^2) = 145 Hz) ppm. EI-MS (matrix: triethylene glycol, ^{120}Sn, *m/e* (%): 579 (62, M + 23), 557 (10, M + H), 541 (26, M − 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}H NMR (CD_3OD): δ 0.7 (s, 6H, $SnCH_3$, ^2J(SnCH) = 69.8 Hz) ppm. ^{31}P NMR: δ 34 (broad, $P^1(O)Ph_2$ and P^2(O)Ph(ring)) ppm. ^{119}Sn NMR: δ −34 (d/d, ^3J(Sn, P^1) = 324 Hz, J(Sn, P^2) = 22 Hz) ppm. Ar FAB MS (matrix: triethylene glycol, ^{120}Sn, *m/e* (%)): 519 (14, M + 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, CH_2Cl_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}H NMR (CD_3OD): δ 0.58 (s, 6H, $SnCH_3$, ^2J(SnCH) = 70.5 Hz) ppm. ^{31}P NMR: δ 17 (broad, $P^1(O)(OH)_2$, J(Sn, P^1) = 183 Hz); 34 (broad, P^2(OH)OH(ring), ^3J(SnCCP^2) = 210 Hz) ppm. ^{119}Sn NMR: δ −34 (t (broad), J(Sn, P^1) and ^3J(SnCCP^2) = 198 Hz) ppm.

XLII: ^{1}H NMR (D_2O): δ 0.7 (s, 6H, $SnCH_3$, ^2J(SnCH) = 68.5 Hz) ppm. ^{31}P NMR: δ 23 ($P^1(O)O^{2-}$ and $P^2(O)O^-$ (ring)) ppm. ^{119}Sn NMR: δ −63 (^3J(SnCCP^1) and J(Sn, P^2(ring) = 215 Hz) ppm.

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References

1 H. Fleisch, *Ther. Umsch.*, *42* (1985) 366.

2 (a) F.A. Ebetino and L.A. Jamieson, *Phosphorus, Sulfur Silicon*, *51–52* (1990) 23; (b) F.H. Ebetino, *Eur. Pat. Appl. EP 298.553*, 1989; *Chem. Abstr.*, *110* (1989) 213077g.

3 (a) H. Weichmann and A. Tzschach, *J. Prakt. Chem., 318* (1976) 87, and references cited therein; (b) H. Weichmann, *J. Organomet. Chem., 262* (1984) 279, and references cited therein; (c) M. Dargatz, H. Hartung, E. Kleinpeter, B. Rensch, D. Schollmeyer and H. Weichmann, *J. Organomet. Chem., 361* (1989) 43, and references cited therein.

4 H. Weichmann and F. Richter, *Z. Chem., 29* (1989) 409.

5 D.K. Hutchinson and P.L. Fuchs, *J. Am. Chem. Soc., 109* (1987) 4755.

6 (a) B. Testa, *Grundlagen der organischen Stereochemie*, Chemie, Weinheim, 1983, p. 54; (b) R. Meusinger, C. Duschek, E. Kleinpeter, R. Borsdorf, K. Pihlaja and J. Mattinen, *Monatsh. Chem., 119* (1988) 1019; (c) R. Göbel, F. Richter and H. Weichmann, *Phosphorus, Sulfur, Silicon, 73* (1992) 67.

7 T. Kauffmann and R. Kriegsmann, *Chem. Ber., 115* (1982) 1810.

8 (a) H. Weichmann and C. Schmoll, *Z. Chem., 24* (1984) 390; (b) B. Jousseaume and P.J. Villeneuve, *J. Chem. Soc., Chem. Commun.*, (1987) 513.

9 (a) D.D. Davis and C.E. Gray, *Organomet. Chem. Rev. A, 6* (1970) 298; (b) M. Pereyre, J.P. Quintard and A. Rahm, *Tin in Organic Synthesis*, Butterworth, London, 1987, p. 16.

10 D. Gloyna, H. Köppel and H.-G. Henning, *J. Prakt. Chem., 316* (1974) 832.

11 (a) R.V. Dubs and W.V. Philipsborn, *Org. Magn. Res., 12* (1979) 326; (b) U. Vögeli and W.V. Philipsborn, *Org. Magn. Res., 7* (1975) 617.

12 C.E. McKenna, M.T. Higa, N.H. Cheung and M.C. McKenna, *Tetrahedron*, (1977) 155.

13 J. Chojnowski, M. Cypryk, J. Michalski, L. Wozniak, R. Corriu and G. Lanneau, *Tetrahedron, 42* (1986) 385.

14 D. Seyferth and S.B. Andrews, *J. Organomet. Chem., 30* (1971) 151.

15 *Organikum*, VEB Deutscher Verlag der Wissenschaften, Berlin, 1986, pp. 473, 478.

16 P. Nylen, *Chem. Ber., 57* (1924) 1023.

17 (a) H.-G. Hennig and G. Hilgetag, *J. Prakt. Chem., 29* (1965) 86; (b) B.A. Arbusov and V.S. Vinogradova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1957) 284.

18 (a) C.H. Roy, *US Patent 3251907*, 1966; *Chem. Abstr., 65* (1966) P3908f; (b) W.J. Stec and A. Okruszek, *Pol. PL 130.983*, 1985; *Chem. Abstr., 109* (1988) 211,219k.

19 M. Mastalerz, *Rocz. Chem., 39* (1965) 1129.

20 (a) W. Hewertson and H.R. Watson, J. Chem. Soc., 1962, 1490; (b) K. Issleib and L. Baldauf, *Pharm. Zent.-halle Deutschl., 99* (1960) 329.

21 R.C. Poller, *The Chemistry of Organotin Compounds*, Logos, London, 1970, p. 154.

22 T.N. Mitchell and G. Walter, *J. Chem. Soc., Perkin Trans. II*, (1977) 1842.

23 B. Hoffmann, *Ph.D. Thesis*, Academy of Sciences, Berlin, 1989.

24 A. Fürstner and H. Weidmann, *J. Organomet. Chem., 354* (1988) 15.

25 H.G. Kuivila, J.L. Considine, R.H. Sarma and R.J. Mynott, *J. Organomet. Chem., 111* (1976) 179.

26 M.R. Kula, E. Amberger and K.K. Mayer, *Chem. Ber., 98* (1965) 634.

27 W. McFarlane, J.C. Maire and M. Delmas, *J. Chem. Soc., Dalton Trans.*, (1972) 1872.