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REACTION OF STANNENES AND PHOSPHASTANNENES WITH ALDEHYDES AND KETONES: NEW TIN FOUR-MEMBERED RING DERIVATIVES

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*Stannene $Tip_2Sn=CR_2$ **1** (Tip = 2,4,6-triisopropylphenyl, CR_2 = fluorenylidene) enters a [2+2] cycloaddition reaction with benzophenone to afford the four-membered ring derivative **2**. This stannaoxetane undergoes a [2+2] decomposition with formation of the corresponding stannanone **8** and alkene **9** and an easy hydrolysis by initial cleavage of the Sn–C bond. Diphenylacetaldehyde also gives with **1** a stannaoxetane, which has been characterized by its hydrolysis products. Phosphastannene $Tip_2Sn=PAr$ **13** (Ar = 2,4,6-tri-tert-butylphenyl) reacts with benzaldehyde according to a [2+2] cycloaddition pattern leading to stannaphosphaoxetane **14**, whereas ene-products **19–21** were obtained with acetaldehyde, acetone, and acetophenone.*

INTRODUCTION

The chemical behavior of double-bonded compounds of the type >M=M' (M = Si, [1, 12], Ge [9, 15] M' = M, C, N, P, O, S, Se, Te) is now well known. It is not yet the case for their tin analogues >Sn=M' [9–13]: due to the difficulty of synthesis and isolation of such derivatives and sometimes to the poor stability of their adducts or cycloadducts, their reactivity is much less known. For example, only one paper has been published on the reactivity of >Sn=M' compounds with saturated aldehydes and ketones, more precisely the reaction of a stannaimine >Sn=N- with benzaldehyde [16].

We report here on the reactivity of stannene **1** and the corresponding phosphastannane with some aldehydes and ketones.

RESULTS AND DISCUSSION

1. STANNENES

a) Benzophenone

The addition of benzophenone to stannene **1** [17] affords the sole stannaoxetane **2**. The first step leading to this four-membered ring derivative is probably the nucleophilic attack of oxygen to the tin atom followed by the cyclization. Such a preliminary step is supported by the easy complexation of the tin atom of **1** by ethers [17]:

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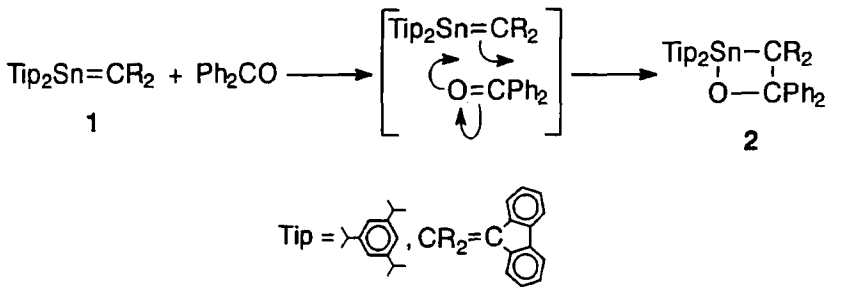
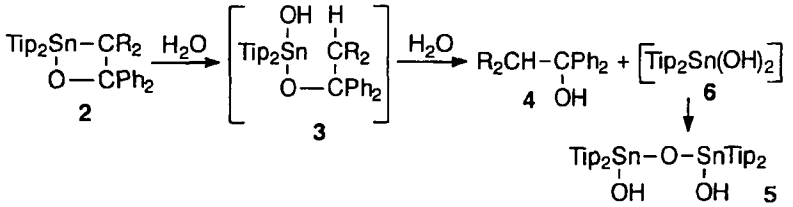


The regiochemistry of this reaction, with, as expected, the oxygen atom bonded to tin, was proved by mass spectrometry, in which the fragments $Ph_2C{=}CR_2$ and Tip_2SnO + 1 being observed. No fragments corresponding to the other type of [2+2] decomposition, leading to the starting stannene and ketone, were detected.

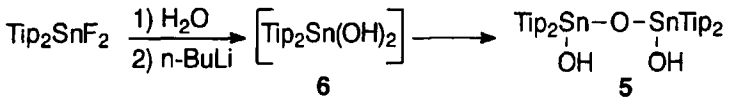
The structure of **2** was also unambiguously proved in ^{13}C NMR with a signal in the expected range (88.8 ppm) for the carbon atom bonded to oxygen. The carbon atom of the fluorenylidene moiety (88.6 ppm) is observed at low field. Similar chemical shifts (70.6 ppm) [17] were observed for this carbon in the four-membered ring 2,4-distanna-1,3-cyclobutane, the head-to-tail dimer of the stannene **1**, whereas signals between 45 and 55 ppm are found in acyclic compounds [18].

In the ^1H NMR, the methyls of the *o*-Pr-*i* groups give a wide multiplet due to the hindered rotation of the two Tip groups because of the large steric hindrance. But a well-resolved doublet (coupling with the CH) is observed for the methyls of the *p*-Pr-*i* groups.

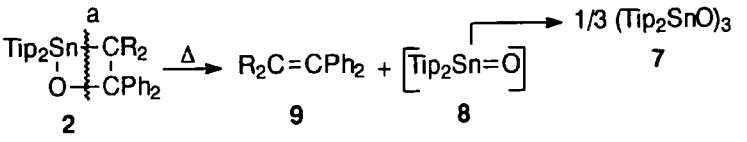
Crystals of **2** are stable under nitrogen at room temperature and can be kept for long periods without change, but its solutions are air and moisture sensitive. Addition of water to **2** leads to the cleavage of the Sn–C bond of the four-membered ring with formation of **3**, which was characterized by proton and tin NMR. After one week at room temperature, NMR analysis of the solution of **3** in Et_2O or pentane showed the formation of two new products: the alcohol **4** and a tin-containing derivative which is assumed to be **5**. The structure of this compound was tentatively assigned on the basis of ^{119}Sn NMR (δ: – 104.6 ppm, corresponding to a tin atom bonded to two oxygens) and ^1H NMR, which displays two diastereotopic methyl groups for every *o*-Pr-*i* group. Such a nonequivalence of these groups proves that the Sn atom is prochiral and excludes the dihydroxide **6**, which is probably an intermediate in this reaction.



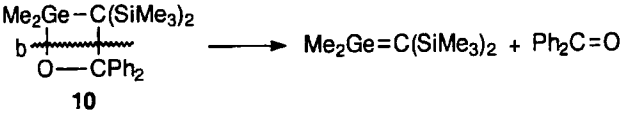
Compound **5** was also obtained by independent synthesis from Tip_2SnF_2 [17] and LiOH prepared in situ from H_2O and *n*-butyllithium:



Fractional crystallization failed to give pure **5**; the latter was always obtained with a small admixture of $(Tip_2SnO)_3$, making elemental analysis ineffective to for unambiguous determination of its structure. Heating **2** in a sealed tube at 100°C leads to its complete decomposition with formation of **7**, the trimer of the stannanone **8**, and the corresponding 9-diphenylmethylenefluorene **9**:



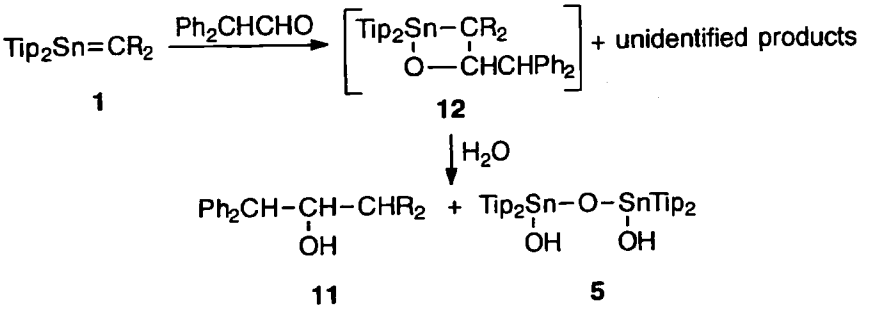
We should note that the four-membered ring derivative germaoxetane **10** [19] including the $OCPh_2$ moiety has a completely different behavior towards the [2+2] decomposition, since a fragmentation of type (b) is observed:



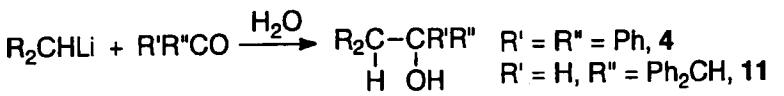
It is interesting to compare the reactivity of the stannene **1** towards benzophenone with the chemical behavior of other double-bonded derivatives of group 14 with thes same ketone. It appears that depending on the group 14 element and on the substituents, various reactions are observed: similar [2+2] cycloadditions as with **1** occur with germene $Mes_2Ge{=}CR_2$ [20] and disilene $Mes_2Si{=}SiMes_2$ [21], an ene reaction with germene $Mes_2Ge{=}CHCH_2tBu$ having allylic protons [22] and unexpected [2+4] cycloadditions involving a Ph group of the benzophenone (the case of $Me_2M{=}C(SiMe_3)_2$, M = Si [23], Ge [19]) or a Ph group of silene $R_2Si{=}C(Ph)OR$ (R = Me_3Si) [24] leading after thermolysis or photolysis to the corresponding [2+2] cycloadduct. No reaction occurs with germaphosphene $Mes_2Ge{=}PAr$, probably for steric reasons.

b) Other Aldehydes and Ketones

With other aldehydes (benzaldehyde, acetaldehyde, and diphenylacetaldehyde) or ketones such as acetone, much less straightforward reactions occurred. A ^{119}Sn NMR analysis immediately after reaction showed the formation of many tin-containing derivatives, and no cycloadduct could be isolated in pure form. Moreover, NMR analysis after a few days showed the occurrence of the reaction mixture with the formation of new unidentified products. However, in the case of Ph_2CHCHO, the two derivatives **5** and **11** (with trace amounts of $(Tip_2SnO)_3$) crystallized after a few days from a pentane solution of the reaction mixture kept at -20°C. The formation of these two derivatives is probably a good indication of the preliminary formation of the air and moisture sensitive stannaoxetane **12** which is easily hydrolyzed:



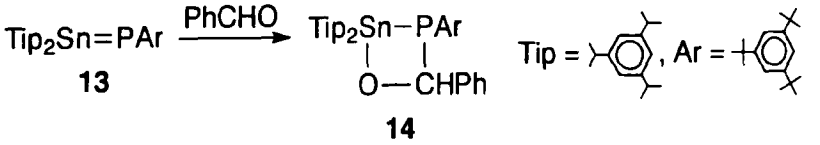
The poor stability of **12** is of course due to the minor steric protection compared to the cycloadduct **2**. Alcohols **4** (synthesized previously by reaction of $R_2CH(Li)AsPhMe_3$ with benzophenone followed by hydrolysis [25]) and **11** have been prepared independently from benzophenone or diphenylacetaldehyde and fluorenyllithium:



2. PHOSPHASTANNAENES

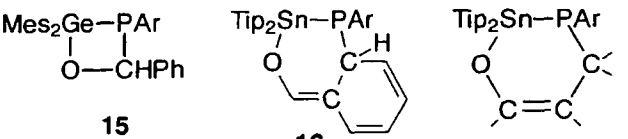
a) Benzaldehyde

Whereas stannene **1** gives a cycloadduct with benzophenone, its phosphorus analogue **13** [26] does not react with this ketone. This is probably due to the low reactivity of the phosphastannene compared to the stannene but also probably to a too large steric hindrance around the Sn=P double bond due to the huge 2,4,6-tri-*tert*-butylphenyl group. By contrast, **13** reacts with benzaldehyde to give the expected [2+2] cycloadduct **14** in a moderate yield according to NMR (65%):



13 **14**

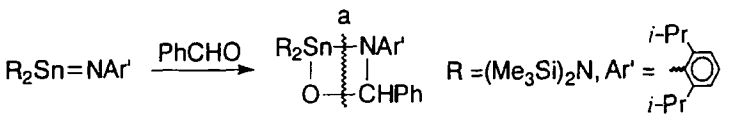
Compound **14** could not be obtained in completely pure form but always with minor amounts of unidentified by-products. However, its structure could be determined by ^{31}P and ^{119}Sn NMR from the signals at 95.8 ppm and - 8.4 ppm respectively. A similar low field δ ^{31}P signal (+82.5 ppm) has been found in the germanium analogue **16** [27]:



15 **16** **17**

The formation of a six-membered ring such as **16** involving the phenyl group of the benzaldehyde can be excluded because similar six-membered ring compounds **17** obtained from **13** and α-ethylenic aldehydes and ketones [28] present completely different ^{31}P and ^{119}Sn NMR data: δ ^{31}P: +6.7 to -21.9 ppm with a very large P–Sn coupling constant ($^{1}J_{SnP}$: 1720 to 1960 Hz), δ ^{119}Sn: -84.6 to -111.5 ppm. The regiochemistry observed corresponds to the $Sn^{\delta+}$–$P^{\delta-}$ polarity of the Sn–P double bond. Only one diastereoisomer was obtained, probably for steric reasons with the phenyl group in a *trans* position in relation to the Ar group. Such a stereochemistry has been previously proved in the case of **15** by examination of the coupling constant $^{2}J_{PH}$ [27], which was not possible for **14** (H under the multiplet of the aromatic group).

As said previously, the only reaction between a double-bonded tin derivative and a saturated aldehyde or ketone reported until now was the reaction between the stannaimine $R_2Sn{=}NAr'$ and benzaldehyde, giving four-membered ring derivative **18** [16] with the similar regiochemistry (oxygen bonded to tin):

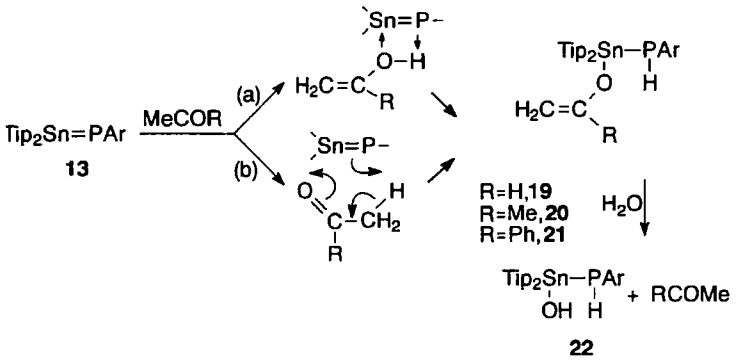


18

It should be noted that by stirring in solution for a few days heterocycle **18** undergoes the same type of fragmentation (a) as **2** with formation in this case of Sn=O and N=C derivatives.

b) Acetaldehyde, Acetone, Acetophenone

By contrast with benzaldehyde, enolizable aldehydes and ketones do not afford with **13** any four-membered ring derivatives but exclusively the acyclic adducts **19–21**:



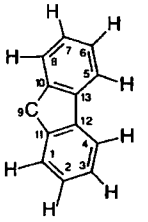
The two mechanisms (a) (reaction of the enolic form with displacement of the keto-enol equilibrium) or (b) (ene-reaction) can be postulated.

Adducts **19** and **20** are highly moisture sensitive and cannot be isolated, leading very easily to **22** previously obtained by hydrolysis of the starting stannaphosphene [26]. Compound **21**, due to the presence of a phenyl group, is less hydrolyzable and, even if it was not possible to isolate it in pure form, was evidenced by ^{1}H and ^{13}C NMR. In ^{1}H NMR, as in the case of the adduct of benzophenone with stannene, the methyls of iPr groups appear as a broad multiplet due to the slow rotation of Tip groups. Compound **19–21** present high-field δ ^{31}P signals (-106.0 to -107.8 ppm) characteristic of the Sn–P(H)Ar moiety.

Very different reactions are observed between acetone and symmetrical unsaturated species such as disilenes >Si=Si< [29] or digermenes >Ge=Ge< [30] since only [2+2] cycloadducts are formed in these cases.

EXPERIMENTAL

All experiments were carried out in flame-dried glassware under N_2 atmosphere with high-vacuum line techniques. Solvents were dried and freshly distilled from sodium benzophenone ketyl and carefully deoxygenated over the vacuum-line by several freeze-pump-thaw cycles. NMR spectra were recorded in $CDCl_3$ or C_6D_6 on the following spectrometers: ^{1}H, Bruker AC 80 (80.13 MHz) and AC 200 (200.13 MHz); $^{13}C\{^{1}H\}$, Bruker AC 200 (50.32 MHz; reference TMS); ^{31}P Bruker AC 200 (81.01 MHz; reference H_3PO_4, 85%); ^{119}Sn, Bruker AC 200 (74.63 MHz; reference Me_4Sn). Mass spectra were obtained on a Hewlett-Packard 5989 A spectrometer by EI at 70 eV or by DCI (CH_4). Melting points were determined on a Wild Leitz-Biomed apparatus. Elemental analyses were performed by the Service de Microanalyse de l'Ecole de Chimie de Toulouse. The numbering scheme for fliorenyl group is shown below:



Reaction of Compound 1 with Benzophenone. Stannene **1** was synthesized according to the procedure already described [17, 18] by addition of one equivalent of tert-butyllithium (1.7 M solution in pentane) to a solution of $Tip_2Sn(F)C(H)R_2$ [17] (1.83 g, 1.31 mmol) in Et_2O (20 ml) cooled to -78°C. After warming to 0°C, the reaction mixture turned deep violet. A ^{119}Sn NMR analysis showed the nearly quantitative formation of **1** (δ: 288 ppm). Extremely air and moisture sensitive solutions of **1** were used without further purification. To this reaction mixture cooled to 0°C was added a solution of benzophenone (0.24 g, 1.31 mmol) in Et_2O (5 ml). After 15 min, the color turned from deep violet to red and then yellow. LiF was eliminated by filtration. White crystals (0.75 g, 63%) of 3-fluorenylidene-4,4-diphenyl-2,2-bis(2,4,6-triisopropylphenyl)-2-stannaoxetane (**2**) were obtained; mp 88-90°C (pentane). PMR spectrum: 0.77-0.99 (24H, m, *o*-$CH\underline{Me}_2$); 1.17 (12H, d, J = 6.8 Hz, *p*-$CH\underline{Me}_2$); 2.43 (4H, sept., J = 6.8 Hz, *o*-$C\underline{H}Me_2$); 2.77 (2H, sept., J = 6.8 Hz, *p*-$C\underline{H}Me_2$); 6.35 (2H, d, J = 7.9 Hz, 1-H, 8-H or 4-H, 5-H); 6.62 (2H, dt, J = 1.3 and 7.9 Hz, 2-H, 7-H or 3-H, 6-H); 6.87 (4H, br. s, arom H Tip); 7.03 (2H, dt, J = 1.3 and 7.9 Hz, 3-H, 6-H or 2-H, 7-H); 7.01-7.16 (10 H, m, arom H Ph); 7.65 (2H, d, J = 7.9 Hz, 4-H, 5-H or 1-H, 8-H).

All the signals of these doublets at 6.35 and 7.65 ppm were broad due to ^4J and ^5J coupling with the other aromatic hydrogen.

^{13}C NMR spectrum: 24.2 (*o*-$CH\underline{Me}_2$); 25.1 (*p*-$CH\underline{Me}_2$); 34.4 (*p*-$\underline{C}HMe_2$); 37.0 (*o*-$\underline{C}HMe_2$); 88.6 ($\underline{C}R_2$); 88.8 ($\underline{C}Ph_2$); 118.9 ($C_{(4)}$, $C_{(5)}$); 122.5 (*m*-C Tip); 124.7; 126.5; 127.7; 128.7 and 129.9 ($C_{(1)}$–$C_{(3)}$, $C_{(6)}$–$C_{(8)}$, *o*-, *m*- and *p*-C Ph); 137.1 (*ipso*-C Ph); 143.8 (*ipso*-C Tip); 144.7 ($C_{(12)}$, $C_{(13)}$); 148.9 ($C_{(10)}$, $C_{(11)}$); 151.1 (*p*-C Tip); 154.5 ppm (*o*-C Tip). ^{119}Sn NMR spectrum (C_6D_6): 27.5 ppm. Mass spectrum: 873 (M + 1, 1), 872 (M^+, 1), 543 (Tip_2SnO + 1, 14), 331 ($Ph_2C{=}CR_2$ + 1, 100), 203 (Tip, 55). Found, %: C 76.88; H 7.11. $C_{56}H_{64}OSn$. Calculated, %: C 77.15; H 7.40.

Hydrolysis of Compound 2. To a solution of stannaoxetane **2** (1.50 g, 1.72 mmol) in Et_2O (20 ml) was added one equivalent of water. After 2 h stirring, an NMR study showed the formation of hydroxy(bis-2,4,6-triisopropylphenyl)stannyl 2-(fluoren-9-yl)-1,1-diphenylethyl ether **3**.

PMR spectrum ($CDCl_3$): 0.94 (12H, d, J = 6.6 Hz, *o*-$CH\underline{Me}Me'$); 1.18 (12H, d, J = 6.6 Hz, *o*-$CHMe\underline{Me}'$); 1.21 (12H, d, J = 6.8 Hz, *p*-$CH\underline{Me}_2$); 2.91 (2H, sept, J = 6.8 Hz, *p*-$C\underline{H}Me_2$); 3.45 (4H, sept, J = 6.6 Hz, *o*-$C\underline{H}Me_2$); 5.25 (1H, s, $C\underline{H}R_2$); 6.99 (4H, s, arom H Tip); 6.45-7.88 (18 H, m, Ph and CR_2). ^{119}Sn NMR spectrum ($CDCl_3$): -104.6 ppm.

The solution of ether **3** was stirred for one week with an excess of water. Crystallization from Et_2O leads to pure alcohol **4** (0.30 g, 51%) and **5** (0.44 g) in about 90% purity according to NMR (~44% yield). Compound **4** was already known [25] but its physicochemical data had not been reported.

Fluorenyl(diphenyl)methanol (4). PMR spectrum ($CDCl_3$): 1.93 (1H, s, OH); 5.29 (1H, s, $\underline{H}CR_2$); 6.50 (2H, d, J = 7.7 Hz, 1-H, 8-H or 4-H, 5-H; all the signals were broad due to ^4J and ^5J coupling with the other aromatic H); 6.95 (2H, dt, J = 1.4 and 7.7 Hz, 2-H, 7-H or 3-H, 6-H); 7.18-7.41 (8H, m, 10H of Ph and 4H of CR_2). ^{13}C NMR spectrum ($CDCl_3$): 56.6 ($\underline{C}R_2$); 80.2 (COH); 119.6 ($C_{(4)}C_{(5)}$); 126.0 (*o*-C Ph); 126.6; 127.2 and 127.8 ($C_{(1)}$-$C_{(3)}$, $C_{(6)}$-$C_{(8)}$, *p*-C Ph); 128.3 (*m*-C Ph); 142.9 and 146.0 ($C_{(10)}$–$C_{(13)}$). Mass spectrum (EI): 330 (M - H_2O, 72), 252 ($PhC{=}CR_2$ - 1, 36), 183 (Ph_2COH, 100), 165 (R_2CH, 34), 105 (PhCO, 46), 77 (Ph, 23). Found, %: C 89.31; H 5.60. $C_{26}H_{20}O$. Calculated, %: C 89.62; H 5.79.

1,3-Dihydroxy-1,1,3,3-tetrakis(2,4,6-triisopropylphenyl)distannoxane (5). PMR spectrum ($CDCl_3$): 0.96 (24 H, d, J = 6.7 Hz, *o*-$CH\underline{Me}Me'$); 1.00 (24 H, d, J = 6.7 Hz, *o*-$CHMe\underline{Me}'$); 1.17 (24 H, d, J = 6.7 Hz, *p*-$CH\underline{Me}_2$); 2.14 (2H, s, OH); 2.79 (4H, sept, J = 6.6 Hz, *p*-$\underline{C}HMe_2$); 3.26 (8H, sept, J = 6.6 Hz, *o*-$\underline{C}HMe_2$); 6.92 (8H, s, $^4J_{H^{119}Sn}$ = 29.1 Hz, arom H Tip). ^{119}Sn NMR spectrum (C_6D_6): - 103.1 ppm.

Synthesis of Carbinol 4 from Ph_2CO and R_2CHLi. To 1.15 g of fluorene R_2CH_2 (6.93 mmol) in Et_2O/THF solution (1:1, 20 ml) cooled to -78°C was added one equivalent of *n*-BuLi (1.6 M solution in hexane). The reaction mixture turned red. The solution of R_2CHLi was then slowly added to a solution of Ph_2CO (1.26 g, 6.93 mmol) in Et_2O cooled to -78°C. After warming to room temperature an excess of water was added and the organic phase was separated and dried over Na_2SO_4. The solvents were removed in vacuo. Compound **4** was recrystallized from Et_2O (1.85 g, 77%).

Thermolysis of Stannaoxetane 2. Compound **2** (1.35 g, 1.55 mmol) and C_6H_6 (5 ml) were heated in a sealed tube at 100°C for 1 h. After elimination of benzene in vacuo, crystallization from benzene afforded **7** (0.44 g, 52%) identified as the derivative previously prepared by Masamune [31], and **9** (0.37 g, 72%) identified by its melting point (230-233°C) [32, 33] and its PMR spectrum [34]. A more detailed PMR spectrum with the ^4J and ^5J coupling constants, which were not reported, is given below. **Compound 9**: PMR spectrum ($CDCl_3$): 6.60 (2H, ddd, J = 0.4, 1.4 and 7.9 Hz, 1-H, 8-H or 4-H, 5-H); 6.90 (2H, dt, J = 1.4 and 7.9 Hz, 2-H, 7-H or 3-H, 6-H); 7.22 (2H, dt, J = 1.4 and 7.9 Hz, 3-H, 6-H or 2-H, 7-H); 7.39 (10 H, br. s, Ph); 7.69 (2H, ddd, J = 0.4, 1.4 and 7.9 Hz, 4-H, 5-H or 1-H, 8-H).

Reaction of Stannene 1 with Diphenylacetaldehyde. Diphenylacetaldehyde (0.22 ml, 1.12 mmol) was added by syringe to a solution of **1** (prepared as previously described from 0.79 g (1.12 mmol) of $Tip_2Sn(F)CHR_2$) [17] in Et_2O (10 ml) cooled at 0°C. The reaction mixture slowly turned from violet to orange and then yellow. After 1 h stirring at room temperature, an excess of water was added; after drying the organic layer over Na_2SO_4, crystallization from pentane gave 0.17 g of 1-fluorenyl-2,2-diphenylethanol (**11**) (45%; mp 120-125°C, white crystals), and 0.25 g of distannoxane **5** mixed with about 10% of $(Tip_2SnO)_3$ [31] (~37%).

Compound 11: PMR spectrum ($CDCl_3$): 1.48 (1H, d, J = 4.0 Hz, OH); 4.26 (1H, d, J = 3.1 Hz, C<u>H</u>R_2); 4.36 (1H, d, J = 9.6 Hz, C<u>H</u>Ph_2); 5.10 (1H, ddd, J = 3.1, 4.0 and 9.6 Hz, OCH); 7.13-7.72 (18 H, m, CR_2 and Ph). ^{13}C NMR spectrum ($CDCl_3$): 51.2 (<u>C</u>HR_2); 56.4 (<u>C</u>HPh_2); 76.3 (CHOH); 119.9 and 120.0 ($C_{(4)}C_{(5)}$); 124.6; 125.7; 126.7; 127.0; 127.4; 127.5; 128.5 and 128.6 ($C_{(1)}$–$C_{(3)}$, $C_{(6)}$–$C_{(8)}$ and *p*-C Ph); 126.6 (*o*-C Ph); 128.7 (*m*-C Ph); 141.7; 141.9; 142.2; 143.1 and 145.0 ($C_{(10)}$–$C_{(13)}$ and *ipso*-C Ph). Mass spectrum (EI): 362 (M, 6), 344 (M - H_2O, 9), 267 (M - H_2O - Ph, 3), 197 (M – CHR_2, 16), 180 (Ph_2CHCH, 13), 166 (R_2CH_2, 100). Found, %: C 89.71; H 6.32. $C_{27}H_{22}O$. Calculated, %: C 89.47; H 6.12.

Synthesis of Compound 11 from Ph_2CHCHO and R_2CHLi. $Ph_2CHCH(OH)CHR_2$ was synthesized by a similar route to **4** using 2.30 g of fluorene (13.86 mmol), 8.7 ml of a solution of *n*-BuLi 1.6 M, and 2.71 g (13.86 mmol) of Ph_2CHCHO. 3.50 g (70%) of **11** was obtained.

Reaction of Phosphastannene with Aldehydes and Ketones. Compound **13** was prepared as previously reported [26, 28] by addition of *tert*-butyllithium (1.7 M solution in pentane, 1 equiv.) to a solution of $Tip_2Sn(F)P(H)Ar$ [26] (1 g, 1.24 mmol) in Et_2O (10 ml) cooled to -78°C. After completion of the addition, warming to room temperature afforded a red solution of **13** that was used directly after checking by NMR (δ ^{31}P: 170.7 ppm, δ ^{119}Sn: 499.5 ppm, $^1J_{P^{119}Sn}$: 2208 Hz). To this crude solution of **13** was added at room temperature by syringe one equivalent of acetaldehyde, acetone, acetophenone, and benzaldehyde, respectively. The reaction mixture slowly turned from intense red to yellow. Solvents were eliminated in vacuo, replaced by 20 ml of pentane, and LiF was filtered out.

Attempts to crystallize **14**, **19**, **20** and **21** failed. These derivatives were characterized by NMR spectra. Hydrolysis of **19**–**21** led quantitatively to $Tip_2Sn(OH)P(H)Ar$ (δ ^{31}P: -119.0, δ ^{119}Sn: -65.1 ppm) [26] and to acetaldehyde, acetone, and acetophenone, respectively.

Bis(2,4,6-triisopropylphenyl)(vinyloxy)stannyl(2,4,6-tri-*tert*-butylphenyl)phosphine (19). ^{31}P NMR spectrum (C_6D_6): -107.8 ppm (d, $^1J_{PH}$ = 204.7 Hz); ($^1J_{P^{117}Sn}$ = 859.6, $^1J_{P^{119}Sn}$ = 902.4 Hz). ^{119}Sn NMR spectrum (C_6D_6): -71.0 ppm (d, $^1J_{P^{119}Sn}$ = 902.4 Hz).

Bis(2,4,6-triisopropylphenyl)(2-propenyloxy)stannyl(2,4,6-tri-*tert*-butylphenyl)phosphine (20). ^{31}P NMR spectrum (C_6D_6): -106.0 ppm (d, $^1J_{PH}$ = 205.9 Hz); ($^1J_{P^{117}Sn}$ = 962.7, $^1J_{P^{119}Sn}$ = 1011.7 Hz). ^{119}Sn NMR spectrum: -81.2 ppm (d, $^1J_{P^{119}Sn}$ = 1011.7 Hz).

Bis-(2,4,6-triisopropylphenyl)(α-styryloxy)stannyl(2,4,6-tri-*tert*-butylphenyl)phosphine (21). PMR spectrum ($CDCl_3$): 0.9-1.3 (36H, m, *o*- and *p*-CH<u>Me</u>$_2$); 1.34 (9H, s, *p*-CMe_3); 1.50 (18H, s, *o*-CMe_3); 2.6-3.1 (6H, *m*, *o*- and *p*-C<u>H</u>Me_2); 3.66 (1H, d, J_{HaHb} = 1.6 Hz, <u>Ha</u>HbC=); 4.23 (1H, d, J_{HaHb} = 1.6 Hz, Ha<u>Hb</u>C=); 6.87 (4H, s, arom H of Tip); 7.1-7.9 ppm (7H, m, arom H of Ph and Ar). ^{13}C NMR spectrum ($CDCl_3$): 24.0; 24.6 and 24.7 (*o*- and *p*-CH<u>Me</u>$_2$); 31.5 (*p*-<u>C</u>Me_3); 33.7 (d, $^4J_{CP}$ = 7 Hz, *o*-<u>C</u>Me_3); 34.2 (*p*-<u>C</u>HMe_2); 34.9 (*p*-<u>C</u>Me_3); 37.2; 37.3 and 37.6 (*o*-<u>C</u>HMe_2); 38.5 (*o*-<u>C</u>Me_3); 88.7 (H_2C=); 122.3 (d, $^3J_{CP}$ = 9.5 Hz, *m*-C Ar); 122.9 and 127.4 (*m*-C Tip); 123.1 (d, $^1J_{CP}$ = 80.0 Hz, *ipso*-C Ar); 142.7 (d, $^2J_{CP}$ = 5.3 Hz, *ipso*-C Tip); 144.3 (d, $^2J_{CP}$ = 4.9 Hz, *ipso*-C Tip); 148.2 (*p*-C Ar); 150.3 and 150.4 (*p*-C Tip); 154.2 ($^2J_{P^{117}Sn}$ = 25.3 Hz, $^2J_{P^{119}Sn}$ = 29.7 Hz); 160.1 ppm (=CO). ^{31}P NMR spectrum

(C_6D_6): -106.0 ppm (d, $^1J_{PH}$ = 206.0 Hz); ($^1J_{P^{117}Sn}$ = 955.6, $^1J_{P^{119}Sn}$ = 997.8 Hz). ^{119}Sn NMR spectrum (C_6D_6): -74.3 ppm (d, $^1J_{P^{119}Sn}$ = 997.8 Hz).

4-Phenyl-2,2-bis(2,4,6-triisopropylphenyl)-3-(2,4,6-tri-*tert*-butylphenyl)-2-stanna-3-phosphaoxetane (14). ^{31}P NMR spectrum ($CDCl_3$): 95.8 ppm ($^1J_{P^{117}Sn}$ = 729.8 Hz, $^1J_{P^{119}Sn}$ = 763.6 Hz). ^{119}Sn NMR spectrum ($CDCl_3$): -8.4 ppm (d, $^1J_{P^{119}Sn}$ = 763.6 Hz).

REFERENCES

1. G. Raabe and J. Michl, *Chem. Rev.*, **85**, 419 (1985).
2. A. G. Brook and M. A. Brook, *Adv. Organomet. Chem.*, **39**, 71 (1996).
3. R. West, *Angew. Chem. Int. Ed. Engl.*, **26**, 1201 (1987).
4. M. Weidenbruch, *Coord. Chem. Rev.*, **130**, 275 (1994).
5. I. Hemme and U. Klingebiel, *Adv. Organomet. Chem.*, **39**, 159 (1996).
6. R. Okazaki and R. West, *Adv. Organomet. Chem.*, **39**, 232 (1996).
7. M. Driess, *Adv. Organomet. Chem.*, **39**, 193 (1996).
8. G. Raabe and J. Michl, in: *The Chemistry of Organic Silicon Compounds*, S. Patai, Z. Rappoport (eds.), Wiley, New York (1989).
9. M. A. Chaubon, H. Ranaivonjatovo, J. Escudié, and J. Satgé, *Main Group Met. Chem.*, **19**, 145 (1996).
10. A. Kandri Rodi, H. Ranaivonjatovo, J. Escudié, and A. Kerbal, *Main Group Met. Chem.*, **19**, 199 (1996).
11. T. Tsumuraya, S. A. Batcheller, and S. Masamune, *Angew. Chem. Int. Ed. Engl.*, **30**, 902 (1991).
12. N. Tokitoh and R. Okazaki, *Main Group Chem. News.*, **3**, 4 (1995).
13. K. M. Baines and W. G. Stibbs, *Adv. Organomet. Chem.*, **39**, 275 (1996).
14. J. Barrau, J. Escudié, and J. Satgé, *Chem. Rev.*, **90**, 283 (1990).
15. J. Escudié, C. Couret, H. Ranaivonjatovo, and J. Satgé, *Coord. Chem. Rev.*, **130**, 427 (1994).
16. G. Ossig, A. Meller, S. Freitag, R. Herbst-Irmer, and G. M. Sheldrick, *Chem. Ber.*, **126**, 2247 (1993).
17. G. Anselme, H. Ranaivonjatovo, J. Escudié, and C. Couret, J. Satgé, *Organometallics.*, **11**, 2748 (1992).
18. G. Anselme, J.-P. Declercq, A. Dubourg, H. Ranaivonjatovo, J. Escudié, and C. Couret, *J. Organomet. Chem.*, **458**, 49 (1993).
19. N. Wiberg and C.-K. Kim, *Chem. Ber.*, **119**, 2980 (1986).
20. M. Lazraq, C. Couret, J. Escudié, J. Satgé, and M. Draeger, *Organometallics.*, **10**, 1771 (1991).
21. A. D. Fanta, D. J. De Young, J. Belzner, and R. West, *Organometallics.*, **10**, 3466 (1991).
22. G. Delpon-Lacaze, C. Couret, J. Escudié, and J. Satgé, *Main Group Met. Chem.*, **16**, 419 (1993).
23. N. Wiberg, G. Preiner, K. Schurz, and G. Fischer, *Z. Naturforsch. B. Chem. Sci.*, **43**, 1468 (1988).
24. A. G. Brook, W. J. Chatterton, J. F. Sawyer, D. W. Hughes, and K. Vorspohl, *Organometallics.*, **6**, 1246 (1987).
25. G. Wittig and H. Laib, *Liebigs Ann. Chem.*, **580**, 57 (1953).
26. H. Ranaivonjatovo, J. Escudié, C. Couret, and J. Satgé, *J. Chem. Soc. Chem. Comm.*, No. 15, 1047 (1992).
27. H. Ranaivonjatovo, J. Escudié, C. Couret, and J. Satgé, *J. Organomet. Chem.*, **415**, 327 (1991).
28. A. Kandri Rodi, H. Ranaivonjatovo, and J. Escudié, *Organometallics.*, **13**, 2787 (1994).
29. M. J. Fink, D. J. De Young, R. West, and J. Michl, *J. Amer. Chem. Soc.*, **105**, 1070 (1983).
30. S. A. Batcheller and S. Masamune, *Tetrah. Lett.*, **29**, 3383 (1988).
31. S. Masamune and L. R. Sita, *J. Amer. Chem. Soc.*, **107**, 6390 (1985).
32. B. Glaser and H. Noth, *Chem. Ber.*, **119**, 3856 (1986).
33. G. Wittig and G. Pieper, *Liebigs Ann. Chem.*, **558**, 207 (1947).
34. M. Luisa, T. M. B. Franco, B. J. Herold, J. C. Evans, and C. C. Rowlands, *J. Chem. Soc. Perkin Trans. II.*, No. 4, 443 (1988).