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SYNTHESIS, MOLECULAR STRUCTURE AND STEREOISOMERIZATION OF 2-PHOSPHINYL AND 2-PHOSPHONYLETHYL DIORGANOTIN HALIDES

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Summary

Functionally substituted triorganotin halides V—IX of type $R_2Sn(X)$-$(CH_2)_2P(O)PhR'$ (R = Me, t-Bu; R′ = OEt, t-Bu; X = Cl, Br) have been synthesized by halogen cleavage of the corresponding tetraorganotin compounds $R_2R^2Sn(CH_2)_2P(O)PhR'$ (R^2 = Me or Ph), I—IV. The solid state structure of Me_2Sn (Br) $(CH_2)_2P(O)PhBu$-t (IX), determined by X-ray diffraction, shows a distorted trigonal-bipyramidal structure at the tin atom, with intramolecular coordination of the P=O group. Spectroscopic data are in agreement with such a structure in solution for compounds V—IX. Upon varying the temperature, concentration or solvent in solutions of compounds V—IX a stereoisomerization is observed. On the basis of NMR (^1H, ^{13}C, ^{31}P, ^{119}Sn), IR and conductivity studies, it is suggested that this stereoisomerization involves a hexacoordinated transition state at the tin atom.

Introduction

Triorganotin halides with a pentacoordinated tin centre resulting from the intramolecular coordination of a donor function D suitably placed in an organic ligand within the same molecule offer interesting structural possibilities. Such compounds may provide good models to study the well-known phenomenon of the configuration instability of triorganotin compounds containing an electronegative fourth ligand [1—4]. In the recent years some triorganotin halides of this type, with a carbonyl [5—8], an oximato [9] or an amino group [1—4] as a built-in donor ligand in at least one of the organo

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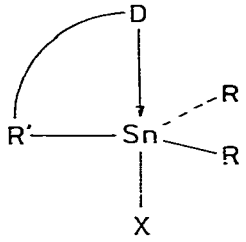


groups have been described. Only in a few cases were detailed studies of the molecular geometry and the molecular mobility of these compounds reported [1, 4, 7, 10].

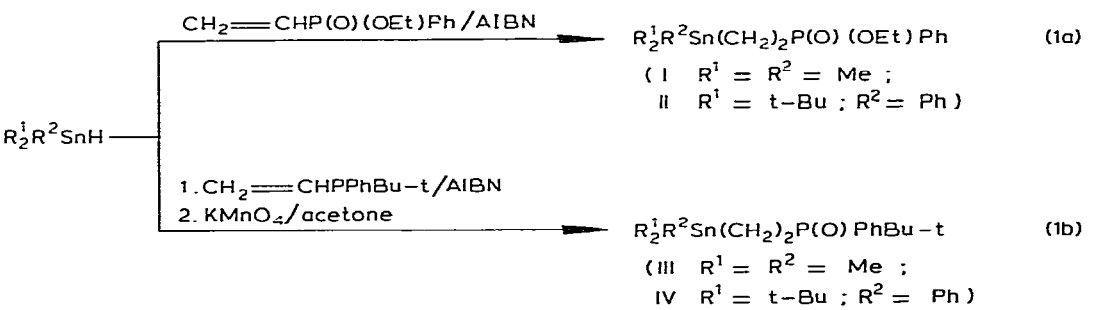
In a previous paper on 2-phosphono and 2-phosphonylethyl diorganotin halides $R_2Sn(X)(CH_2)_2P(O)(OEt)R'$ (R' = OEt, Ph) [11] we reported, without detailed structural studies, the intramolecular coordination of the P=O group to the tin atom. These molecules are interesting starting materials for new types of functionally substituted triorganotin hydrides and tin phosphorus heterocycles [12]. More recently, we described an example of intramolecular P=O → Sn coordination and of molecular mobility in triorganotin halides $R^1R^2Sn(X)$-$C_6H_4CH_2P(O)R^3_2$-*o* [13].

In continuation of this work we report below the synthesis, structure and stereoisomerization of 2-phosphinyl and 2-phosphonylethyl diorganotin halides $R_2Sn(X)(CH_2)_2P(O)PhR'$ (V—IX) *.

Results and discussion

Synthesis of the triorganotin halides V—IX

The main method for the synthesis of the 2-phosphinyl and 2-phosphonylethyl diorganotin halides V—IX involves the halogen cleavage of the corresponding 2-phosphinyl and 2-phosphonylethyl triorganotin compounds I—IV. Compounds I—IV can be obtained by hydrostannation of the appropriate vinylphosphinic esters (eq. 1a) [11], or by oxidation of the addition products of triorganotin hydrides and vinyl-t-butylphenylphosphine oxide (eq. 1b), respectively [15]. The halogenation was performed with bromine or hydrogen chloride in organic solvents such as chloroform, ether or methanol (eq. 2).



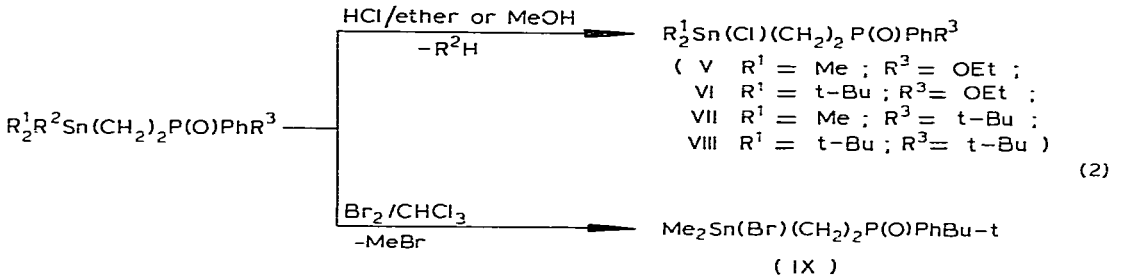
$R^1_2R^2Sn(CH_2)_2P(O)(OEt)Ph$ (1a)

(I $R^1 = R^2 = Me$;
II $R^1 = t\text{-}Bu$; $R^2 = Ph$)

$R^1_2R^2Sn(CH_2)_2P(O)PhBu\text{-}t$ (1b)

(III $R^1 = R^2 = Me$;
IV $R^1 = t\text{-}Bu$; $R^2 = Ph$)

* For preliminary results see ref. 14.



V—IX are crystalline solids which are monomeric in solution.

Structural study

X-ray structure determination of compound IX

The solid state structure of compound IX consists of discrete monomeric units separated by normal Van der Waals contacts. The final refined atomic coordinates and thermal parameters are listed in Table 1. An overall view of the molecule is shown in Fig. 1. The bond distances and bond angles are given in Tables 2 and 3.

The geometry of the bonds around the tin atom shows a slightly distorted trigonal bipyramid. The phosphinyl oxygen and the bromine atoms occupy the apical positions; the three carbon atoms lie in the equatorial idealized trigonal-bipyramid stereochemistry with the three in plane angles (120.3(4), 115.2(4), 122.8(4)°; Σ = 358.3(12)°), the axial Br—Sn···O bond angle (172.5(2)°), and the equatorial to axial C—Sn—Br angles (98.1(3), 92.3(3), 92.7(3)°), instead of the ideal values 120, 180 and 90°, respectively. The tin atom lies 16.2 pm away from the equatorial plane defined by the three carbon atoms attached to the tin. The Sn—C bond distances of 213.9(9), 214.9(9) and 217.5(10) pm, respectively, are in agreement with those observed for trimethyltin structures. The Sn—Br bond distance (268.4(1) pm) is significantly longer than the covalent Sn—Br bond distance in tetrahedral trialkyltin bromides (249 pm in Me_3SnBr [16], 250.4(5) pm in $Me_2Sn(Br)C_4Ph_4Br$ [17]). But the Sn—Br bond distance of compound IX is in good agreement with the corresponding value in intramolecular coordinated triorganotin bromides of formula $RR'Sn(Br)C_6H_4$ $CHZNMe_2$-*o*, reported by Van Koten and Noltes (263.0(2) pm for R = R' = Ph, Z = H [10], and 268.3(1) pm for R = Ph, R' = Me, Z = Me [3]). The Sn—O bond distance (232.4(6) pm) corresponds to the values reported for pentacoordinated triorganotin halide complexes with axial ligands coordinated by a P=O or a C=O group (235.7(3) pm for 2 $Ph_3SnCl \cdot Ph_2P(O)(CH_2)_2P(O)Ph_2$ [18], 234.6(6)pm for $Ph_3SnCl \cdot$ *cis*-$Ph_2P(O)CH{=}CHP(O)Ph_2$ [19], 233.2(6) pm for $Me_3SnCl \cdot Ph_3P{=}CHCOPh$ [20]). It is noteworthy that the X-ray structure determination of compound VII * shows a Sn—O bond distance (239 pm) longer than in compound IX. The shorter distance in IX may be explained by the higher polarizability of the Sn—Br bond as compared with the Sn—Cl bond. The torsion angles

* Unpublished results.

TABLE 1

FRACTIONAL COORDINATES ($X10^4$) AND THERMAL PARAMETERS FOR THE NON-HYDROGEN ATOMS (Estimated standard deviations in parentheses)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	6021(1)	2865(1)	3517(1)	13(1)	69(1)	64(1)	1(1)	3(1)	0(1)
Br	5655(1)	614(1)	3383(1)	22(1)	76(1)	160(2)	−7(1)	−4(1)	7(1)
P	6319(1)	5377(2)	2373(2)	14(1)	66(2)	44(2)	−1(1)	−1(1)	1(2)
O	6390(2)	4768(5)	3422(5)	16(1)	66(6)	41(5)	−1(2)	0(2)	5(5)
C(1)	6770(3)	2283(9)	4149(9)	12(2)	10(12)	10(10)	10(4)	−6(4)	8(10)
C(2)	5419(3)	3570(9)	4529(8)	13(2)	106(12)	64(9)	11(4)	13(3)	−3(9)
C(3)	5898(4)	3193(9)	1855(8)	23(3)	96(11)	38(7)	−2(4)	−1(3)	−13(7)
C(4)	5824(4)	4556(9)	1629(8)	18(2)	86(11)	63(9)	−11(4)	−8(4)	7(9)
C(5)	6119(4)	6938(8)	2570(9)	21(2)	64(10)	74(9)	3(4)	1(4)	−5(8)
C(6)	5965(4)	7534(10)	1481(9)	32(3)	107(11)	83(9)	14(5)	−17(5)	31(1)
C(7)	6593(4)	7608(9)	3100(9)	21(2)	66(10)	100(11)	−7(4)	−11(4)	−10(9)
C(8)	5633(4)	6921(9)	3323(9)	18(2)	107(12)	99(11)	6(4)	17(4)	−37(10)
C(9)	6936(4)	5303(8)	1652(9)	16(2)	68(10)	63(10)	−7(4)	0(4)	−13(9)
C(10)	6961(5)	5701(10)	591(9)	27(3)	98(12)	59(10)	−8(5)	16(5)	4(10)
C(11)	7447(6)	5644(12)	71(10)	31(3)	124(15)	83(12)	−17(6)	19(6)	−32(12)
C(12)	7902(5)	5234(11)	568(12)	30(3)	100(14)	100(14)	−15(6)	24(6)	−45(12)
C(13)	7876(4)	4808(10)	1625(11)	18(2)	104(13)	115(13)	−4(4)	16(5)	−46(12)
C(14)	7388(4)	4856(9)	2175(8)	14(2)	89(11)	75(10)	1(4)	0(4)	19(9)

TABLE 2

BOND DISTANCES (in pm) (with estimated standard deviations in parentheses)

Distance		Distance	
Sn—C(1)	214.9(9)	C(9) —C(10)	142.7(14)
Sn—C(2)	213.9(9)	C(10)—C(11)	139.2(15)
Sn—C(3)	217.5(10)	C(11)—C(12)	138.6(17)
Sn—Br	268.4(1)	C(12)—C(13)	143.3(17)
Sn—O	232.4(6)	C(13)—C(14)	141.3(13)
C(3)—C(4)	156.1(13)	C(14)—C(9)	140.9(13)
C(4)—P	181.4(10)	C(5) —C(7)	156.3(13)
P—O	151.3(6)	C(5) —C(6)	158.9(14)
P—C(5)	183.3(10)	C(5) —C(8)	155.3(13)
P—C(9)	180.5(10)		

quoted in Table 4 and the molecular geometry shown on Fig. 1 indicate that the five-membered chelate ring in compound IX is close to a half chair conformation. The P, O, Sn and C(3) atoms are nearly coplanar and the ring is puckered at the C(4) edge.

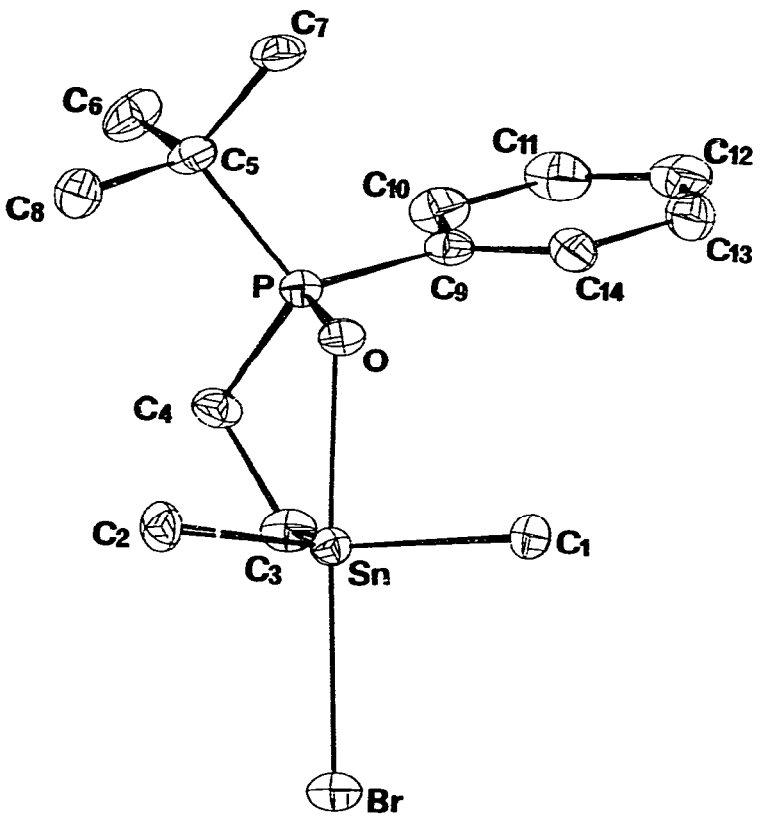


Fig. 1. Molecular geometry of $Me_2Sn(Br)(CH_2)_2P(O)PhBu\text{-}t$ (IX).

TABLE 3

BOND ANGLES (in °) (with estimated standard deviations in parentheses)

Angle		Angle	
Br—Sn—O	172.5(2)	P—C(9)—C(14)	117.9(9)
Br—Sn—C(1)	92.3(3)	P—C(9)—C(10)	120.4(9)
Br—Sn—C(2)	98.1(3)	C(9)—C(10)—C(11)	118.5(12)
Br—Sn—C(3)	92.7(3)	C(10)—C(11)—C(12)	121.4(13)
C(1)—Sn—C(2)	120.3(4)	C(11)—C(12)—C(13)	120.2(12)
C(1)—Sn—C(3)	122.8(4)	C(12)—C(13)—C(14)	119.7(12)
C(2)—Sn—C(3)	115.2(4)	C(13)—C(14)—C(9)	118.6(11)
		C(14)—C(9)—C(10)	121.6(10)
O—Sn—C(1)	86.9(3)		
O—Sn—C(2)	88.7(3)	P—C(5)—C(6)	110.2(7)
O—Sn—C(3)	81.5(3)	P—C(5)—C(7)	107.8(7)
		P—C(5)—C(8)	106.8(7)
Sn—C(3)—C(4)	111.2(7)		
C(3)—C(4)—P	108.4(7)	C(6)—C(5)—C(7)	111.3(9)
C(4)—P—O	108.5(4)	C(6)—C(5)—C(8)	110.8(9)
P—O—Sn	114.2(3)	C(7)—C(5)—C(8)	109.8(9)
O—P—C(9)	109.2(4)		
O—P—C(5)	109.8(4)		
C(5)—P—C(9)	110.5(5)		
C(5)—P—C(4)	111.4(5)		
C(4)—P—C(9)	107.5(5)		

Spectroscopic data of compounds V—IX

The Mössbauer data of compound IX, with an isomer shift of 1.67 mm sec^{-1} (relative to SnO_2) and a quadrupole splitting of 3.39 mm sec^{-1} confirm the trigonal-bipyramid structure of compounds V—IX in the solid state [21,22].

Several arguments, based on IR and NMR data and results reported in the literature [3,4,10], strongly suggest that compounds V—IX also exist in solution in a trigonal-bipyramid structure. Upon comparing the vibrational spectra of compounds V—IX to those of the tetracoordinated species I—IV (Table 5) it appears that the IR frequency attributed to the P=O group is shifted to lower frequency values. Such a shift indicates the presence of an intramolecular coordination between the P=O group and the halogenated tin atom.

The NMR coupling constants $^2J(^{119}SnC^1H_3)$ in V and VII and $^1J(^{119}Sn^{13}CH_3)$ in VII (Table 5) are characteristic of five-coordinated methyl substituted tin

TABLE 4

TORSION ANGLES [a] (in °) IN THE FIVE-MEMBERED CHELATE RING OF COMPOUND IX

Sn—C(3)—C(4)—P	44.0(8)
C(3)—C(4)—P—O	—37.3(8)
C(4)—P—O—Sn	13.8(5)
P—O—Sn—C(3)	6.9(4)
O—Sn—C(3)—C(4)	—29.7(7)

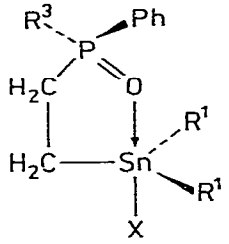
[a] The torsion angle A(1)—A(2)—A(3)—A(4) is viewed along the A(2)—A(3) bond with the rotation of A(1) to A(4) taken to be positive.

TABLE 5

SELECTED INFRA-RED AND ^{1}H NMR DATA FOR COMPOUNDS I–VIII

Compound	IR [b] ν(P=O) (cm^{-1})	^{1}H NMR				
		Solvent	$\delta(SnCH_3)$ (ppm)	$\delta(SnCCH_3)$ (ppm)	$^2J(^{119}SnC^1H_3)$ (Hz)	$^3J(^{119}SnCC^1H_3)$ (Hz)
I	1228	$CDCl_3$	0.10(s)		54.0	
V	1182	$CDCl_3$	1.02(s)		69.9	
		Pyridine	0.92(s)		68.8	
II	1230	$CDCl_3$		1.16(s)		65.3
				1.19(s)		65.2
VI	1186	$CDCl_3$		1.33(s)		88.2
				1.39(s)		87.0
		Pyridine		1.52(s)		84.0
III [a]	1181	$CDCl_3$	0.09(s)		53.9	
VII [a]	1138	$CDCl_3$	0.73(s)		71.0	
			0.81(s)		71.1	
		Pyridine	0.84(s)		70.5	
IV	1133	$CDCl_3$		1.18(s)		65.0
				1.22(s)		64.9
VIII	1135	$CDCl_3$		1.11(s)		87.2
				1.38(s)		88.6
		Pyridine		1.47(s) [c]		82.5

[a] ^{13}C NMR: III($CDCl_3$): $\delta(SnCH_3)$ — 9.71 ppm(s); $^1J(^{119}Sn^{13}CH_3)$ 344.4 Hz; VII($CDCl_3$): $\delta(SnCH_3)$ 1.43 ppm(s), 2.90 ppm(s); $^1J(^{119}Sn^{13}CH_3)$ 539.4 Hz, 511.1 Hz. [b] In CCl_4. [c] Broadened signal.



compounds [23,24]. As the phosphorus atom in compounds V—IX is a chiral center the two methyl or t-butyl groups attached to the tin atom are diastereotopic. They show two signals in the ^{1}H and ^{13}C NMR spectra, with nearly the same value for the corresponding coupling constants with the tin atom. This indicates that both the methyl and t-butyl groups occupy equatorial positions in the trigonal-bipyramidal arrangement. In case of an axial-equatorial disposition, the values of the coupling constants would be very different [25].

The intramolecular coordination of the P=O group in compounds V—IX is also confirmed by the ^{31}P and ^{119}Sn NMR data (Table 6). The high field shift of the ^{119}Sn NMR signal of VII and VIII when compared to those of Me_3SnCl ($\delta^{119}Sn$ 164.2 ppm in $CDCl_3$ [26]) and n-Bu_3SnCl ($\delta^{119}Sn$ 141.2 ppm in CCl_4 [27]) indicates the pentacoordination at the tin atom. In agreement with the P=O group coordination is the low field shift of the ^{31}P NMR signal of compounds V—IX as compared to those of compounds I–IV. In compounds V—IX the $J(^{119}Sn{\sim}^{31}P)$ coupling constant is considerably smaller than the value for $^{3}J(^{119}SnCC^{31}P)$ observed in compounds I—IV. Several factors may give rise to

TABLE 6

^{31}P NMR PARAMETERS FOR COMPOUNDS I—VIII

Compound	Solvent	δ (ppm)	$^{3}J(^{119}SnCC^{31}P)$ (Hz)	$J(^{119}Sn{\sim}^{31}P)$ (Hz)
I	$CDCl_3$	45.7	234.8	
V	$CDCl_3$	53.4		55.4
	Pyridine	55.4		85.4
	HMPT/C_6D_6 (1/1)	47.3		283.5
II	$CDCl_3$	41.8	210.2	
VI	$CDCl_3$	51.3		38.1
	Pyridine	54.3		39.2
III	$CDCl_3$	47.8	99.1	
VII [a]	$CDCl_3$	60.0		38.8
	Pyridine	63.2		41.3
	HMPT/C_6D_6 (2/1)	61.6		51.8 [b]
IV	$CDCl_3$	46.5	160.4	
VIII [a]	$CDCl_3$	57.6		20.0 [b]
	Pyridine	59.2		21.2 [b]
	HMPT/C_6D_6 (2/1)	60.3		27.6 [b]

[a] ^{119}Sn NMR: VII($CDCl_3$): δ 2.9 ppm (d); $J(^{119}Sn{\sim}^{31}P)$ 36.6 Hz; VIII($CDCl_3$): δ — 21.9 ppm (d); $J(^{119}Sn{\sim}^{31}P)$ 14.8 Hz. [b] Unresolved satellites.

this difference between the two families of compounds: (i) the difference in the coordination state of the tin atom; (ii) the difference in the Sn–C—C—P dihedral angles; (iii) the fact that in compounds V—IX, because of the intramolecular coordination, the $J(^{119}Sn\sim^{31}P)$ coupling is the contribution of two couplings, namely ^3J and ^2J, of opposite sign [28].

Stereochemical study

In agreement with the well-known stabilization of triorganotin halides by intramolecular coordination [1—4], compounds VI—IX are configurationally stable at room temperature in non-nucleophilic solvents (hydrocarbons, carbon halides). This configurational stability is indicated by the separated signals of the diastereotopic t-butyl and methyl groups in the ^1H NMR spectra. In contrast, V undergoes a stereoisomerization in all solvents.

The stereochemistry of compounds V—IX is highly dependent upon the solvent. The presence of traces of nucleophiles in the solution of these compounds causes the coalescence of the H methyl and t-butyl signals. In non-nucleophilic solvents the stereoisomerization of compounds V–IX can be induced by increasing the concentration of the solutions. As an example, on a spectrum recorded at 200 MHz, the methyl signals of compound VII coalesce in $CDCl_3$ for a concentration equal to 0.2 mol l^{-1}. Furthermore, the nature of the substituents at the tin and phosphorus atoms have a significant influence on the stereochemical stability of compounds V—IX. Because the P=O donor ability is higher for a phosphinyl group than for a phosphonyl group, compounds VII–IX are more stable than compounds V and VI. Compounds VI and VIII with t-butyl substituents at the tin show a higher stability than the corresponding methyl substituted compounds V, VII and IX. At room temperature and in all solvents compound V undergoes an inversion. Even at –90°C in toluene there is a single methyl signal in a 100 MHz ^1H NMR spectrum. In contrast compound VIII is stable in toluene up to 120°C. The configurational stability of the title compounds decreases with increasing the atomic number of the halogen attached to the tin atom.

In order to examine the possible existence of ionic species in solutions of compounds V—IX in the presence of nucleophiles, conductometric titrations of a 0.1 *M* solution of HMPT in CH_2Cl_2 against VII and VIII were carried out. In both cases, the conductivity of the pure HMPT solution in CH_2Cl_2 (λ 35—38 × 10^{-6} ohm^{-1} cm^{-1}) is not increased upon the progressive addition of organotin halide solutions.

The molecular mobility of compounds V–IX could be due to various rearrangement processes. A Berry type pseudorotation or a turnstile-rotation [29] for the ligand exchange at a pentacoordinated tin atom can be excluded. Such processes would involve energetically and sterically unfavourable structures of V—IX in which both the strongly electronegative halogen and oxygen atoms and the five-membered chelate ring occupy equatorial sites [28, 1–4].

The following arguments support a stereoisomerization process of compounds V—IX which involves hexacoordinated intermediates (transition states) with intact intramolecular Sn—O coordination formed by attack of an external nucleophile in donor solvents (Fig. 2 (A)) or by association of two molecules

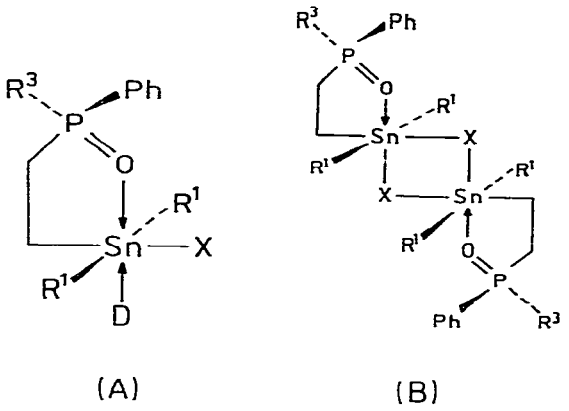


Fig. 2. Intermediates in the stereoisomerization of V—IX.

of V—IX in non-nucleophilic solvents (Fig. 2 (B)): (i) The energy barrier for the stereoisomerization is lowered by nucleophiles ($\Delta G^{\ddagger}_{coal.}$ of compound VIII: 72.4 kJ mol^{-1} in $CDCl_3$ and 58.5 kJ mol^{-1} in pyridine) or by increasing the concentration of the solutions, respectively. (ii) The $J(^{119}Sn{\sim}^{31}P)$ coupling constant in compound VI--VIII is nearly independent of the donor ability of the solvent (Table 6). (iii) Even in presence of strong nucleophiles (DMSO) the IR spectra of VI--IX show no absorption bands of uncoordinated P=O groups. (iv) The results of the conductometric study clearly exclude a nucleophile-induced dissociation of the tin halogen bond in V—IX.

Intermediates of type (A) and (B) were previously postulated by Van Koten, Noltes [3] and Corriu [30]. However, the solvent dependence of $J(^{119}Sn{\sim}^{31}P)$ in compound V (Table 6) indicates a second alternative for the stereoisomerization of this compound in donor solvents which involves a nucleophile-induced opening of the intramolecular Sn—O coordination followed by inversion of the configuration at the tin atom. Inversion at the tetracoordinated phosphorus atom while conceivable, is energetically unlikely [31].

Experimental

General

All reactions were carried out under dry nitrogen or argon. Solvents were purified and distilled before use under nitrogen.

The NMR spectra were recorded using the following spectrometers: Varian HA-100 (^1H), Varian XL-100 (^{13}C), Bruker WP-200 (^1H, ^{31}P, ^{119}Sn) and Bruker WP-60 (^{31}P). As references were used TMS (^1H, ^{13}C), 85% H_3PO_4 (^{31}P) and Me_4Sn (^{119}Sn). Low-field shifts are positive.

Infrared spectra were obtained with a Carl Zeiss UR-20 instrument.

The conductometric measurements used a Tacussel conductometer and a conductance cell with a constant of 1.07 cm^{-1}. For titrations of the CH_2Cl_2 solutions the compounds VII and VIII were added by a calibrated syringe to the HMPT *.

* The conductometric studies were carried out by Prof. R.J.P. Corriu (University of Languedoc, Montpellier, France).

X-ray structure determination of compound IX

Preliminary unit cell dimensions and space group *Pccn* were determined from Weissenberg photographs. Cell parameters were refined by a least-squares fitting of the angular position of 25 reflexions.

Crystal data: $C_{14}H_{24}OPBrSn$, M = 437.92; orthorhombic, *a* 25.137(2), *b* 11.174(1), *c* 12.760(1) Å; *V* 3584.04 Å^3; d_{exp} 1.624 g cm^{-3}, d_{calc} 1.624 g cm^{-3}; *Z* = 8; *F*(000) = 1696; space group *Pccn*. The intensity of 3576 reflexions ($2° < \theta < 25°$) was collected on an automatic ENRAF NONIUS CAD-4 diffractometer, with graphite monochromatized Mo-K_α radiation. The intensities of three standard reflexions (295; 1275; 1573) were recorded periodically, and no decrease was observed during the data collection. The data were corrected for Lorentz and polarization factors and for anomalous dispersion, but not for absorption. The structure was solved by heavy atom method. Fourier synthesis allowed the location of all non-hydrogen atoms. The structure was refined using the XFLSN program [32], with Sn, Br, P, O, C atoms anisotropic. Refinement with 1858 reflexions $F_0 > 36$ (F_0) reached and R_w value of 0.045 ($R_w = \Sigma(w(F_0 - F_c)^2/\Sigma wF_0^2)^{1/2}$) and an *R* value of 0.044 ($R = \Sigma|F_0 - F_c|/\Sigma F_0$).

Materials. Trimethyltin hydride was prepared by $LiAlH_4$ reduction of trimethyltin chloride in dibutyl ether..

Di-t-butylphenyltin hydride

A solution of 27.5 g (0.08 mol) of di-t-butylphenyltin chloride [33] in 50 ml of ether was added dropwise at —20°C to a stirred suspension of 1.5 g (0.04 mol) lithium aluminium hydride in 250 ml of ether. Reflux for 1 h and work up by hydrolysis in the usual fashion afforded 14.2 g (57%) di-t-butylphenyltin hydride; b.p. 99—101°C/2.7 mmHg; ^{1}H NMR(CD_2Cl_2): 1.25 ppm (s, 18H, t-C_4H_9Sn, ^3J(SnCCH) 86Hz); 5.32 ppm (m, 1H, SnH); 7.28—7.70 ppm (m, 5H, SnC_6H_5). (Found: C, 54.37; H, 7.59; Sn, 38.41. $C_{14}H_{24}Sn$ calcd.: C, 54.07; H, 7.78; Sn, 38.16%).

t-Butylphenylvinylphosphine

To the stirred Grignard reagent prepared from 24.3 g (1 mol) of magnesium and vinyl chloride in 250 ml of tetrahydrofuran, and diluted with further 250 ml of tetrahydrofuran before use, was slowly added a solution of 126 g (0.63 mol) of t-butylphenylphosphine chloride in 100 ml of benzene. The mixture was then stirred 15 h at 50°C. After hydrolysis with 10% aqueous HCl the organic phase was dried over anhydrous sodium sulfate and distilled; b.p. 83—84°C/2 mmHg; ^{1}H NMR (C_6D_6): 0.95 ppm (d, 9H, PC_4H_9-t, ^3J(PCCH) 11.7 Hz); 5.47—6.01 ppm (m, 2H, CH=CH_2); 6.37—6.75 ppm (m, 1H, C*H*=CH_2); 7.01—7.54 (m, 5H, PC_6H_5). (Found: C, 75.31; H, 8.86; P, 15.73. $C_{12}H_{17}P$ calcd.: C, 74.99; H, 8.92; P, 16.12%).

Ethyl (2-phenylphosphonylethyl)triorganostannanes I and II

A mixture of 0.15 mol trimethyltin or di-t-butylphenyltin hydride and 0.1 mol ethyl phenylvinylphosphinate was slowly warmed to 70°C for 8—15 h with stepwise addition of 3 mol% of AIBN. The product mixture was distilled in vacuum (cf. Table 7).

TABLE 7

PHYSICAL CONSTANTS, YIELDS AND ANALYTICAL DATA OF COMPOUNDS I–IX

Compound	R^1	R^2	R^3	X	B.p. (°C/mmHg)	M.p. (°C)	Yield (%)	Analyses (Found (calcd.) (%))			
								C	H	P	X
I	Me	Me			113–115/0.02		81	43.12 (43.25)	6.39 (6.42)	8.71 (8.58)	
II	t-Bu	Ph			166–168/0.02		53	56.62 (56.83)	7.21 (7.35)	6.23 (6.11)	
III	Me	Me			102–104/0.02	76–77	79	48.71 (48.29)	7.63 (7.29)	8.21 (8.30)	
IV	t-Bu	Ph				114–116	72	60.53 (60.14)	8.25 (7.96)	6.21 (5.97)	
V	Me		OEt	Cl	132–134/0.05	45–47	64	37.63 (37.79)	5.24 (5.29)		9.12 (9.30)
VI	t-Bu		OEt	Cl		104–106	73	46.51 (46.43)	6.81 (6.93)		6.38 (7.62)
VII	Me		t-Bu	Cl		149–151	76	42.89 (42.73)	6.47 (6.15)		8.81 (9.01)
VIII	t-Bu		t-Bu	Cl		196–198	86	50.86 (50.30)	8.02 (7.60)		7.21 (7.42)
IX	Me		t-Bu	Br		160–162	81	38.40 (38.49)	5.52 (6.01)		18.25 (18.57)

(2-t-Butylphenylphosphinylethyl)triorganostannanes III and IV

(a). In the manner described above, from t-butylphenylvinylphosphine and trimethyltin hydride or di-t-butylphenyltin hydride, in a molar ratio of 1/1 for the first step, were obtained (2-t-butylphenylphosphinoethyl)trimethylstannane (b.p. 106—108°C/0.2 mmHg; Found: 50.63; H, 7.71; P, 8.51. $C_{15}H_{27}PSn$ calcd.: C, 50.45; H, 7.62; P, 8.68%) and (2-t-butylphenylphosphinoethyl)di-t-butylphenylstannane (b.p. 143—145°C/0.04 mmHg; Found: C, 62.21; H, 8.18; P, 6.27. $C_{26}H_{41}PSn$ calcd.: C, 62.05; H, 8.21; P, 6.16%).

(b) The oxidation of the compounds prepared above to III and IV was performed in acetone at room temperature by dropwise addition of a saturated solution of $KMnO_4$ in the same solvent. The reaction was complete when the solution over the precipitate of MnO_2 became violet. The mixture was then filtered and the filtrate distilled (cf. Table 7).

(2-Phosphonyl and 2-phosphinylethyl)diorganotin chlorides V—VIII

A solution of 0.1 mol of hydrogen chloride in ether was added at 0°C to 0.1 mol of I—IV in 50 ml of ether and the resulting suspension or clear solution was stirred for 1 h at room temperature. After removal of the solvent the white solids were recrystallized from methylene chloride/hexane (cf. Table 7).

(2-t-Butylphenylphosphinylethyl)dimethyltin bromide IX

To a solution of 0.1 mol of III in 50 ml of $CHCl_3$ was added at —5°C 0.1 mol of bromine in 50 ml of the same solvent. After standing at room temperature for 2 h the solvent was removed and the residual white solid was recrystallized from methylene chloride/hexane (cf. Table 7).

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