α-Alkoxytin Compounds in Organic Synthesis: an Efficient Synthesis of α-Ethoxyalkenyl- and α-Ethoxyalkynyl-tin Compounds

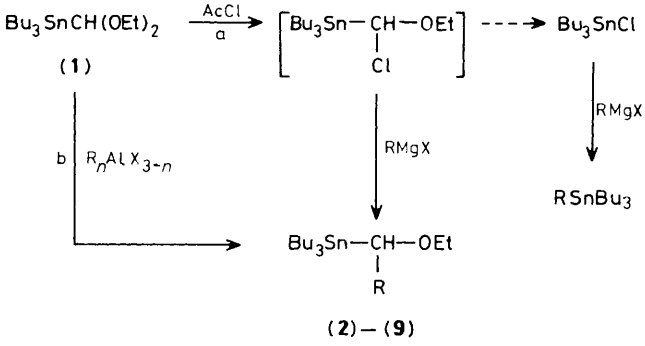
Alain Duchêne[a] and Jean-Paul Quintard*[b]

[a] *Laboratoire de Chimie Organique et Biologique, Faculté des Sciences de Tours, Parc de Grandmont, 37200 Tours, France*

[b] *Laboratoire de Chimie Organique du Silicium et de l'Etain, UA 35 du CNRS, Université de Bordeaux I, 351, Cours de la Libération, 33405 Talence, France*

Alkenyl- and alkynyl-aluminium reagents react with diethoxymethyltributyltin to afford the corresponding α-ethoxyalkenyl- and α-ethoxyalkynyl-tin compounds in high yields; the but-3-ynyltin derivative has been modified to give new bis(tributyltin) precursors useful for selective organic synthesis.

α-Alkoxyorganotin reagents have important synthetic applications because of their ready transmetallation with butyllithium[1] and their ability to take part in transition metal-catalysed cross-coupling reactions.[2] We have already reported the use of α-alkoxymethyl- and α-ethoxybutenyl-tin compounds in the synthesis of aldehydes or enones *via* transmetallation,[3,4] while α-alkoxyallyltin compounds have been used in the functionalization of aryl halides, acyl halides, and aldehydes with remarkable chemo-, regio- and stereo-selectivities.[5—7] Thus, α-alkoxyorganotin compounds are of considerable interest in organic synthesis and although analogous compounds containing an acetal group are readily obtained, derivatives with simple alkoxy groups (*e.g.* ethoxy) have until now been less accessible.

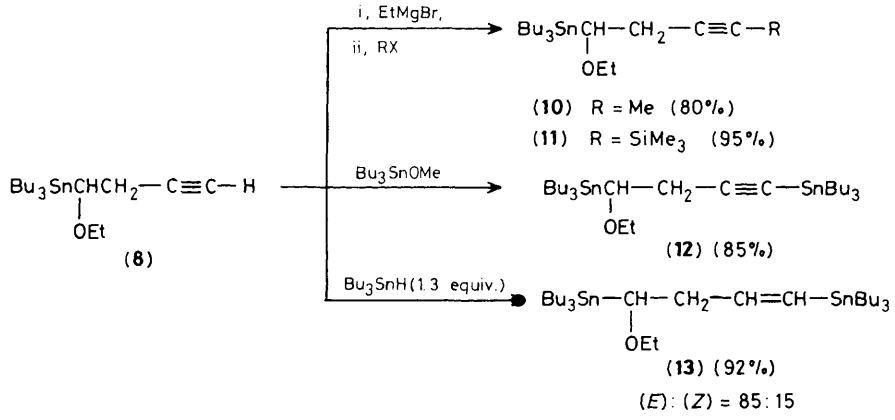


Scheme 1

Table 1. Preparation of α-ethoxyalkenyl- and α-ethoxyalkynyl-tin compounds.

RX or RH	R_nAlX_{3-n},[a] experimental conditions	Bu_3Sn–CH(R)–OEt	% Yield[b]
Me_2C=CHBr	Method A, tetrahydrofuran, 40 °C	(**2**) R = –CH=CMe_2	(70)
Ph–C≡C–H	Method A, EtMgBr, diethyl ether, 20 °C	(**3**) R = –C≡C–Ph	90
CH_2=CH–CH_2Br	Method B, diethyl ether, 35 °C	(**4**) R = –CH_2–CH=CH_2	95
CH_2=C(Me)–CH_2Br	Method B, diethyl ether, 35 °C	(**5**) R = –CH_2–C(Me)=CH_2	95
Me–CH=CH–CH_2Br	Method B, diethyl ether, 35 °C	(**6a,b**) R = –CH(Me)–CH=CH_2	95
Me_2C=CH–CH_2Br	Method A, diethyl ether, 25 °C	(**7**) R = –CMe_2–CH=CH_2	(75)
H–C≡C–CH_2Br	Method B, diethyl ether, 35 °C	(**8**) R = –CH_2–C≡C–H	(85)
H–C≡C–CH(Me)Br	Method B, diethyl ether, 35 °C	(**9a,b**) R = –CH(Me)–C≡C–H	(84)

[a] Method A: R_nAlX_{3-n} is obtained from an exchange between the Grignard reagent (obtained conventionally from RBr or RH) and $AlCl_3$. Method B: R_nAlX_{3-n} is obtained directly from organic halide and aluminium. [b] Yields in parentheses are isolated yields after distillation or liquid chromatography; the other values are conversion rates (R_nAlX_{3-n} is used in 20% excess).



Scheme 2

Our previous route to these reagents employed tributyl[chloro(ethoxy)methyl]tin as a key intermediate[4—6] but its propensity to decompose (with formation of tributyltin chloride) decreased the yields and introduced a contaminating organotin side product according to path a in Scheme 1. To avoid this drawback, we have treated diethoxymethyltributyltin (**1**) (readily accessible on a one molar scale[8]) with organoaluminium reagents (path b, Scheme 1) and concentrated on unsaturated derivatives, which afford interesting possibilities in organic synthesis. Using this organoaluminium route, the reaction occurs as a clean substitution of an ethoxy group as already described with organic acetals[9] but without transmetallation of the tin–carbon bond (see Table 1).†

The 3-methylbut-2-enyltin derivative (**2**) has been obtained as a pure distilled product in 70% yield while the crude prop-2-ynyl derivative (**3**) has been obtained uncontaminated with the allenic isomer. In addition the but-3-enyltin derivatives (**4**)—(**7**) have been obtained efficiently from prop- and but-2-enylaluminium reagents in high yields. In contrast with the synthesis involving Grignard reagents and tributyl[chloro(ethoxy)methyl]tin (for which coupling occurs without rearrangement), the substitution of (**1**) by but-2-enylaluminium reagents occurs with complete rearrangement leading to the branched products (**6**) and (**7**). It should be noted that the composition of the diastereoisomeric mixture (**6a**,**b**)‡ is substantially modified by experimental factors. For instance, when the reaction was performed in diethyl ether at 0 °C, the ratio of (**6a**) : (**6b**) is 95 : 5 while the same reaction performed in refluxing ether gave a 67 : 33 mixture. Emphasising the usefulness of butenyl type reagents, compound (**7**) provides access to the artemisyl skeleton, after transmetallation and reaction with methylallyl bromide or α-methylacrylaldehyde.

Furthermore, the but-3-ynyltin derivative (**8**) can be modified to afford other useful organotin precursors (Scheme 2).

The above organotin compounds are promising synthetic reagents because they are expected to allow a stepwise functionalization which should be amenable to control by varying the experimental conditions. Thus, this new route to unsaturated α-ethoxyorganotributyltin compounds provides new perspectives in the application of organostannanes in organic synthesis.

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† All α-ethoxyorganotin compounds described have been identified on the basis of physicochemical data and their structures firmly established by i.r., ^{1}H n.m.r. (200 MHz), and ^{119}Sn n.m.r. (33.54 MHz) data. ^{119}Sn N.m.r. data in p.p.m. (Me_4Sn, C_6D_6): (**1**), −57.8; (**2**), −33.9; (**4**), −38.4; (**5**), −35.1; (**6a**), (**6b**), −37.4 and −37.6; (**7**), −31.2; (**8**), −31.1; (**9a**), (**9b**), −34.0 and −34.9; (**10**), −33.0; (**11**), −30.8; (**12**), −31.3 and −71.2, $^5J_{Sn-Sn}$ 65.4 Hz; (*E*)-(**13**) −35.34 and −50.73, $^5J_{Sn-Sn}$ 11.7 Hz; (*Z*)-(**13**), −35.00 and −60.98, $^5J_{Sn-Sn}$ unobserved.

‡ (**6a**) is believed to be the *threo* isomer (*SS* + *RR*) and (**6b**) the *erythro* isomer (*RS* + *SR*).

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