www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 585 (1999) 35–42

Journal of Organometallic Chemistry

Evidence of single electron transfer in the diastereoselective synthesis of β-stannylketones

A.B. Chopa *, A.P. Murray, M.T. Lockhart

Instituto de Investigaciones en Química Orgánica, Universidad Nacional del Sur, Avenida Alem 1253, 8000 Bahía Blanca, Argentina

Received 9 November 1998

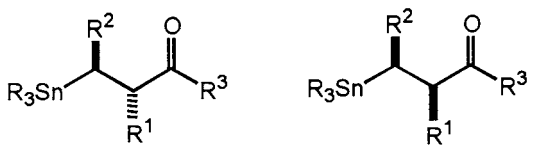
Abstract

The reaction of trimethyl- and triphenylstannylpotassium with mono and disubstituted enones (**1**–**5**) in acetonitrile as solvent was studied. In a few seconds and under mild conditions these reactions lead in nearly quantitative yields either to a mixture of diastereomers or to a pure diastereomer of β-stannylketones **6**–**16**. The reactions with triphenylstannylpotassium gave higher yields than trimethylstannylpotassium. The partial or total inhibition of the reactions by addition of a free radical scavenger (galvinoxyl) or a radical–anion scavenger (*p*-dinitrobenzene) leads us to believe that these reactions could follow a two-stage reaction mechanism involving an initial electron transfer step. Our results indicate that these reactions are stereoselective but certainly not stereospecific. Full ^{1}H- and ^{13}C-NMR data of the new β-stannylketones are given.

Keywords: Organotin anions; 1,4-Addition; Single electron transfer

1. Introduction

In the course of our studies we found it necessary to prepare diastereoisomers of the series of β-triphenyl- and β-trimethylstannyl-α,β-disubstituted ketones shown in Fig. 1.



R = Me, Ph; R^1 = Me, Ph; R^2 = Me, Ph; R^3 = Me, Ph

Fig. 1. Stereochemistry of compounds **6**–**16**.

The 1,4-addition of trialkylstannyllithium to α,β-unsaturated carbonyl compounds in THF [1,2] is known to be a simple and efficient way to functionalize organostannanes. The subsequent treatment of the intermediate enolates with electrophiles such as a proton or alkyl halides results in high anti selectivity [3]. Taking into account these antecedents, we carried out the reaction of triphenylstannyl- and trimethylstannyllithium [1] with enones **1**–**5**, quenching the enolates with the appropriate electrophile using THF as solvent. We observed that although the stereochemical results were promising, the reactions always gave rather low yields of 1,4-addition products (0–51%) except with (*E*)-1,2,3-triphenylpropenone (**3**) (78%).

Previous results obtained in our laboratory regarding the reactivity of triorganostannyl anionoids in polar aprotic solvents such as acetonitrile (ACN) and dimethylsulphoxide (DMSO) toward different substrates [4] encouraged us to carried out the addition reactions in ACN. We prefer to use the latter solvent over DMSO because ACN is easier to purify and

* Corresponding author. Tel.: +54-291-4595-187; fax: +54-291-4595-187.

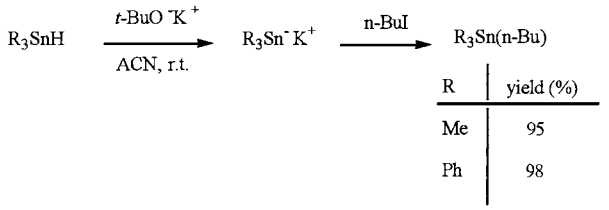
E-mail address: achopa@criba.edu.ar (A.B. Chopa)

0022-328X/99/$ - see front matter
PII: S0022-328X(99)00186-2

handle. As far as we know there are no reports about the generation of stannylanionoids in ACN [5]. In the present paper we report the results obtained in the course of these studies.

2. Results and discussion

We generated triphenyl- and trimethylstannylpotassium by reaction of potassium *t*-butoxide with the corresponding triorganostannanes (R_3SnH) [6]. The resulting anions were trapped with *n*-butyl iodide and quantified by GLC (Fig. 2).



R	yield (%)
Me	95
Ph	98

Fig. 2. Results obtained in the generation of triphenyl- and trimethylstannylpotassium.

The reaction of the enones **2**–**5** with the triphenylstannylpotassium followed by quenching of the intermediate enolates with methyl iodide or water led in nearly quantitative yields either to a mixture of diastereomers or to a pure diastereomer of the desired β-stannylketones in a rather instantaneous reaction (Table 1, Entries 3,7, 11 and 14). For example, the addition at room temperature of (*E*)-1,2,3-triphenylpropenone (**3**) to a solution of 1.2 equivalents of triphenylstannylpotassium in ACN followed after a few seconds by quenching with water, afforded a mixture (98.3%) of diastereomers **11** (75%) and **12** (25%) (Entry 7). The reaction with enone **1** led to the pure diastereomer **6** but in rather low yield (18,2%) (Entry 1). Similar reactions involving enones **1**–**4** and trimethylstannylpotassium in ACN were also carried out, showing that while ketones **2** and **3** gave mixtures of diastereomers in high yields (Table 1, Entries 5 and 9), ketone **4** gave only adduct **16** in 45% yield (Entry 13), and ketone **1** failed to react (Entry 2). Attempts to increase the yields by either increasing reaction times or lowering the temperature proved to be unfruitful.

Moreover, the results summarized in Table 1 show that trimethylstannylpotassium is less reactive than triphenylstannylpotassium toward the substrates studied under these reaction conditions.

Triorganostannyl anions have been proven to be excellent one-electron donors toward alkyl halides [7]. Nevertheless, as far as we know there are no examples in the literature of a single electron transfer (SET) mechanism in the reaction between triorganostannyl anions and enones. In our view 1,4-conjugate addition of triphenyl- and trimethylstannylpotassium to enones **1**–**5** in ACN takes place clearly via a SET mechanism. The partial or total inhibition of the reactions by addition of a free radical scavenger (galvinoxyl) or a radical anion scavenger (*p*-dinitrobenzene, *p*-DNB) (Table 1, Entries 4, 6, 8, 10, 12 and 15) leads us to believe that the conjugate addition of triphenyl- and trimethylstannylpotassium to the enones studied could be an example of a two-stage reaction involving an initial electron transfer step (Scheme 1). The electron transfer nature of this reaction appears to be a function of the reduction potential of the ketone. Thus, while ketones **2**–**5** (E_{red} within the range -1.0 to -1.4 V [8]) give high yields, ketone **1** ($E_{red} = -2.2$ V [8]) gives low yields or no product either with triphenyl- or trimethylstannylpotassium.

Moreover, the reaction of triphenylstannylpotassium with butenone ($E_{red} = -2.25$ V [8]) in ACN led (1 h) to 4-(triphenyltin)butanone in 76.6% yield. This reaction was not inhibited by the addition of galvinoxyl or *p*-DNB. Probably, the reaction takes place by a direct nucleophilic addition which is favoured in less hindered ketones [9]. It is to be noted that we could not detect any of di-addition product (conjugate addition of the enolate anion to a second molecule of ketone) as had been observed when the reaction was carried out in THF [10].

The analysis of the diastereomeric mixtures gave valuable information about the stereochemistry of these reactions. Product analysis showed that one diastereomer or mixtures of diastereomers with a relatively high predominance of one of them were always obtained (Table 1). The diastereomeric ratios in the product mixtures were identical independently of the starting olefin configuration. Consequently, these reactions are stereoselective but certainly not stereospecific. When the reactions were carried out using limiting amounts of stannyl anion (olefin/anion: 1/0.5), the addition products were detected together with the starting olefin which showed no appreciable isomerization. These stereochemical results indicate that the collapsing rate of the SET intermediates (radical–radical anion pair) to give products is faster than the isomerization rate of *cis* and *trans* ketyl and that the diastereomeric ratios of the products would depend only on the stereochemistry of the electrophilic attack (Scheme 1).

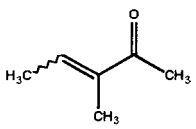
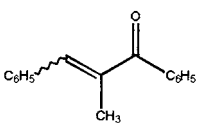
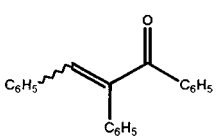
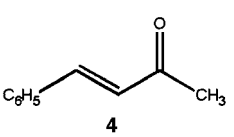
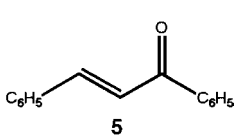
The ^{1}H-and ^{13}C-NMR characteristics of the new β-stannylketones are summarized in Tables 2 and 3. The ^{13}C-NMR chemical shifts were assigned by means of DEPT experiments and taking into account the magnitude of ^nJ (^{13}C, ^{119}Sn) coupling constants.

The configuration of the diastereoisomers was defined unambiguously on the basis of ^{13}C- and ^{1}H-NMR data. Thus, the correlation existing between the coupling constants and the dihedral angles [11] enabled us to assign the configuration *threo* to compounds **8**,

10, **12, 14** and **15** and *erythro* to compounds **6**, **7**, **9, 11** and **13**.

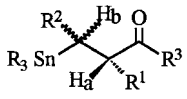
The diastereoselectivity of the additions has been explained taking into account the stability of the enolate intermediates as well as the stereoselection of the electrophilic attack. The stability of the enolate intermediates could be rationalized in terms of the steric requirements of the substituents attached to the chiral carbon [12] (Fig. 3, eclipsed-conformer **I**) and/or of electronic factors (Fig. 3, conformer **II**). As for the electronic factors, theoretical studies carried out by Houk et al. [13] and experimental results obtained by Fleming et al. [14] and McGarvey et al. [3] showed that the lower energy transition states are the ones originated from those conformers in which the electron donor substituent (R_3Sn) is located in the least crowded *anti*-conformational posi-

Table 1
Reaction of trimethyl- and triphenyltin–potassium with enones **1**–**5** [e]

Entry	Enone	Reaction conditions	*Erythro*/*threo* No. (%)	Yield (%) [a]
1	 **1**	$Ph_3Sn^-\ K^+$, H_2O	**6** (100)/0	18
2		$Me_3Sn^-\ K^+$, H_2O	–	0
3	 **2**	$Ph_3Sn^-\ K^+$, H_2O	**7** (97)/**8** (3)	97
4		$Ph_3Sn^-\ K^+$, H_2O [b,c]	–	0
5		$Me_3Sn^-\ K^+$, H_2O	**9** (67)/**10** (33)	77
6		$Me_3Sn^-\ K^+$, H_2O [b]	**9** (67)/**10** (33)	8
7	 **3**	$Ph_3Sn^-\ K^+$, H_2O	**11** (75)/**12** (25)	98
8		$Ph_3Sn^-\ K^+$, H_2O [b,c]	–	0
9		$Me_3Sn^-\ K^+$, H_2O	**13** (43)/**14** (57)	86
10		$Me_3Sn^-\ K^+$, H_2O [b]	**13** (43)/**14** (57)	41
11	 **4**	$Ph_3Sn^-\ K^+$, MeI	0/**15** (100)	99
12		$Ph_3Sn^-\ K^+$, MeI [b]	0/**15** (100)	34
13		$Me_3Sn^-\ K^+$, MeI	0/**16** [d] (100)	45
14	 **5**	$Ph_3Sn^-\ K^+$, MeI	0/**8** (100)	99
15		$Ph_3Sn^-\ K^+$, MeI [b]	0/**8** (100)	27

[a] Yields refer to isolated, purified material by column chromatography.
[b] Addition of 20% mol of galvinoxyl.
[c] The same results were obtained in the presence of 20% mol of *p*-DNB.
[d] *Erythro*/*threo*: 1/10, 60%, in THF [2].
[e] Stereochemical results and yields.

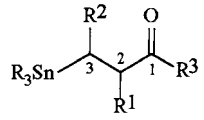
Table 2
^{1}H-NMR data of compounds **6**–**15** [a]



Number	R	R^1	R^2	R^3	H_a ^3J(Sn, H)	H_b ^2J(Sn, H)	J(Ha, Hb)	Others
6	Ph	Me	Me	Me	2.72 (59.7)	2.20 (62.0)	7.3	1.15 (3H, d, ^3J(H,H) 7.0); 1.26 (3H, d, ^3J(H,H) 7.8); 1.95 (3H, s); 7.15–7.28 (9H, m); 7.36–7.56, (6H, m)
7	Ph	Me	Ph	Ph	4.43 (35.1)	3.92 (61.7)	11.0	1.38 (3H, d, ^3J(H,H) 7.0); 6.94–7.11 (5H, m); 7.31–7.47 (18H, m); 7.33 (2H, d, ^3J(H,H) 7.2)
8					4.17 (81.3)	3.37 (71.8)	5.3	1.13 (3H, d, ^3J(H,H) 7.3); 6.83–7.45 (23H, m); 7.77 (2H, d, ^3J(H,H) 7.5)
9 [b]	Me	Me	Ph	Ph	4.23 (NO)	3.13 (58.4)	10.6	0.07 (9H, s, ^2J(Sn,H) 51.9); 1.35 (3H, d, ^3J(H,H) 6.8); 6.88–7.14 (3H, m); 7.34–7.54 (5H, m); 7.81–7.88 (2H, m)
10 [b]					4.21 (50.5)	2.80 (64.8)	8.0	−0.03 (9H, s, ^2J(Sn,H) 52.0); 1.26 (3H, d, ^3J(H,H) 7.1); 6.99–7.06 (3H, m); 7.34–7.54 (5H, m); 7.81–7.88 (2H, m)
11	Ph	Ph	Ph	Ph	5.55 (29.7)	4.36 (57.4)	12.8	6.94–7.43 (28H, m); 7.76 (2H, d, ^3J(H,H) 8.2)
12					5.20 (54.4)	3.77 (70.8)	9.2	6.84–7.39 (28H, m); 7.58 (2H, d, ^3J(H,H) 7.2)
13 [b]	Me	Ph	Ph	Ph	5.37 (23.4)	3.68 (56.0)	12.3	0.13 (9H, s, ^2J(Sn,H) 50.0); 6.83–7.51 (15H, m)
14 [b]					3.88 (34.1)	3.34 (60.6)	12.1	0.12 (9H, s, ^2J(Sn,H) 51.6); 6.74–7.21 (15H, m)
15	Ph	Me	Ph	Me	3.28 (59.7)	3.14 (72.3)	8.3	1.02 (3H, d, ^3J(H,H) 7.0); 1.77 (3H, s); 6.84–7.04 (5H, m); 7.15–7.33 (15H, m)

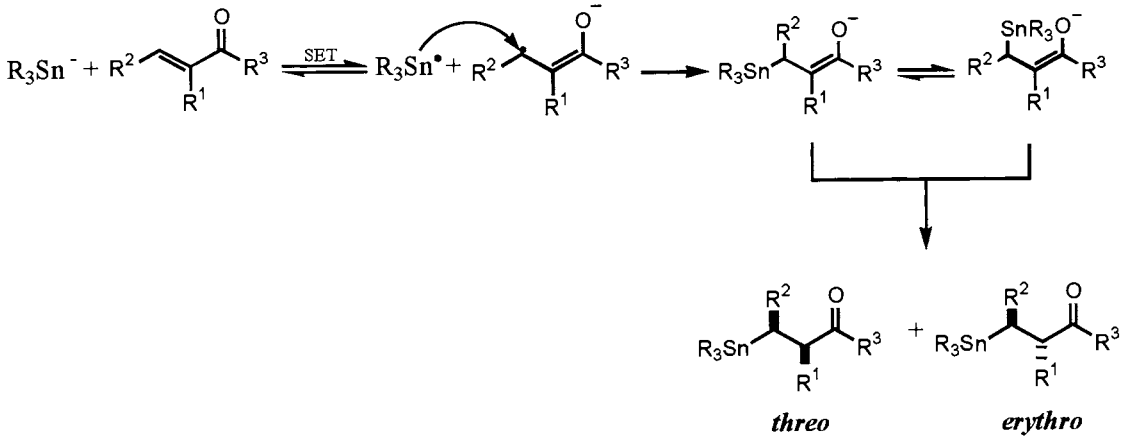
[a] Chemical shifts in ppm versus TMS, ^nJ in Hz. In $CDCl_3$. Multiplicity: s stands for singlet, d for doublet and m for multiplet.
[b] From Ref. [15].

Table 3
^{13}C-NMR data of compounds **6**–**15** [a]



Number	R	R^1	R^2	R^3	C-1	C-2	C-3	C-1′	C-2′	Others
6	Ph	Me	Me	Me	213.38 (37.9)	51.57 (14.6)	26.19 (439.3)	16.64 (15.5)	17.44 (35.9)	139.72, 137.27 (33.0), 128.64, 128.58, 128.33 (46.6)
7	Ph	Me	Ph	Ph	204.35 (50.1)	43.95 (NO)	41.69 (NO)	20.67 (16.5)	143.29 (28.8)	138.74 (484.0), 137.15 (35.0), 132.70, 128.84 (10.7), 128.48, 128.43 (47.6), 127.93, 124.85 (13.6)
8					204.43 (20.3)	44.91 (16.9)	40.70 (NO)	19.91 (28.8)	143.62 (35.6)	140.77 (495.1), 137.25 (34.8), 133.01, 128.41, 128.36, 128.09 (11.9), 127.82 (49.2), 127.14 (25.4), 124.38 (15.3)
9 [b]	Me	Me	Ph	Ph	204.40 (50.9)	43.51 (NO)	39.70 (332.3)	19.61 (19.5)	144.90 (29.6)	136.94, 132.35, 130.00, 129.10, 128.21, 128.08, 127.76, 126.54 (24.2), 123.86 (13.1), −9.16 (323.0).
10 [b]					204.28 (13.3)	44.25 (13.6)	38.75 (334.8)	20.11 (33.9)	145.12 (31.7)	135.89, 132.93, 128.56, 128.26, 126.42 (23.2), 123.76 (13.5), −8.40 (328.1)
11	Ph	Ph	Ph	Ph	199.90 (68.7)	55.88 (NO)	43.24 (362.8)	137.39 (10.2)	143.22 (33.9)	138.74 (487.4), 137.19 (34.8), 132.64, 129.44, 128.95, 128.58 (11.0), 128.39, 128.23, 128.13, 127.99, 127.89, 124.98 (14.4)
12					200.54 (14.4)	58.27 (11.9)	42.53 (377.2)	139.41 (44.9)	142.76 (31.4)	142.76 (31.3), 140.15 (493.4), 137.35 (34.7), 132.60, 128.71, 128.51, 128.27, 128.24, 128.15, 126.67, 124.52 (14.4)
13 [b]	Me	Ph	Ph	Ph	199.87 (56.0)	55.52 (NO)	40.07 (337.4)	138.62 (11.0)	144.55 (29.7)	137.39, 132.30, 128.97, 128.72, 128.19, 128.14, 127.99, 127.50, 126.34, (22.9), 123.97 (12.7), −10.06 (324.7)
14 [b]					200.37 (9.2)	59.68 (11.0)	35.39 (373.8)	140.69 (56.8)	145.74 (33.1)	143.69, 140.49, 128.63, 128.34, 127.13, 126.78, 126.22, 125.58, 122.54 (15.3), −8.45 (326.8)
15	Ph	Me	Ph	Me	213.55 (17.5)	50.91 (14.6)	39.99 (384.8)	18.26 (40.8)	143.38 (31.0)	140.30 (490.8), 137.36 (34.0), 128.57(11.7), 128.35, 128.04 (48.6), 127.59 (26.2), 124.57 (14.6)

[a] Chemical shifts in ppm with respect TMS; ^nJ, in brackets, in Hz; solvent, $CDCl_3$; NO: not observed. C-1′ and C-2′ are the 'first' carbons in R^1 and R^2, respectively.
[b] From Ref. [15].



Scheme 1. Reaction of triphenyl- and trimethylstannyl–potassium with enones **1**–**5**.

tion, i.e. perpendicular to the double bond. Then in order to minimize torsional strains in the transition state, the electrophile would attack on the same side of the organotin moiety in conformer **I** and on the opposite side in conformer **II**, leading to the *syn* and *anti* addition products, respectively.

Our experimental results indicate that in the reactions of the triphenyltin anion with activated ketones the products are predominantly those resulting from an *anti* attack, i.e. the attack on the preferred conformation **II** (Scheme 2). The rather diminished stereoselection found in the reaction of this anion with 1,2,3-triphenylpropenone (**3**) (*erythro*/*threo*: 75/25), could be explained taking into account that due to the larger steric requirements of the phenyl groups in conformation **II** ($R^1 = R^2 = Ph$), the attack of the electrophile to conformations **I** and **II** would lead to transition states of comparable energy.

The reaction of the trimethyltin anion with 4-phenylbutenone followed by quenching with methyl iodide gave as only product the *threo* diastereomer (45%), confirming the preference of electrophilic attack to conformer **II**. However, whereas the reaction of trimethylstannylpotassium with 1,3-diphenyl-2-methylpropenone (**2**) led also to the *anti* addition but with diminished stereoselection (*erythro*/*threo*, 67/33), the reaction with 1,2,3-triphenylpropenone (**3**) gave the *syn* addition product (*erythro*/*threo*, 43/57) in higher yield. The observed stereoselection could be explained by the attack of the electrophile to conformer **I** shown in Scheme 3.

These results suggest that the diastereocontrol observed in the addition of stannyl anions to the acyclic activated ketones studied arises from stereoelectronic and steric effects. Thus, stereoelectronic effects highly prevail over the steric hindrance when the triphenyltin group acts as a donor group, while the opposite situation exists in the case of the trimethyltin group. On the basis of these results, we could also assume that under these reaction conditions, the triphenyltin group acts as a better donor electron group than the trimethyltin group.

This study provides experimental support for the existence of a single electron transfer mechanism in the 1,4-addition of triphenyl- and trimethyltinpotassium over different enones, in ACN as solvent. The possibility of SET depends on the one-electron donor ability of the nucleophile and the electron-acceptor ability of the ketone. Sterically hindered molecules with low reduction potential (enone **1**) lead to low or null yields. On the other hand, uncrowded ketones yield the 1,4-addition products through a direct nucleophilic attack.

3. Experimental

3.1. General

^1H and ^{13}C-NMR spectra were determined with a Bruker AC200 instrument at IQUIOS (Rosario, Argentina) and a Bruker AM300 instrument at Dortmund University (Germany). Ph_3SnH and Me_3SnH were prepared by the reaction of Ph_3SnCl (Fluka) and Me_3SnCl (Fluka) and $LiAlH_4$ as reported [16]. Acetonitrile was vacuum distilled from H_2Ca and put in storage over molecular sieves. Commercial 1,3-diphenylpropenone and 4-phenyl-3-buten-2-one were recrystallized before used. The olefins used were synthesized by known procedures [17–19].

All the reactions were monitored by thin-layer chromatography (TLC) and judged complete when starting

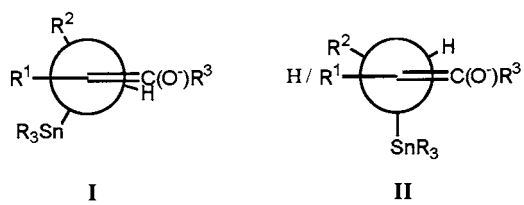
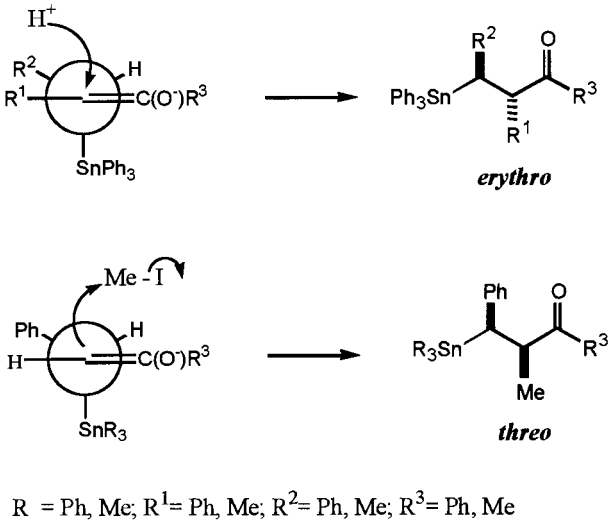


Fig. 3. Eclipsed and perpendicular models for enolate conformations.



R = Ph, Me; R^1= Ph, Me; R^2= Ph, Me; R^3= Ph, Me

Scheme 2. Preferred intermediate enolates and major products in the reaction of enones **1**–**5** with triphenylstannyl–potassium.

material was no longer visible in the reaction mixture. Analytical TLC was performed using precoated silica gel plates with phosphomolibdic acid in ethanol as indicator. The diastereoisomers ratios were determined by GLC.

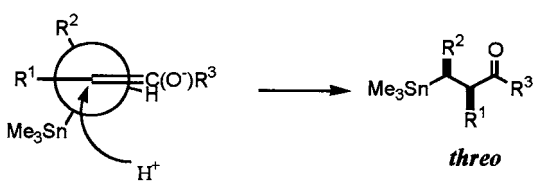
All the reactions were carried out following the same procedure. One experiment is described in detail in each case in order to illustrate the method used.

*3.2. Reaction of triphenylstannylpotassium with 1,3-diphenyl-2-methylpropenone (**2**). Synthesis of erythro- and threo-1,3-diphenyl-2-methyl-3-(triphenylstannyl) propanone (**7** and **8**)*

The reactions were carried out in a two-necked, 25 ml, round-bottomed flask equipped with a nitrogen inlet, a magnetic stirrer and septums. To a solution of 0.088 g (0.78 mmol) of *t*-BuOK in 5 ml of ACN was added, by syringe, a solution of 0.27 g (0.2 ml, 0.78 mmol) of Ph_3SnH in 4.8 ml of ACN. After 5 min, a solution of 0.144 g (0.65 mmole) of **2** in 5 ml of ACN was added. The resulting mixture was quenched immediately by adding 5 ml of water. The mixture was extracted with ether, dried over magnesium sulphate and the solvent was removed by distillation under reduced pressure. Column chromatography on silica gel 60 of the crude mixture yielded 0.35 g (0.61 mmol, 94%) of compound **7** and 0.011 g (0.019 mmol, 2.9%) of **8**.

The reaction of triphenylstannylpotassium with 1,3-diphenylpropenone (**5**) was carried out under similar conditions. The resulting mixture was quenched by adding 0.1 ml (0.22 g, 1.6 mmol) of methyl iodide instead of water and was stirred during 15 min. After usual work up the reaction conduced to a quantitative yield of isomer **8**.

Addition reactions in the presence of galvinoxyl or *p*-DNB. The procedure was similar to that for the previous reactions, except that 20 mol% of galvinoxyl or *p*-DNB was added to the solution of the anion prior to the substrate addition.



Scheme 3. Preferred intermediate enolate and major product in the reaction of enone **3** with trimethylstannyl–potassium.

Acknowledgements

This work was partially supported by CIC, CONICET and UNS (Argentina). The CIC is thanked for a research fellowship to A.P.M. The authors thank Dr T.N. Mitchell (University of Dortmund, Germany) and Dr M. González Sierra (IQUIOS, Argentina) for the NMR spectra.

References

[1] W.C. Still, J. Am. Chem. Soc. 99 (1977) 4836.
[2] I. Fleming, C.J. Urch, J. Organomet. Chem. 285 (1985) 173.
[3] G.J. Mc Garvey, J.M. Williams, J. Am. Chem. Soc 107 (1985) 1435.
[4] M.T. Lockhart, Thesis (1998). Results to be published
[5] A.G. Davies, Organotin Compounds, VCH, Weinheim, 1997. E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 11, Elsevier, Amsterdam, 1995, p. 356. M. Pereyre, J.P. Quintard, A. Rahm, Tin in Organic Synthesis, Butterworths, London, 1987.
[6] The pK_a of Ph_3SnH is ca. 16 (E.S. Petrov, M.I. Terekhova, R.G. Mirskov, M.G. Voronkov, A.I. Shatenshtein, Dokl. Akad. Nauk. SSSR 221 (1975) 111; Chem. Abstr. 82 (1975) 155040e; Me_3SnH ca. 25 (M.S. Alnajjar, H.G. Kuivila, J. Am. Chem. Soc., 107 (1985) 416), lower than *t*-BuOH (32.2) (F.G. Bordwell, Acc. Chem. Res. 21 (1988) 456).
[7] E.C. Ashby, Acc. Chem. Res. 21 (1988) 414 and references cited therein.
[8] H.O. House, L.E. Huber, M.J. Umen, J. Am. Chem. Soc. 94 (1972) 8471.
[9] A. Pross, Acc. Chem. Res. 18 (1985) 212.
[10] E. Piers, H.E. Morton, J.M. Chong, Can. J. Chem. 65 (1987) 78.
[11] T.N. Mitchell, J.C. Podestá, A. Ayala, A.B. Chopa, Magn. Reson. Chem. 26 (1988) 497.
[12] The *A* value of the phenyl group is 2.8 kcal mol^{-1}: M.E. Squillacote, J.M. Neth, J. Am. Chem. Soc. 109 (1987)198. The *A* value of the methyl group is 1.74 kcal mol^{-1}: H. Book, J.R. Everett, J. Chem. Soc. Chem. Commun. (1976) 278. The *A* values of Me_3Sn- and Ph_3Sn- are 1.0 kcal mol^{-1} and 1.44 kcal mol^{-1}, respectively: W. Kitching, H.A. Olszowy, K. Harvey, J. Org. Chem. 47 (1982) 1893.

[13] K.N. Houk, N.M. Paddon-Row, N.G. Rondan, Y.D. Wu, F.K. Brown, D.C. Spellmeyer, J.T. Metz, R.J. Loncharich, Science 231 (1986) 1108.
[14] (a) I. Fleming, J.J. Lewis, J. Chem. Soc. Chem. Commun. (1985) 149. (b) I. Fleming, J.H.M. Hill, D. Parker, D. Waterson, J. Chem. Soc. Chem. Commun. (1985) 318.
[15] A.B. Chopa, A.P. Murray, Main Group Metal Chem. 21 (1998) 347.
[16] (a) H.G. Kuivila, O.F. Beumel, J. Am. Chem. Soc. 83 (1961) 1246. (b) H.G. Kuivila J.E. Dixon, P.L. Maxfield, N.M. Scarpa, T.M. Topka, K-H. Tsai, K.R. Wursthorn, J. Organomet. Chem. 86 (1975) 89.
[17] G.F. Hennion, R.B. Davis, D.E. Maloney, J. Am. Chem. Soc. 71 (1949) 2813.
[18] W.B. Black, R.E. Lutz, J. Am. Chem. Soc. 75 (1953) 5990.
[19] R.D. Abell, J. Chem. Soc. 79 (1901) 928.