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Preparation and some reactions of neophyltin anions ☆

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Abstract

A study on the preparation of trineophyltin and mixed methylneophyltin anions and subsequent reactions of these anions is reported. It was found that whereas mixed hydrides $Me_nNph_{3-n}SnH$ ($n = 1,2$) react with NaH in DMSO to give the corresponding organotin sodium anions (60–70% yield), trineophyltin hydride reacts with NaH to give hexaneophylditin as the only product (32%). The reaction of tin halides $Me_nNph_{3-n}X$ (X = Cl, Br; $n = 0$, 1, 2) with lithium in THF yields the corresponding organotinlithium anions (70%). The tin anions were reacted with various alkyl halides. The 1,4 addition of trineophyltinlithium (**10***) to α,β-unsaturated enones followed by the reaction of the intermediate carbanions with methyl iodide, leads with benzylideneacetone to a mixture of the corresponding *threo* (34%) and *erythro* (25%) diastereoisomers. Under the same reaction conditions, the addition of **10*** to chalcone proceeded with complete stereoselectivity to give the diastereoisomer *threo* (60%) as the only product. Full ^1H and ^{13}C NMR data of the new organotins are given.

Keywords: Tin; Stereoselective synthesis

1. Introduction

Organotin anions, i.e. compounds with tin–metal bonds, are useful for making carbon–tin bonds via stannylation of electrophilic substrates [1]. Thus, these anions react with primary and secondary alkyl halides to give the corresponding substitution products, i.e. mixed tetraorganotins. With tertiary alkyl halides, organotin anions usually give elimination products.

In previous studies carried out with trineophyltin hydride [2] and deuteride [3], as well as with mixed methylneophyltin hydrides [4], we have found that the size of the organic ligands attached to the tin atom affects not only the reactivity but also the stereoselectivity of the reactions of these compounds.

In order to determine whether a similar relationship exists in the case of organotin anions with regard to their reactivity and selectivity, we considered it to be of interest to carry out a study on the generation of trineophyltin and mixed methylneophyltin anions, and then to study some reactions of the more hindered ones.

2. Results and discussion

Taking into account that the reactivity of the organotin anions prevents their isolation, in order to assess the amount of anion formed they were made to react with methyl iodide. In Eqs. (1)–(3) are summarized the results obtained in the reactions between the organotin hydrides **1–3** [2,4] and sodium hydride carried out in dimethyl sulfoxide (DMSO).

$$\underset{\mathbf{1}}{Nph_3SnH} + NaH \xrightarrow[3h]{DMSO} \underset{\mathbf{4}\ (32\%)}{Nph_3Sn-SnNph_3} \qquad (1)$$

$$\underset{\mathbf{2}}{MeNph_2SnH} + NaH \xrightarrow[1.5h]{DMSO} \underset{\mathbf{2}^*}{[MeNph_2SnNa]}$$

$$\xrightarrow{MeI} \underset{\mathbf{5}\ (60\%)}{Me_2SnNph_2} \qquad (2)$$

☆ Dedicated to the memory of Prof. Dr. Wilhelm Paul Neumann.

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$$Me_2NphSnH + NaH \xrightarrow[1.5h]{DMSO} [Me_2NphSnNa]$$

3 **3***

$$\xrightarrow{MeI} Me_3SnNph \quad (3)$$

6 (70%)

Nph = Neophyl = $PhMe_2C-CH_2$

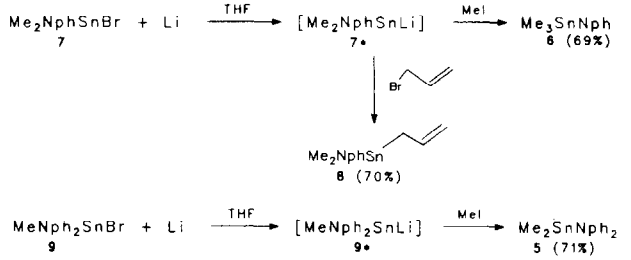
The yields stated are an average of five reactions. As can be seen, the tin–sodium compound was obtained in reasonably good yields (60–70%) only in the case of the less hindered hydrides **2** and **3**. Trineophyltin hydride (**1**) did not lead to the expected anion: after 3 h only hexaneophylditin (32%) was isolated.

All the attempts made to prepare trineophyltinlithium through the reaction of hydride **1** with lithium diisopropylamide (LDA) (Eq. (4)) also failed.

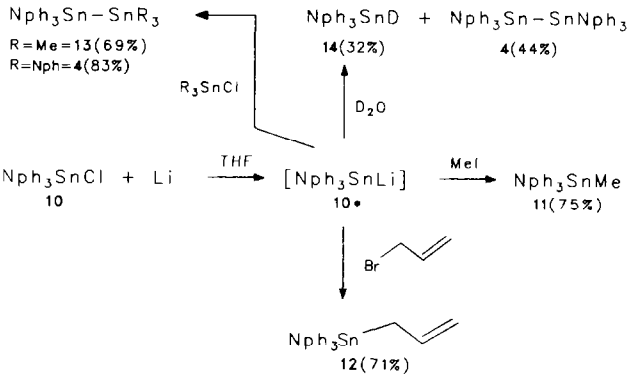
$$Nph_3SnH + LDA \not\longrightarrow [Nph_3SnLi] + {}^iPr_2NH \quad (4)$$

1

The generation of organotinlithium compounds was achieved starting from the corresponding organotin halides. The reactions of dimethylneophyltin bromide (**7**), methyldineophyltin bromide (**9**) [4] (Scheme 1), and trineophyltin chloride (**10**) [5] (Scheme 2) with lithium

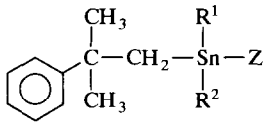


Scheme 1.



Scheme 2.

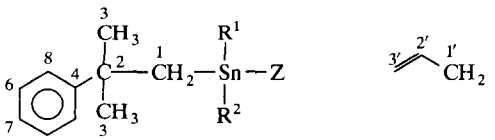
Table 1
^1H NMR data of compounds **8**, **12** and **13**



Comp. n°	R^1	R^2	Z	Chemical shifts, δ, ppm versus TMS [a]
8	Me	Me	Allyl	−0.11 [s, 6H, ^2J(Sn,H) 53.8]; 1.42 (s, 6H); 1.49 (s, 2H); 1.57 [d, 2H, ^3J(H,H) 8.2]; 4.61 (m, 2H); 5.13 (m, 1H); 7.30 (m, 15H)
12	Nph	Nph	Allyl	0.95 [s, 6H, ^2J(Sn,H) 48.9]; 1.18 (s [b], 20H); 4.60 [d, 2H, ^3J(H,H) 23.9]; 5.50 (m, 1H); 7.17 (m, 15H)
13	Nph	Nph	Me_3Sn	−0.12 [s, 9H, ^2J(Sn,H) 47.2, ^3J(Sn,Sn,H) 13.7; 1.04 [s, 6H, ^2J(Sn,H) 42.0, ^3J(Sn,Sn,H) 17.6]; 1.21 (s, 18H); 7.17 (m, 15H)

[a] Coupling constants, ^nJ, in Hz; the spectra were recorded in $CDCl_3$. [b] is a broad singulet.

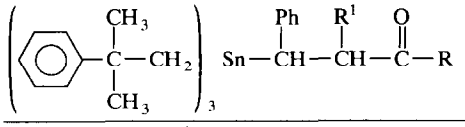
Table 2
^{13}C NMR characteristics of compounds **8**, **12**, and **13** [a]



No.	R^1	R^2	Z	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	CH_3Sn	C(1′)	C(2′)	C(3′)
8	Me	Me	Allyl	30.89 (349.2)	37.95 (16.5)	32.75 (35.1)	151.10 (22.0)	125.45	125.02	125.32	−10.06 (315.0)	18.24 (280.2)	137.51 (46.3)	109.22 (48.3)
12	Nph	Nph	Allyl	30.42 (310.2)	37.88 (17.8)	33.19 (35.6)	151.15 (16.5)	127.93	125.20	125.33	–	20.20 (249.2)	137.81 (43.2)	109.67 (47.6)
13	Nph	Nph	Me_3Sn	32.09 (239.7) [b]	38.06 (16.0)	32.99 (32.4)	151.37 (21.0)	128.00	125.18	125.62	−8.50 (239.1) [c]	–	–	–

[a] In $CDCl_3$; chemical shifts, δ, in ppm with respect to TMS; $^nJ(^{119}Sn, ^{13}C)$ coupling constants in Hz (in parentheses). [b] ^2J(Sn,Sn,C) 43.6 Hz. [c] ^2J(Sn,Sn,C) 47.0 Hz.

Table 3
^{1}H NMR data of compounds **16–19**



No.	R	R^1	Chemical shifts, δ, ppm versus TMS [a]
16	Me	H	0.92 [q, 6H, AB sist., $\Delta\delta$ A,B = 0.14 ppm; J(A,B) 13.2]; 1.07 (s, 9H); 1.12 (s, 9H); 1.77 (s, 3H); 1.86 [dd, 1H, part X of an ABX syst., J(A,X) 16.3); J(B,X) 3.2]; 2.59 [m, 2H, part AB of an ABX syst., $\Delta\delta$ A,B = 0.32 ppm; J(A,B) 12.9; J(A,X) 16.2); J(B,X) 3.2]; 6.80–7.35 (m, 20H)
17	Me	Me	0.95–1.20 (m + s, 27H); 2.12 (s, 3H); 2.55 [d, 1H, ^3J(H,H) 8.6; ^2J(Sn,H) 58.0); 3.00 (m, 1H); 6.75–7.40 (m, 20H)
18	Me	Me	0.85 [d, 3H, ^3J(H,H) 6.9); 0.95–1.20 (m, 24H); 2.23 [d, 1H, ^3J(H,H) 12.3]; 2.98 (m, 1H); 6.70–7.40 (m, 20H)
19	Ph	Me	0.99 (s, 24H); 1.11 [d, 3H, ^3J(H,H) 7.0); 2.88 [d, 1H, ^3J(H,H) 10.2; ^2J(Sn,H) 57.0]; 4.15 (m, 1H); 6.80–8.10 (m, 25H)

[a] In $CDCl_3$; coupling constants, ^nJ, iin Hz.

in THF led to the corresponding anions with ca. 70% yield in all cases.

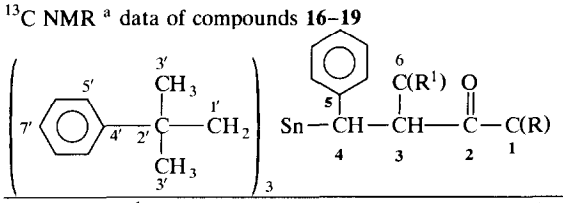
The results indicate that the generation of the organotin anions depends upon the reactivity of the starting organotins and the nature of the reaction products. Thus, the increasing number of neophyl ligands attached to tin stabilizes the organotin hydrides **1–3** and diminishes their reactivity, as shown by the fact that the trineophyltin hydride (**1**) reacts with sodium hydride to give hexaneophylditin (**4**) and not the anion. However, for the reactions of organotin halides with lithium, the driving force could be the formation of the strong lithium–halide bond.

^{1}H and ^{13}C NMR data of those compounds included in Schemes 1 and 2 not reported previously are summarized in Tables 1 and 2.

The 1,4-addition of organotin anions to α,β-unsaturated carbonyl systems followed by the reaction of the intermediate carbanion with an alkyl halide leads to the corresponding adducts with high stereoselectivity [6]. In order to determine the degree of stereoselectivity that can be achieved in the additions of trineophyltinlithium (**10***) to α,β-unsaturated carbonyl systems, we carried out a study on the reaction of **10*** with the enones [14] and [15] according to Fig. 1.

Fig. 1A shows that the addition of trineophyltin-

Table 4
^{13}C NMR [a] data of compounds **16–19**



No.	R	R^1	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	C(7′)	Others
16	Me	H	29.22	208.83 (60.1)	45.98 (NO)	30.15 (257.2)	145.07 (27.1)	–	30.15 (299.8)	37.68 (17.8)	33.08 (31.4) 33.36 (37.4)	150.90 (16.2)	128.04	125.21	125.39	– [b]
17	Me	Me	28.41	211.27 (20.8)	50.04 (NO)	38.67 (272.1)	143.96 (23.9)	17.97 (31.3)	31.09 (294.6)	37.78 (18.2)	32.74 (32.4) 32.94 (33.9)	151.38 (22.9)	127.85	125.28	125.16	– [c]
18	Me	Me	26.39	213.30 (57.0)	50.97 (NO)	40.82 (258.9)	144.75 (NO)	18.64 (NO)	31.11 (295.2)	37.75 (NO)	32.98 (NO) 33.07 (NO)	150.89 (19.0)	127.88	124.99	125.21	– [d]
19	Ph	Me	136.19	202.85 (NO)	43.99 (NO)	39.44 (264.6)	144.50 (24.8)	20.32 (37.8)	31.15 (292.7)	37.72 (18.2)	32.66 (32.7) 32.46 (31.3)	151.59 (25.2)	127.84	125.32	125.10	– [e]

[a] In $CDCl_3$; chemical shifts, δ, in ppm versus TMS; $^nJ(^{119}Sn, ^{13}C)$, in Hz; NO = not observed. [b] 123.94 (12.6), 126.65 (20.6) and 128.17. [c] 124.15, 128.05 and 128.47 (22.9). [d] 124.20 (12.7), 127.35 (20.7) and 127.55. [e] 124.07, 128.24, 128.44, 128.50, 128.61, and 132.83

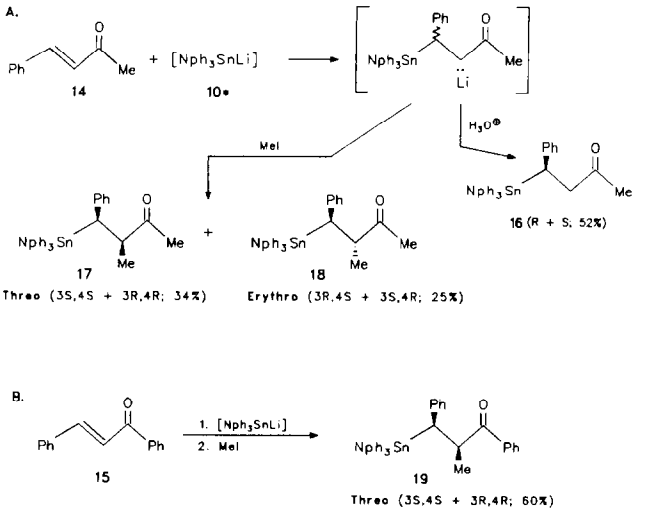


Fig. 1. Addition of trineophyltinlithium to: (A) bencylidenacetone; (B) chalcone.

lithium (**10***) to benzylideneacetone (**14**) followed by the reaction with methyl iodide gives a mixture of *threo* **17** (34% yield) and *erythro* **18** (25%) adducts.

This result indicates that the stereoselectivity of the addition of **10*** to this substrate is low: just 15.2% of diastereoisomeric excess. The total yield of the reaction (59%) is similar to that obtained using trimethylstannyllithium (60%) and substantially higher to the yield obtained in the addition of tributyltinlithium (12%) to the same substrate [6].

Fig. 1A also shows that acid hydrolysis of the intermediate carbanion leads to 4-phenyl-4-(trineophylstannyl)butan-2-one (**16**) in 52% yield as a mixture of the corresponding enantiomers (4R and 4S).

Fig. 1B, shows that the addition of trineophylstannyllithium (**10***) to chalcone (**15**) followed by reaction with methyl iodide gave as only product *threo*-2-methyl-3-(trineophylstannyl)-2,3-dihydrobenzalacetophenone (**19**) (60% yield), as a mixture of the corresponding enantiomers (3S, 4S and 3R, 4R). This clearly indicates that in this case the sequence of reactions takes place with complete stereoselectivity.

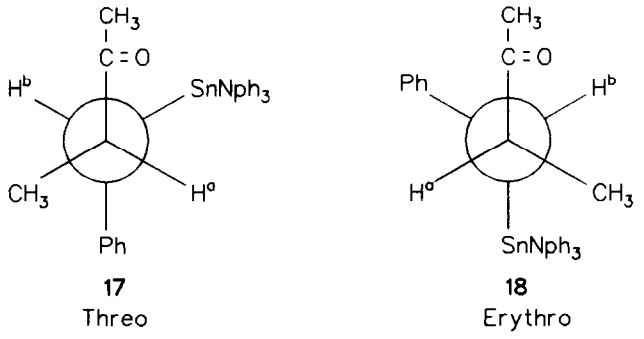


Fig. 2. Preferred conformations of *threo* and *erythro* 3-methyl-4-phenyl-4-(trineophylstannyl)butan-2-ones (**17** and **18**) (only one isomer of each is shown).

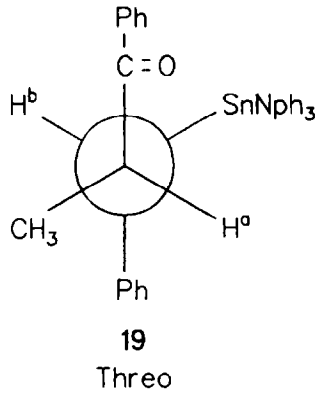


Fig. 3. Prefered conformation of *threo* 2-methyl-3-(trineophylstannyl)-2,3-dihydrobenzalacetophenone (**19**) (only one isomer is shown.

^1H and ^{13}C NMR characteristics of the new stannyl ketones **16–19**, are collected in Tables 3 and 4.

The configurations of compounds **17** and **18** were assigned as follows. The coupling constants for protons H^a and H^b in the isomeric stannyl ketones **17** and **18** are 8.6 and 12.3 Hz, respectively (Table 3). This indicates that the preferred conformation for both diastereoisomers are those where H^a and H^b are antiperiplanar to each other (Fig. 2).

In the ^{13}C NMR (Table 4), the observed $^3J(^{119}Sn–C–C–^{13}C{=}O)$ coupling constants for compounds **17** and **18** were 20.8 and 57 Hz, respectively. These values, according to our previous work [7], correspond to a dihedral angle close to 60° in the case of compound **17** and of 120° in the case of **18**. Similarly, the value of $^3J(Sn–C–C–CH_3)$ coupling constant for compound **17** was 31.3 Hz suggesting a dihedral angle of approx. 130°. This coupling was not observed in the case of compound **18** indicating an angle close to 60°. Taking these values into account, it is possible to attribute the *threo* configuration (Fig. 2) to compound **17**, and the *erythro* (Fig. 2) to compound **18**.

Considering the NMR characteristics of the stannyl ketone **19**, it is possible to propose for this compound a threo configuration like the one depicted in Fig. 3.

Thus, the coupling constant for protons H^a and H^b (Table 3) is 10.2 Hz, indicating that the preferred conformation is that in which these protons are antiperiplanar. The fact that the $^3J(Sn–C–C–C{=}O)$ is not observed (Table 4) suggests a dihedral angle close to 60° between the tin moiety and the carbonyl group, and the value of 37.8 Hz of the $^3J(Sn–C–C–CH_3)$ coupling constant indicates an angle of about 60°.

2. Experimental section

^1H and ^{13}C NMR spectra were determined with a Bruker AC 200 instrument at IQUIOS (Rosario, Argentina). Infrared spectra were recorded with a

Perkin-Elmer 599B spectrophotometer. The melting points were determined on a Kofler hot stage and are uncorrected. Microanalyses (C, H) were performed at Dortmund University (Dortmund, Germany). All the solvents and reagents used were analytical reagent grade. Organotin hydrides **1–3** and organotin halides **7**, **9–19** [2,4] as well as enones **14** and **15** [8] were synthesized by known procedures. Mixed methylneophylorganotin compounds **5**, **6**, and **11** [4], and hexaneophylditin (**4**) [9], used as reference, have also been reported previously.

2.1. Preparation of organotinsodium anions via the reaction between organotin hydrides and sodium hydride in DMSO

All the reactions were carried out following the same procedure. One experiment is described in detail to illustrate de method used.

Reaction between dimethylneophyltin hydride (3) and sodium hydride in DMSO. Synthesis of trimethylneophyltin (6)

To sodium hydride (0.125 g of an 80% suspension, 0.042 mol), previously washed three times with dry hexane, was added dry DMSO (10 ml), under nitrogen, in the dark, and with magnetic stirring. Then, a solution of **3** (0.996 g, 0.00352 mol) in DMSO (10 ml) was added dropwise. After 90 min at room temperature, the solution developed a strong yellow colour. The addition of 0.4 ml (0.0065 mol) of methyl iodide produced a colourless solution. Then distilled water (0.5 ml) was added and the solution was extracted with ether (50 ml). After five washings with water, the organic layer was dried (magnesium sulphate) and the solvent removed under reduced pressure. Kugelrohr distillation of the residue gave pure **6** (0.727 g, 70% yield), as shown by comparison with an authentic sample [4].

Under the same reaction conditions, methyldineophyltin hydride (**2**) gave dimethyldineophyltin (**5**) (60% yield), and trineophyltin hydride (**1**) (after 3 h) only gave hexaneophylditin (**4**) (32% yield).

2.2. Preparation of organotinlithium anions via the reaction between organotin halides and lithium in THF

All the reactions were carried out following the same procedure. One experiment is described in detail to illustrate the method used.

Reaction of methyldineophyltin bromide (9) with lithium. Synthesis of dimethyldineophyltin (5)

Lithium in the form of fine shavings (Ref. [8], p. 835) (0.201 g, 0.029 atg) was introduced into a two-necked round-bottom flask containing dry THF (2 ml), under nitrogen and with magnetic stirring. Then, a solution of 9 (1.98 g, 0.00414 mol) in dry THF (4 ml) was added dropwise. After 1 h at room temperature, the mixture developed a dark-green colour. MeI (0.5 ml) was then added (the colour disappeared) and after the same work-up as previously, kugelrohr distillation of the residue gave pure **5** (1, 20 g, 71.5% yield), as shown by comparison with an authentic sample [4].

Similarly, dimethylneophyltin bromide (**7**) gave after 1 h the corresponding lithium anion (**7***) which on reaction with methyl iodide yielded trimethylneophyltin (**6**) (69%). The reaction of **7*** with allyl bromide led to allyldimethylneophyltin (**8**). In this case, the residue obtained after elimination of the solvent was purified by column chromatography using silica gel 60. **8** was eluted with petroleum ether 30–60 as an oily colourless liquid (70% yield); n_D^{20} 1.5483. Anal.: Found: C, 55.45; H, 7.41. $C_{24}H_{34}Sn$ Calc.: C, 55.76; H, 7.49%.

Under the same reaction conditions, trineophyltin chloride (**10**) after 3 h gave the corresponding trineophyltinlithium anion (**10***), which on reaction with methyl iodide gave **11** (75% yield) and with **10**, after 2 h stirring at room temperature, yielded hexaneophylditin (**4**). The reaction of **10*** with trimethyltin chloride gave after 3.5 h reflux trimethyltrineophylditin (**13**). **13** was purified by column chromatography (silica gel 60), the compound being eluted with Petroleum ether 30–60°, as a colourless liquid (69% yield); n_D^{25} 1.5909. Anal.: Found: C, 58.25; H, 6.85. $C_{33}H_{45}Sn_2$ Calc.: C, 58.36; H, 6.68%.

The stannyl anion **10*** reacted with allyl bromide to give allyltrineophyltin (**12**), which was purified by column chromatography (silica gel 60). **12** was eluted with Petroleum ether 30–60°, as a white solid, m.p. 52–54 °C. Anal.: Found: C, 70.61; H, 7.85. $C_{33}H_{44}Sn$ Calc.: C, 70.85; H, 7.93%.

The anion **10*** reacted with deuterium oxide to give a mixture of trineophyltin deuteride (**14**) [3] in 32% yield and hexaneophylditin (**4**) (44%).

2.3. Reactions of trineophyltinlithium (10) with α,β-unsaturated enones*

All the reactions were carried out following the same procedure. One experiment is described in detail to illustrate the method used.

Addition of trineophyltinlithium (10) to 4-phenyl-3-buten-2-one (14). Synthesis of (3RS, 4RS)- and (3RS, 4SR)-3-methyl-4-phenyl-4-(trineophylstannyl)butan-2-one (17 and 18)*

To a solution of **10*** in THF prepared from trineophyltin chloride (**10**) (2.85 g, 0.005 mol) following the procedure given in 2.2, under nitrogen and with magnetic stirring, was added a solution of 14 (0.47 g, 0.0032 mol) in THF (1 ml). The mixture was stirred at room

temperature for 72 h, and then methyl iodide (0.2 ml, 0.46 g, 0.0032 mol) was added, and the mixture was stirred for a further 2.5 h. Then, water was added and the mixture was extracted with ether, dried with sodium sulphate, and the solvent was eliminated under reduced pressure. Column chromatography on silica gel 60 of the crude mixture, yielded 0.74 g (0.0011 mol, 34%) of isomers *threo* **17**, eluted with petroleum ether 30–60°/benzene (97:3), as a solid, m.p. 73–75°. IR (KBr disc), ν(C=O) 1712 cm^{-1}. Anal.: Found: C, 72.55; H, 7.49. $C_{41}H_{52}OSn$ Calc.: C, 72.46; H, 7.71%. Isomers *erythro* 18, 0.54 g (0.008 mol, 25%), were eluted with petroleum ether 30–60°/benzene (4:1), m.p. 68–70 °C.IR (KBr disc), ν(C=O) 1690 cm^{-1}. Anal.: Found: C, 72.21; H, 7.39. $C_{41}H_{52}OSn$ Calc.: C, 72.46; H, 7.71%.

The addition of 10% hydrochloric acid to the intermediate carbanion, generated as above, gave (±)-4-phenyl-4-(trineophylstannyl)butan-2-one (**16**) in 52% yield, which was purified by column chromatography (silica gel 60); **16** was eluted with petroleum ether 30–60°/ethyl ether (92:8), as a solid, m.p. 64–65 °C. IR (KBr disc), ν(C=O) 1700 cm^{-1}. Anal.: Found: C, 72.15; H, 7.65. $C_{40}H_{50}OSn$ Calc.: C, 72.18; H, 7.57%.

Similarly, the addition of the stannyllithium anion **10*** followed by the reaction with methyl iodide, gave to **15** *threo* or (3S, 4S and 3R, 4R)-2-methyl-3-(trineophylstannyl)-2,3-dihydrobenzalacetophenone (**19**). Column chomatography (silica gel 60) of the crude product yielded **19** (60%), in the fraction eluted with petroleum ether/ethyl ether (98:2), as a solid, m.p. 80–82 °C. IR (KBr disc), ν(C=O) 1675 cm^{-1}. Anal.: Found: C, 74.62; H, 7.20. $C_{46}H_{54}OSn$ Calc.: C, 74.49; 7.34%.

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