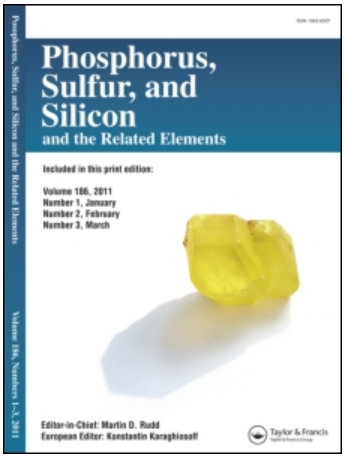

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Functional Organotrialkynyltins: Preparation by Transmetallation of Tetraalkynyltins with Grignard Reagents and Transformation into Organotin Oxides, Alkoxides and Oxocarboxylates

PASCALE JAUMIER, BERNARD JOUSSEAUME and MOHAMED LAHCINI

Laboratoire de Chimie Organique et Organométallique, UMR 5802 CNRS, Université Bordeaux I, 351, cours de la Liberation, 33405 – Talence-Cedex (France)

Functional monoorganotin alkoxides and oxides, and monoorganooxotins carboxylates have been synthesized in high yield by reaction of the corresponding trialkynylorganotins respectively with water, alcohols and carboxylic acids. Functional starting trialkynylorganotins were obtained either by alkynylation of organotin trichlorides or by a new selective transmetallation of tetraalkynyltins by Grignard reagents. By changing the stoichiometry of the reactants, the transmetallation can selectively give dialkynyldiorganotins.

Keywords: Organotins; oxides; alkoxides; alkynyltins; Grignard reagents; transmetallation

INTRODUCTION

Organotin oxides, alkoxides and oxocarboxylates represent an important class of organotin compounds for their applications in organic synthesis and in industry as catalysts, and for structural studies.[1] Several routes are available for the synthesis of these derivatives. Organotin oxides were first obtained by alkaline hydrolysis of the corresponding chlorides,

hydroxyde intermediates undergoing spontaneous dehydration. Then, milder method appeared, involving tin alkoxides and stannylamines highly susceptible to protolysis. Triorganotin oxides are well characterized compounds, but, except with bulky substituent were trimers are formed, insoluble polymeric diorganotin oxides are not well defined. The same is true for monoorganotin oxides, except for clusters with twelve tin atoms and fourteen oxygen atoms which can be isolated at the early stage of the hydrolysis. Tin alkoxides can also be prepared from organotin halides by reaction with alkali metal alkoxides although specific preparation of triorganotin alkoxides by decomposition of triorganostannyl alkyl carbonate is by far easier. It is also possible to treat labile stannylamines, where dialkylamino group can be easily displaced, by alcohols, which is advantageous when a volatile amine is formed but necessitates the preparation of reactive organotin amides. Di- and triorganotin alkoxides are conveniently obtained from the corresponding di- and triorganostannanes, by addition to aldehydes and ketones under radical or polar conditions. However, this reaction has not been extended to monoorganotin alkoxides.While many monoalkyl or monoaryltin oxide or alkoxides have been described the number of functional examples prepared up to now is rather limited.

On the other hand, the sol-gel process is suitable for the preparation of almost all metallic oxides, with metallo-organic compounds being commun starting materials.[2] Upon hydrolysis a metal-oxo based macromolecular network is formed through condensation reactions. However, materials prepared according to this method present mechanical defects due to shrinkage and cracking upon solvent removal. Organic phases incorporated in these materials improve their mechanical properties, as it has been shown with silicon-based materials where links between the organic and the inorganic phase are established through silicon-oxygen-carbon or silicon-carbon-silicon bonds.[3] Tin affording stable carbon-metal bonds, we were interested in preparing precursors of such hybrid materials based on the existence of metal-carbon-metal bonds. Two ways are possible, the first involving a pre-established polymeric organic network linked to metallic centers bearing hydrolyzable groups,[4] and the other using organotin compounds where

the metal bears both hydrolyzable and polymerizable groups.[5] However, in the last case, available synthetic routes only allowed the preparation of 3-butenyltrialkoxytin,[6] the introduction of alkoxyl groups on the tin being incompatible with the presence of more reactive functional groups such as styryl or unsaturated ester groups. Therefore, it was necessary to find a more accessible route to functional organotin oxides, using other precursors rather than alkoxides. These precursors should be easily cleaved by water to give organotin oxides, and easily introduced onto the tin by a reaction tolerant to as many functional groups as possible. Alkynylorganotins should fill all these requirements. The tin-alkynyl bonds are easily cleaved by water,

$$(R^2C{\equiv}C)_3SnR^1 \xrightarrow{H_2O} R^1SnO_{3/2} + 3\ R^2C{\equiv}CH$$

and trialkynylorganotins are accessible from conveniently obtained organotin trichlorides.[6], [7] They are prepared from better nucleophiles, such as alkynyllithiums, than alkoxides which should allow shorter reaction time and use of lower temperatures of reaction.

$$R^1SnCl_3 + R^2C{\equiv}CLi \longrightarrow R^1Sn(C{\equiv}CR^2)_3$$

Here are described two ways of preparation of functional trialkynylorganotins and their transformation in organotin oxides, alkoxides and oxocarboxylates.

RESULTS

The first entry to organotrialkynyltins involves alkynylation of trichloroorganotins, prepared from uncommon organotricyclohexyltins as starting materials by treatment with tin tetrachloride, which is tolerant to styryl, hydroxyl and ester groups. Classical substitution[8] of chlorine atoms by alkynyl groups was conveniently achieved with alkynyllithium and allowed the preparation of styryl and ester-substituted organotrialkynyltins irrespective of the nature of the alkynyl groups, propynyl, butynyl or phenylethynyl (Table 1).[9]

$$Cl_3Sn(CH_2)_nOAc + 3\ BuC{\equiv}CLi \longrightarrow (BuC{\equiv}C)_3Sn(CH_2)_nOAc$$

n = 3(1), 4(2), 5(3)

In the case of ester-substituted compounds a slight excess of lithium reagent (3.5 eq) was used in order to improve the yield of the reaction. Oxygen must be carefully excluded from the reaction as lithium butanolate formed by oxydation of butyllithium induced transesterification of esters, especially with (2-(methoxycarbonyl)-ethyl)trichlorotin.

Functional organotrialkynyltins were purified either by recrystallization or by rapid chromatography on Florisil. Crystalline triphenylethylnyl-stannylated compounds were more stable in air than the corresponding tripropynyl- or tributynylstannyl derivatives.

TABLE I Organotrialkynyltins from the corresponding trichlorides.

Product	$(MeC{\equiv}C)_3SnBu$	$(BuC{\equiv}C)_3SnBu$	$(BuC{\equiv}C)_3SnPh$
Yield(%)	83	79	75
Product	(1)	(2)	(3)
Yield(%)	36	45	42

When hydroxyl-substituted organotrichlorotins were used, the corresponding trialkynyltins could not be isolated. Suspecting a displacement reaction between the hydroxyl and the alkynyl group avoiding the isolation of hydroxyl-substituted organotrialkynyltins, a less acidic hydroxyl-substituted organotrichlorotin was prepared. However, alkynylation of 5-(2-hydroxy-2-methylhexyl)trichlorotin only led to 5-(2-methylhex-2-enyl)trihexynyltin, dehydration taking place during the reaction or the work-up.

$$Cl_3Sn(CH_2)_3\text{-}CH_2\text{-}\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}\text{-}CH_3 \longrightarrow (nBuC{\equiv}C)_3Sn(CH_2)_3CH{=}C\overset{CH_3}{\underset{CH_3}{\diagdown}}$$
$$\underset{CH_3}{}$$

The above described route was very useful when organotin trichlorides were available. However, functional organotrichlorotins are

sometimes too unstable to be isolated as for instance in the case of (ω-styrylalkyl)trichlorotins which undergo premature oligomerization upon isolation. Thus a more direct route to organotrialkynyltins was necessary to broaden the scope of functional groups present in these compounds. The preparation of vinyl,[10] allyl[11] or α-heteroalkyllithiums[12] using the reaction of organotins with organolithium reagents is a very common reaction in organic synthesis.

$$Bu_3SnAr + BuLi \rightleftharpoons ArLi + Bu_4Sn$$

In this transmetallation reaction, a tetraorganotin is formed as a by-product, which would be very useful if a transmetallation could be achieved from a tetraalkynyltin and an organolithium reagents. In this way an organotrialkynyltin might be formed. Butyllithium was then reacted with tetralkynyltins in various conditions but mixtures of mono-, di- and trialkylation products were obtained.

$$(RC{\equiv}C)_4Sn + BuLi \longrightarrow (RC{\equiv}C)_3SnBu + (RC{\equiv}C)_2SnBu_2 + RC{\equiv}CSnBu_3 + RC{\equiv}CLi$$

The reaction was as unselective than alkylation of tin tetrachloride. So, less nucleophilic Grignard reagents were used with successfull results, as tetrapropynyltin reacted with one equivalent of butylmagnesium bromide in diethylether to give butyltripropynyltin in 68% yield with a 95% selectivity. The use of a Grignard reagent in a preparative transmetallation process involving an organotin compound is reported here for the first time.

$$(MeC{\equiv}C)_4Sn + BuMgX \longrightarrow (MeC{\equiv}C)_3SnBu + MeC{\equiv}CMgX$$

The reaction was not limited to primary alkyl Grignard reagents: secondary and tertiary alkylmagnesium compounds reacted as well, at a somewhat slower rate. THF, used instead of diethylether allowed the reaction to complete at a faster rate. The transmetallation succeeded whatever the nature the alkynyl moiety, propynyl, hexynyl or phenylethynyl. However, better yields and selectivity were obtained with tetrakis(phenylethynyl)tin (Table 2).[13]

$$(R^1C{\equiv}C)_4Sn + R^2MgX \longrightarrow (R^1C{\equiv}C)_3SnR^2 + R^1C{\equiv}CMgX$$

TABLE 2 Organotrialkynyltins by transmetallation of tetraalkynyltins.

R^1	R^2	Solvent	Selectivity(%)	Yield (%)
Me	Me	Et_2O	85	41
Me	n-Bu	Et_2O	95	68
Me	i-Pr	Et_2O	88	70
Bu	n-Bu	Et_2O	92	43
Ph	Me	Et_2O	100	87
Ph	n-Bu	Et_2O	100	75
Ph	i-Pr	THF	95	89
Ph	t-Bu	THF	100	82

The reaction was then applied to (4-styrylbutyl)magnesium bromide and tetrakis(phenylethyltin). It furnished (4-styrylbutyl)tris(phenylethynyl)tin in 60% yield after rapid chromatography on florisil to get rid of 1,8-distyryloctane, a by-product present in the Grignard reagent.

$$(RC{\equiv}C)_4Sn + sty\text{-}(CH_2)_4MgBr \longrightarrow sty\text{-}(CH_2)_4Sn(C{\equiv}CR)_3$$

R = Ph Yield = 60 %
R = Me Yield = 46%

Extension to aromatic or unsaturated Grignard reagents as phenylmagnesium bromide or allylmagnesium bromide was less successful. In both cases the reaction did not show any selectivity as mixtures of mono-, di- and trialkylation products were isolated. The alkyl substituent in alkyltrialkynyltins probably diminishes the electrophilic properties of the tin while aryl or allyl substituent show a reverse effect, which makes the nucleophilic attack of Grignard reagents easier.

The nature of the halogen in the organomagnesium compound had also a strong influence on the rate of the reaction. With the same conditions, diethylether as solvent and a reaction time of five hours, butylmagnesium chloride reacted faster than butylmagnesium bromide,

which itself transmetallated faster than butylmagnesium iodide. Such a reactivity scale is in agreement with known data on the reactivity of Grignard reagents.[14] However butylmagnesium chloride was less selective as 12% of dialkylation product was formed (Table 3).

TABLE 3 Influence of the halogen of the Grignard reagent.

Grignard reagent	$(PhC{\equiv}C)_4Sn$	$(PhC{\equiv}C)_3SnBu$	$(PhC{\equiv}C)_2SnBu_2$
BuMgCl	0	88	12
BuMgBr	0	100	0
BuMgI	40	60	

The reaction could also be driven cleanly to dialkylation. Using two equivalents of Grignard reagent the corresponding diorganodialkynyltins were recovered in good yield with a very high selectivity. As for monotransmetallation, the use of THF was necessary to complete the reaction.

$$(R^1C{\equiv}C)_4Sn + 2\ R^2MgX \longrightarrow (R^1C{\equiv}C)_2SnR^2_2 + 2\ R^1C{\equiv}CMgX$$

Alkyltrialkyltins could be used instead of tetraalkynyltins. Reactions with one equivalent of Grignard reagent led to the corresponding dialkylation product, which would allow the preparation of unsymmetrical diorganodialkynyltins in two steps from symmetrical tetraalkynyltins (Table 4).

TABLE 4 Diorganodialkynytins from organotrialkynyltins or tetraalkynyltins.

Product	Solvent	Selectivity(%)	Yield (%)
$(MeC{\equiv}C)_2SnBu_2$	Et_2O	93	70
$(MeC{\equiv}C)_2SnBu_2$ (1)	Et_2O	95	62
$(BuC{\equiv}C)_2SnBu_2$	Et_2O	85	38
$(PhC{\equiv}C)_2SnPr_2$	THF	86	75

(1) from $(MeC{\equiv}C)_3SnBu$ as starting reagent and 1 eq. of BuMgCl

Cleavage of organotrialkynyltins with alcohols was then investigated. Acidic alcohols as trifluoroethanol gave rapid reactions at room temperature with evolution of the corresponding alkynes. The same reaction conducted with unhalogenated primary and secondary alcohols had to be conducted at moderate temperature, 60°C, to give good results. However, tertiary alcohols did not give complete cleavage. Organotrialkoxytins were recovered by distillation (Table 5).

$$(R^1C{\equiv}C)_3SnR^2 + R^3OH \longrightarrow R^2Sn(OR^3)_3 + R^1C{\equiv}CH$$

TABLE 5 Organotrialkoxytins from organotrialkynyltins.

R^1	R^2	R^3	Yield
Me	Ph	sec-Bu	65
Me	Ph	i-Pr	59
Bu	Me	sec-Bu	76
Bu	Me	Benzyl	80
Bu	Me	i-Bu	55

Then functional organotrialkynyltins were hydrolyzed with the objective to get closo clusters $[(R^1Sn)_{12}(\mu_3O)_{14}(\mu_2O)_6](OH)_2$ more useful and well characterized than organostannic acids, the ultimate products of hydrolysis.[15] Treatment of organotrialkynyltins either by aqueous tetrahydrofuran in chloroform or by aqueous alcohols resulted in a total cleavage of tin-alkynyl bonds and formation of tin-oxygen-tin bonds.[6] Hydrolysis conditions were mild enough to allow the formation of closo clusters identified by ^{119}Sn NMR by their characteristic signals around -280 and -450 ppm, accompanied by two sets of satellites corresponding to ^2J(Sn-Sn) couplings. Low-field and high-field peaks correspond respectively to five- and six-coordinate tin atoms.

$$AcO(CH_2)_5Sn(C{\equiv}CBu)_3 \longrightarrow \{(AcO(CH_2)_5Sn)_{12}O_{14}(OH)_6\}(OH)_2$$

(3-Acetoxypropyl)tributynyl- and (2-(methoxycarbonyl)ethyl)tributynyltin show a different behavior from other ester-substituted compounds as they do not give the expected

closo cluster but a soluble oxo-polymer where all the tin atoms have a coordination number six. It has been known for a long time that (2-(methoxycarbonyl)ethyl)trichlorotin has a strong intramolecular coordination bond between the tin and the oxygen of the carbonyl.[16] The same effect, somewhat weaker, was also more recently described with (3-acetoxypropyl)trichlorotin. Thus, intramolecular coordination of the tin atom by the carbonyl of ester group would favor six-coordination at tin and then disfavor the formation of the cluster where six tin atoms show a five-coordination.

Organotrialkynyltins allowed also the preparation of functional organooxotin carboxylates.[17] Up to now these compounds were only functionalized on the carboxylate moieties, not on the organic group. It was thus of interest to determine what was the influence of functional groups on the structure of clusters, which can be either tri-, tetra-, or hexameric with hexacoordinated tin atoms.[18] Organotrialkynyltins, either non functional or bearing an ester carbonyl in either β, γ, or ε position where hydrolyzed in wet isopropanol for a few minutes and treated with acetic acid after evaporation of the solvent. Viscous gel was obtained, characterized in ^{119}Sn NMR by signals arounds -487 ppm surrounded by the waited sets of satellites corresponding to ^{2}J(Sn-Sn). Chemical shifts and coupling constants were almost identical to those previously reported for unsubstituted organotin carboxylates in the drum form. Large ^{1}J(Sn-C) of ca 1200 Hz are consistent with hexacoordinated tin atoms.

$$6\,(R^1C{\equiv}C)_3SnR^2 \xrightarrow[2:\ -\,CH_3CO_2H]{1:\,H_2O} [R^2Sn(O)O_2CCH_3]_6$$

R^1 = n-Bu,
$R^2 = CH_2CH_2CO_2Me$, 85%
$R^2 = CH_2CH_2CH_2O_2CCH_3$, 91%
$R^2 = CH_2CH_2CH_2CH_2CH_2O_2CCH_3$, 88%

Thus, even when a carbonyl is present in an ideal position to establish a strong coordination bond as with a 2-methoxycarbonyl group, oxo and carboxylato bridges are retained and the tin atoms do not increase their

coordination to seven. Stabilization of the drum structure is strong enough not to be disturbed.

In summary, it has been shown here that functional organotrialkynyltins could be prepared either by alkynylation of the corresponding organotrichlorotins or by a new transmetallation reaction from Grignard reagents and tetraalkynyltins. This transmetallation could also lead to dialkylated compounds by adjusting the stoichiometry of the reagents. These functional organotrialkynyltins could then give the corresponding alkoxides, oxides or oxocarboxylates upon treatment with alcohols, water or carboxylic acids respectively.

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