Triphenylstannyl Anions and Related Moieties as Leaving Groups in Elimination Reactions

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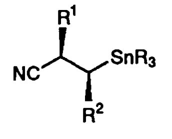
Reactions of strong bases with β-triphenylstannyl substituted propionitriles give high yields of alkenes under mild conditions through, probably, an E1cB mechanism; under the same reaction conditions, β-trialkylstannyl substituted propionitriles give substantially lower yields of elimination products.

Alkene forming elimination reactions are generally associated with a number of well characterized leaving groups, some of which, *e.g.* F, do not really operate as nucleofuges in substitution reactions at saturated carbon. In the present work we have investigated the reactions of a number of substituted propionitriles (**1–5**) of known relative stereochemistry,[1] that carry diverse R_3Sn groups on C-3, with different bases. We have uncovered a synthetically useful elimination reaction in which the R_3Sn moiety acts as leaving group and report our results herein.



threo

Comp.	R	R^1	R^2
1	Me	Ph	Ph
2	Ph	Ph	Ph
3	Ph	Ph	Me
4	Bu	Ph	Me
5	Ph	H	H

In the first instance we found that *threo*-**1** reacted with lithium diisopropylamide (LDA) at low temperature (see Table 1, entry 2) to give an *erythro*: *threo* isomer mixture in a 70:30 ratio. We considered that this result was readily explicable in terms of abstraction of a proton on C-2 of *threo*-**1** to give a carbanion. Subsequent isolation of the *erythro* and *threo* isomers after reprotonation of the carbanion, enabled the relative thermodynamic stabilities of the isomers to be assessed from their ratios.

We were particularly intrigued by the observation of alkene products (isomers) from the reaction of *threo*-**1** with $NaBu^tO/Bu^tOH$ at 25 °C (see Table 1, entry 4) since the ability of Me_3Sn^- to function as a leaving group in alkene forming reactions appears unknown. It is noteworthy that although in the chemical literature there are references to elimination reactions of organotin compounds *via* both carbonium ions[2] and free radicals,[3] we could not find any reference to eliminations *via* carbanions.

Accordingly we sought to optimize the parameters for elimination under convenient conditions. Thus, we found that with the same reagents but increasing the temperature up to 70 °C, *threo*-**1** gave 58% of elimination, with a *Z*/*E* ratio 90:10. Other results shown in Table 1 demonstrate the viability of the method, with virtually exclusive observation of alkene when, *e.g.*, the organotin **2** is treated with $NaBu^tO/Bu^tOH$ at 70 °C, or with LDA at ambient temperature (see Table 1, entries 7 and 9 respectively). Other alkene yields could be increased by use of more prolonged reaction times.

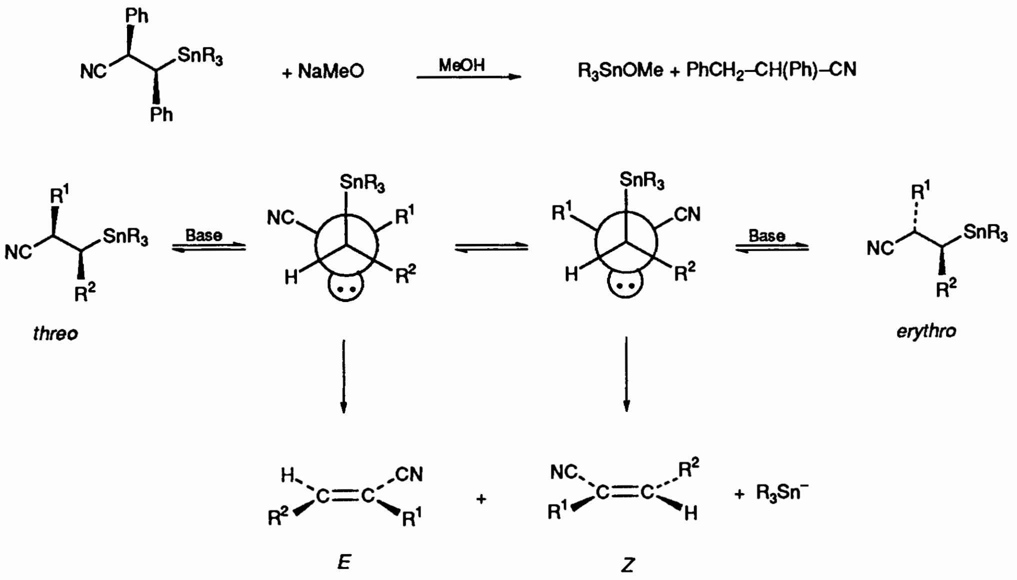
The data presented here demonstrate the unrecognized potential of the trialkyl- or triaryl-tin group as leaving group under base conditions, and support an E1cB mechanism in which proton abstraction from C-2 is reversible and the leaving group is R_3Sn^-, according to Scheme 1.

In order to obtain direct evidence for the existence of trialkylstannyl anions (R_3Sn^-), the elimination reaction was carried out in the presence of allyl bromide. We considered that this alkylating agent would not interfere at the early steps of the

Table 1 Isomerization and elimination reactions of *threo*-β-triorganostannyl substituted propionitriles **1–5**

Entry	Comp.	Base/solvent	*T*/°C	% Isomerization[a] (*erythro*: *threo*)	% Elimination (*Z*: *E*)
1	**1**	NaMeO/MeOH[b]	25	100 (80:20)	—
2	**1**	LDA/THF[c]	−78	100 (70:30)	—
3	**1**	LDA/THF[c]	25	76 (83:17)	24 (90:10)
4	**1**	$NaBu^tO/Bu^tOH$[d]	25	86 (80:20)	14 (89:11)
5	**1**	$NaBu^tO/Bu^tOH$[d]	70	42 (75:25)	58 (90:10)
6	**2**	$NaBu^tO/Bu^tOH$[d]	25	64 (100)	36 (89:11)
7	**2**	$NaBu^tO/Bu^tOH$[d]	70	—	100 (86:14)
8	**2**	LDA/THF[c]	−78	30 (76:24)	70 (85:15)
9	**2**	LDA/THF[c]	25	—	100 (85:15)
10	**3**	$NaBu^tO/Bu^tOH$[d]	25	47 (60:40)	53 (92:8)
11	**3**	$NaBu^tO/Bu^tOH$[d]	70	38 (58:42)	62 (85:15)
12	**4**	$NaBu^tO/Bu^tOH$[d]	25	82 (60:40)	18 (95:5)
13	**4**	$NaBu^tO/Bu^tOH$[d]	70	67 (61:39)	33 (90:10)
14	**5**	$NaBu^tO/Bu^tOH$[d]	25	*e*	13
15	**5**	$NaBu^tO/Bu^tOH$[d]	70	*f*	62

[a] Indicates just the amount of organotin compound in the product and not the actual degree of isomerization from the starting *threo* compounds. [b] Molar ratio organotin:base: 0.32:0.35, 3 h. [c] 0.24:0.26, 1 h. [d] 0.20:0.22, 3 h. [e] 87% of starting organotin recovered. [f] 38% of starting organotin recovered.



Scheme 1

sequence shown in Scheme 1, but would react with R_3Sn^- to give a distinct product. We found that *threo*-2,3-diphenyl-3-(triphenylstannyl)propionitrile (**2**) and LDA in dry tetrahydrofuran (THF) in the presence of an equimolecular amount of allyl bromide, gave 33% of triphenylallytin.

The choice of the base is important to the observation of these elimination reactions. Thus, we found that whereas LDA/THF and NaBu^{t}O/Bu^{t}OH, both promoted elimination, the use of NaMeO/MeOH produced only isomerization at ambient temperature. At higher temperature methanolysis took place, as indicated in Scheme 1, to give products parallel to those obtained by Eaborn[4] in systems in which alkene formation was not possible.

As shown in Scheme 1, it is probable that *trans* elimination from the intermediate carbanions to give the corresponding olefins occurs, and that these carbanions are interconvertible.

It is noteworthy that these eliminations could be considered as the reverse of the hydrostannation of polar alkenes under polar conditions.[5] Our results demonstrate, to our knowledge for the first time, the ability of, *e.g.*, Ph_3Sn^- to sustain a negative charge within an elimination reaction sequence. Further studies are directed to obtain more information about the stereochemistry of the reaction and to carry out kinetic studies on these systems.

The organotin substrates **1**–**5** were prepared as described previously.[6] LDA was prepared according to House *et al.*[7] All the experiments were carried out under a N_2 atmosphere. Reaction conditions are given in Table 1. The reaction mixtures were checked by quantitative GLC using organotin compounds as internal standards. The reactions were performed following the same procedure in all cases, and one experiment is described in detail to illustrate the method used.

To a solution of the propionitrile **2** (1.203 g, 3.25 mmol) in Bu^{t}OH (10 cm^3), a solution of NaBu^{t}O in Bu^{t}OH (2.4 cm^3; 1.5 mol dm^{-3}; 3.6 mmol) was added. After 3 h of stirring at 70 °C, the reaction was quenched with water and worked up as usual. ^{1}H NMR and GLC showed that elimination had occurred quantitatively, giving a mixture of *Z* (86%) and *E* (14%) isomers.

With LDA the reverse order of addition was used, *i.e.*, the organotin compound in dry THF was added to a solution of LDA in THF.

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