Allylstannanes and vinylstannanes from stannylcupration of C–C multiple bonds. Recent advances and applications in organic synthesis

Asunción Barbero* and Francisco J. Pulido*

Received 27th July 2005
First published as an Advance Article on the web 13th September 2005
DOI: 10.1039/b506622k

The stannylcupration of allenes and alkynes has emerged as a powerful tool for the synthesis of allyl- and vinylorganostannanes. The regio- and stereoselectivity of this reaction depends upon the nature of the cuprate, the temperature and the structure of the allene or alkyne. The versatility and synthetic scope of the tin-synthons thus obtained is very wide. These intermediates have been employed as precursors in the key step of the stereoselective synthesis of many natural products, heterocycles or conjugated polyenes. This *tutorial review* shows a general survey of the recent advances in this area together with the contribution of our lab to this field.

1 Introduction

The demand for organotin compounds in organic chemistry has increased greatly in the last two decades, due to the large number of transformations that the Sn–C bond can undergo.[1] The development of new methodologies that allow the synthesis of these synthons has attracted the attention of the scientific community. One of the most interesting ways of forming a C–Sn bond is the stannylmetalation of an alkyne or allene. This methodology provides efficient procedures for introducing tin into organic molecules, giving raise to a wide range of allyl- and vinylstannanes of much potential. Stannylmetalation of multiple bonds can be divided into two categories: stoichiometric stannylcupration and catalytic stannylmetalation in the presence of a transition-metal. As the catalytic stannylmetalation of multiple bonds has been widely reported,[1,2] in this review we highlight some of the recent development in the area of the stoichiometric stannylcupration of alkynes and allenes.

Departamento de Química Orgánica, Facultad de Ciencias, c/Dr Mergelina s/n, 47011 Valladolid, Spain. E-mail: barbero@qo.uva.es; pulido@qo.uva.es; Fax: 34 83 423013; Tel: 34 83 423210

2 Stannylcupration of C–C multiple bonds

2.1 Stannylcupration of alkynes

The stannylcupration of triple bonds was first reported by Piers in 1980.[3] He studied the reaction of α,β-acetylenic esters with lower order stannylcuprates **1** and discovered that the reaction can be experimentally controlled so as to produce stereoselectively either the *Z* or the *E*-β-stannyl-α,β-unsaturated esters. Thus, when the reaction is carried out under kinetic conditions (−100 °C) the *E* isomer is obtained as the major product (97 : 3). However, under thermodynamically controlled conditions (−48 °C) the *Z* isomer is the major one (98 : 2). Apparently, at low temperatures the organocopper species **1** adds kinetically to the carbon–carbon triple bond in a *cis* fashion to provide a vinylcopper intermediate **2**, which may

Asunción Barbero

Asunción Barbero was born in Burgos, Spain. She studied chemistry at the University of Valladolid and received, in 1992, a PhD from the same university under Francisco J. Pulido. During 1993–1995 she held Postdoctoral Fellowships at the University of Cambridge working with Prof. Ian Fleming. She came back to Valladolid as Assistant Professor in 1995 and was promoted to Associate Professor in 2001. Her current interests include metalocupration of multiple bonds and the synthesis of natural products.

Francisco J. Pulido

Francisco J. Pulido obtained his first degree in chemistry at the University of Valladolid, where also he obtained his doctoral degree in 1979 under the supervision of Professor Angel Alberola. He then was awarded with a Fulbright postdoctoral fellowship, working with Professor Gilbert Stork at Columbia University during 1982–83. Later, in 1985 he joined Ian Fleming's research group at Cambridge University supported by a NATO grant. Soon after, he was promoted to Associate Professor at the UVA where he began his independent scientific research. His interests are the development of new synthetic methodologies in organometallic chemistry and the application of organosilicon and organotin compounds to the synthesis of natural products.

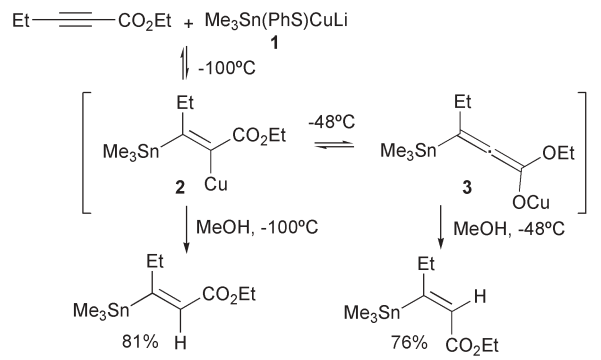
rearrange to the corresponding allenoate **3**. Protonation of the kinetic intermediate provides the *E*-isomer, while protonation of the allenoate affords the *Z*-isomer (Scheme 1). The stereochemistry of this type of reactions varies with a number of factors such as the nature of the reagent, the solvent, the reaction conditions (time and temperature) and the substituents of the acetylenic ester.[4,5]

The stannylcupration of α,β-acetylenic amides with lower order cuprates shows a similar reactivity pattern.[6] Thus, under kinetic conditions (−78 °C, THF) the product of *cis*-addition is formed (the *E*-β-stannyl-α,β-unsaturated amide) whereas addition of a less polar solvent (hexane or ether) to the reaction medium, along with a temperature increase (0 °C) leads to the stereoselective formation, after protonation, of the *Z*-isomer (Scheme 2).

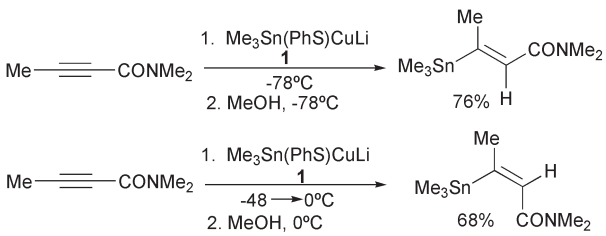
The use of a higher order cuprate **4** in the stannylcupration of acetylenic acids, at −78 °C, leads to the *E*-β-stannyl-α,β-unsaturated acid,[7] resulting from a *cis*-addition (Scheme 3).

The stannylcupration of acetylenic ketones has also been screened.[8] In contrast to the corresponding alkynoates, the reaction of either a lower order or a higher order stannylcuprate with alkynones leads exclusively to the corresponding *Z*-β-stannyl-α,β-unsaturated ketones under all reaction conditions tested. Initial *cis*-addition followed by fast enolate isomerization might account for the selectivity observed (Scheme 4).

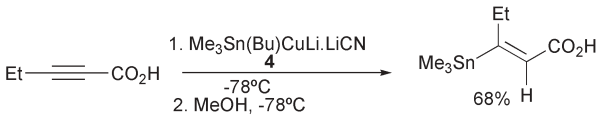
Stannylcopper reagents also add to simple non activated acetylenes. The process has unequivocally established to be reversible both by spectroscopic and chemical evidence.[9] The reaction proceeds *via* reversible addition to yield equilibrium mixtures of the alkyne and the copper-adduct which may be driven to the product by the presence of a protic solvent (such as MeOH). The proton source methanolyses the vinylcopper intermediate but not the stannylcuprate. Thus, reaction of a



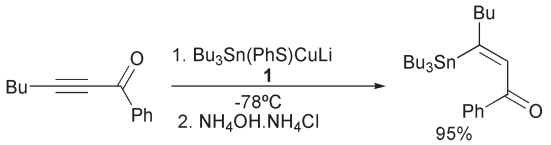
Scheme 1



Scheme 2



Scheme 3



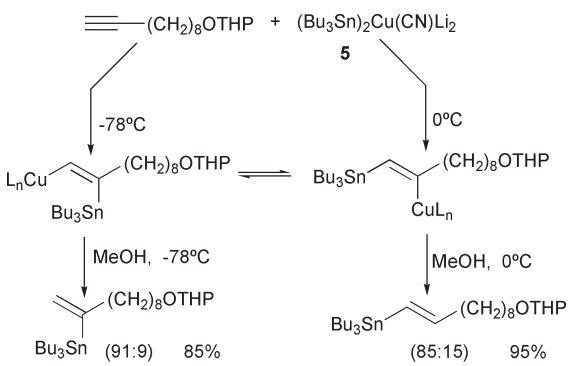
Scheme 4

terminal alkyne with the higher order cuprate **5** under kinetic control (−78 °C) leads to a 91 : 9 mixture, in which the major product is the one that has the tin group linked to the internal carbon of the acetylenic moiety. However, the same reaction under thermodynamic conditions (0 °C) leads this time to a 85 : 15 mixture, where the major product, resulting from a *syn*-addition process, bears the tin group connected to the terminal carbon of the acetylenic unit[9] (Scheme 5).

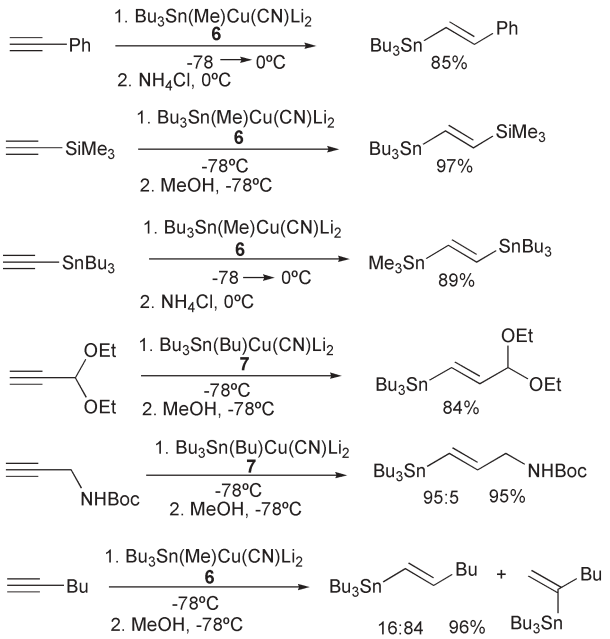
The regioselectivity of the addition of stannylcuprates to alkynes has been extensively studied by ourselves[10] and others.[11] The reaction is not only dependent on the temperature, but also on the structure of the alkyne and the nature of the stannylcopper species. Thus, the reaction of the mixed higher order cuprate **6** or **7** with several monosubstituted alkynes leads regioselectively to the product of *syn* addition where the tin moiety is bonded to the less hindered acetylenic carbon. The only example which is just moderately regioselective is the reaction with alkylacetylenes, where a mixture of the two possible regioisomers is obtained (Scheme 6).

Dienylstannanes are interesting building blocks in the construction of some unsaturated fragments of several natural products. Their stereoselective synthesis has been achieved through stannylcupration of conjugated enynes.[12,13] The use of lower order cuprates is not synthetically useful, but higher order cuprates provided very good yields of the 1-stannyldienyl derivatives with high stereoselectivity (97 : 3) (Scheme 7).

For a long time, one of the major limitations of these powerful reactions has been the difficulty in persuading the vinyl-copper intermediate to react with anything more interesting than a proton.[14] This is especially true, when a lower



Scheme 5



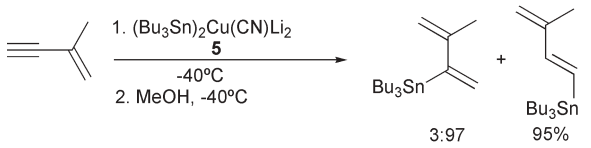
Scheme 6

order cuprate is used. The problem appears to be the reversibility of the stannylcupration step and the fact that the stannylcopper reagent is more reactive than the vinylcopper intermediate towards most of the electrophiles. The use of a higher order cuprate, instead of the lower order cuprate used in the first attempts, has allowed the capture of the vinylcuprate intermediate with a great variety of electrophiles such as acetyl chloride, alkyl halides, halogens, epoxides, α,β-unsaturated ketones and esters, *etc*.[10,15] The reaction goes well for acetylene itself, for monosubstituted acetylenes and even for internal alkynes, though yields are lower in this last case (Scheme 8).

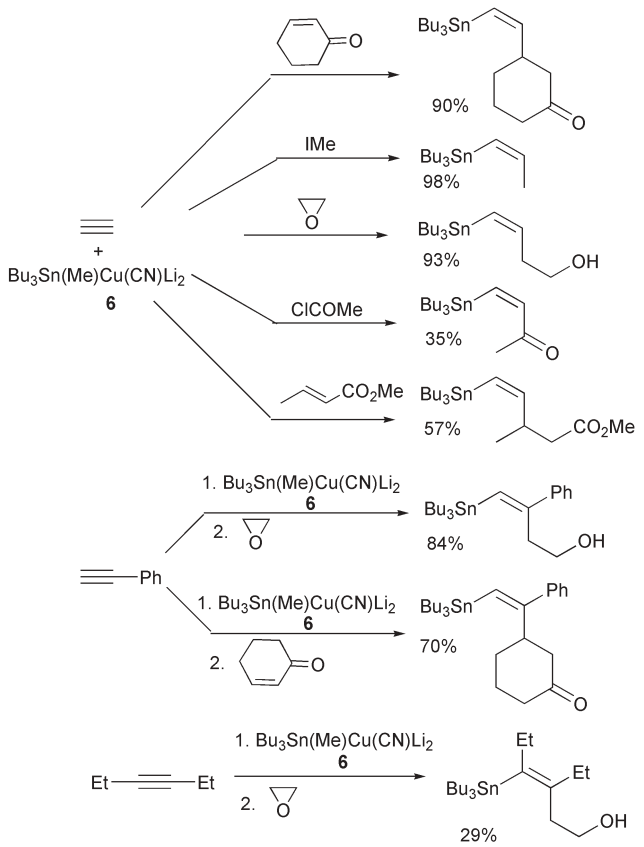
This methodology has been succesfully applied to the preparation of synthetic equivalents of ethene dianions and trianions such as *cis*-distannylethylenes, *cis*- and *trans*-silylstannylethylenes[10,16] and silyldistannylethylenes[16] (Scheme 9).

2.2 Stannylcupration of allenes

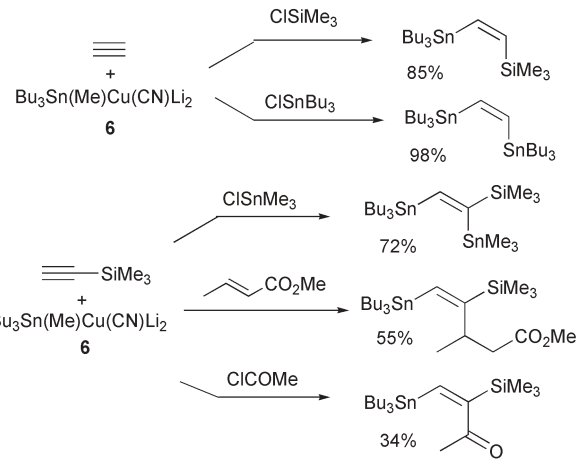
Other metallo-metallations of multiple bonds such as the stannylcupration of allenes have also been reported.[17] The regiochemistry of the reaction depends upon the temperature, the nature of the stannylcuprate reagent and the substitution of the allene. The two modes by which stannylcupration of an allene can occur are the addition of tin to the central sp-hybridized carbon, which leads to the formation of a vinylstannane, and the addition to the terminal sp^2-hybridized carbon, which gives an allylstannane. Substituted allenes react



Scheme 7

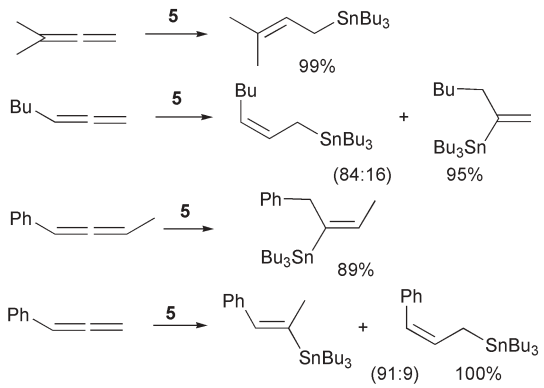


Scheme 8



Scheme 9

with bis(tributylstannyl)cuprate **5** to give either vinyl- or allylstannanes depending upon the structure of the allene. Thus, the stannylcupration of alkylallenes from −78 to 0 °C gives allylstannanes as the major products. However under the same conditions the reaction with phenylallenes leads to the regioisomeric vinylstannanes. The stereochemistry of the products is reasonable if we assume that the stannyl reagent attacks from the less hindered face of the allene. Moreover, the formation of allylstannanes is regioselective in the sense that the stannyl group is placed at the less substituted end of the allene (Scheme 10).[17]

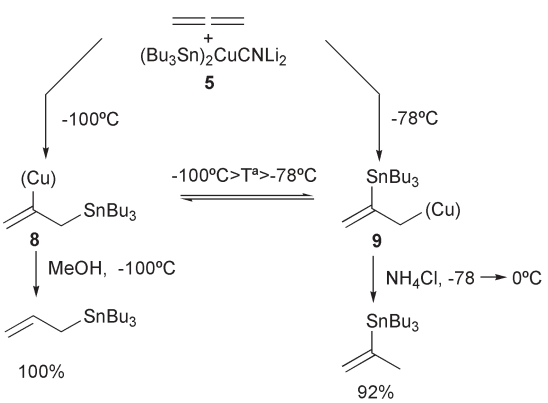


Scheme 10

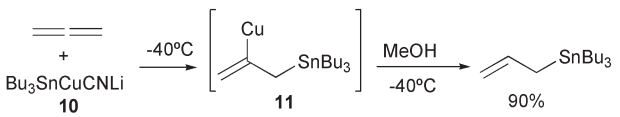
The reaction of allene itself with the higher order stannyl reagent **5** depends strongly upon the temperature. Thus, when the reaction is carried out at −100 °C allyltributylstannane is the only product obtained. However, if the experiment is repeated at −78 °C, either quenching at this temperature or warming the reaction from −78 °C to 0 °C before quenching the intermediate at 0 °C, the only compound present in the reaction mixture is 2-tributylstannyl-1-propene. Therefore, the stannylcupration of allene seems to be a reversible process in which the allylstannane-vinylcopper intermediate **8** is the kinetic product and the vinylstannane-allylcopper intermediate **9** is the thermodynamic product (Scheme 11).[17] Fast interconversion between species **8** and **9** takes place at the range temperature of −100 °C to −78 °C.

The regioselectivity of the reaction is also dependent upon the nature of the stannylcopper reagent. Thus, the stannylcupration of allene itself at −40 °C using the lower order cuprate **10** gives in high yield the allylstannane **11** instead of the vinylstannane analogous to **9** obtained with the higher order cuprate **5**.[18] By this way, the overall regiochemistry of the stannylcupration of 1,2-propadiene is easily controlled in either sense to give vinylstannanes or allylstannanes (Scheme 12).

Interestingly, the intermediate cuprates **8**, **9** and **11** can be captured for various electrophiles. Thus, the cuprate **9** reacts cleanly with a wide variety of electrophiles, such as alkyl halides, carbonyl compounds, halogens, epoxides, acid chlorides, *etc.*, giving the corresponding vinylstannanes. It should



Scheme 11



Scheme 12

be noted that α,β-unsaturated ketones give selectively the product of carbonyl addition in their reaction with the allylcuprate intermediate **9** (Scheme 13).[17]

However, there is a very limited range of electrophiles (bromine and acetyl chloride) which are reactive enough at −100 °C toward intermediate **8**. Fortunately, intermediate **11** resulting from addition of the lower order cuprate **10** to allene, reacts with different electrophiles at −40 °C, thus opening a route to the synthesis of functionalized allylstannanes (Scheme 14). In contrast with **9** the vinylcopper intermediate **11** reacts with α,β-unsaturated oxocompounds giving the products of conjugate addition.[18]

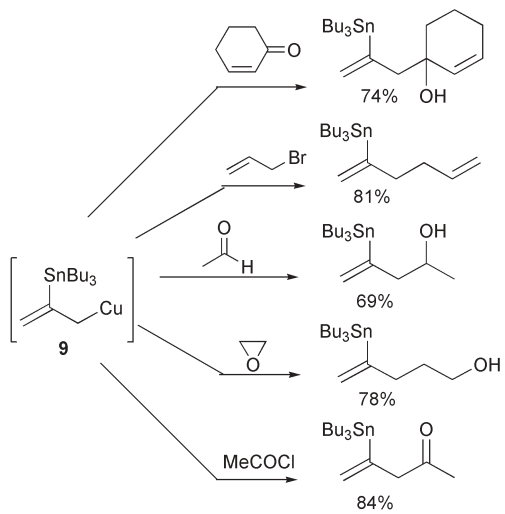
The intermediate cuprates obtained in the stannylcupration of substituted allenes can also be captured with several electrophiles[17] (Scheme 15).

Recent observations carried out in our lab show that unactivated alkenes as well as 1,3-dienes are not reactive enough toward tincuprates.

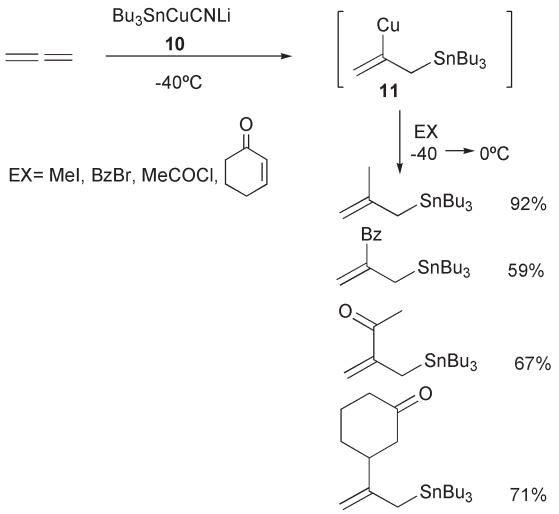
3 Synthetic applications

3.1 Synthesis of natural products or related compounds

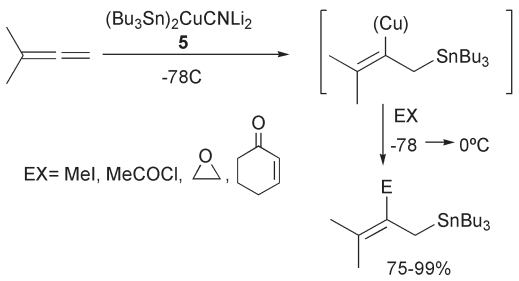
The search and development of efficient and highly selective methods for the synthesis of complex molecules of both natural and unnatural origin continues to be a challenge in organic synthesis and much effort has been directed towards this goal. In this sense, the stereospecific synthesis of conjugated dienes is of considerable importance since a great variety of aliphatic natural products contain the 1,3-diene unit or even higher degrees of conjugation. Some of the recent strategies proposed for the construction of unsaturated fragments are based on the preparation of vinyltin derivatives,



Scheme 13



Scheme 14

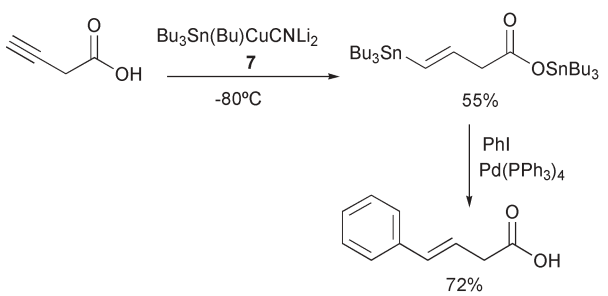


Scheme 15

followed by the palladium-catalyzed cross-coupling with aryl or vinyl halides and triflates. Although the so called Stille reaction,[19] has been extensively explored and huge advances have been made in the stereocontrolled synthesis of polyene systems, the discovery of new naturally occurring products with polyunsaturated moieties clearly shows that research in this area is far from being at the end.

An example of this chemistry is reported by Duchêne, who uses the stannylcupration of homopropargylic acids to control the introduction of the stannyl group in the terminal acetylenic carbon through a *cis*-addition process. Finally, the vinylstannanes thus formed are subjected to cross coupling with aryl halides, under catalysis with palladium complexes, to cleanly afford the homocinnamyl skeleton (Scheme 16).[20]

Similarly Reginato[21] studied the addition of higher order stannylcuprates to naturally occurring amino-acids in order to

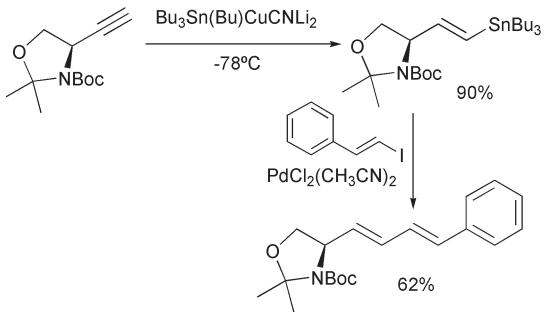


Scheme 16

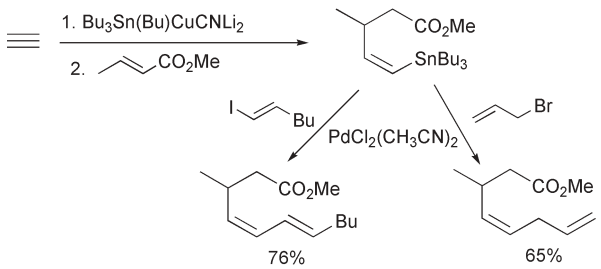
obtain γ-stannylated (*E*)-allylic amines. The corresponding γ-substituted (*E*)-allylic amines, obtained through Stille coupling, are interesting compounds both for their therapeutic properties and as useful intermediates in the synthesis of conformationally restricted peptide isosters (Scheme 17).

We[10] and others[22] have used this methodology to obtain 1,3- and 1,4-dienes. These synthons are synthetically useful building blocks which can be employed for the design and synthesis of biologically active compounds (Scheme 18).

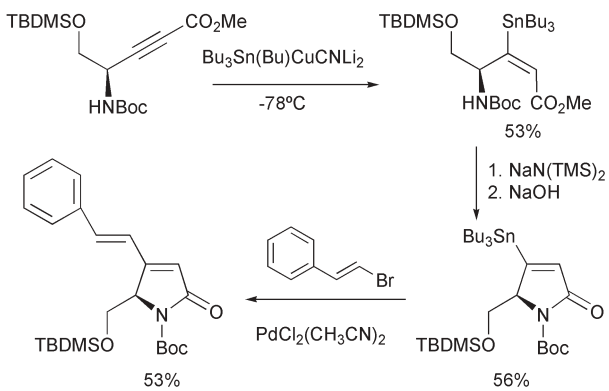
In the stannylcupration of chiral γ-heterosubstituted acetylenic esters, the presence of MeOH as well as the use of higher order stannylcuprates are necessary to obtain with high stereoselectivity the *E*-β-stannyl alkenoates of *cis*-addition. These compounds[23] have been used as intermediates in the synthesis of five membered N- and O-heterocycles, such as 4-substituted pyrrolinones and furanones, *via* ring closure and Stille cross-coupling reactions (Scheme 19).



Scheme 17



Scheme 18



Scheme 19

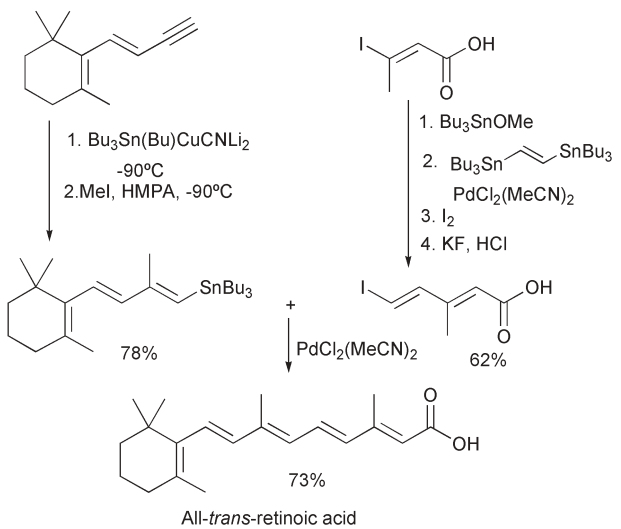
Retinoids are metabolites that modulate proliferation and differentiation of a variety of cell types by activation of their intracellular retinoid receptors. Parrain *et al.* have described the stereoselective synthesis of these derivatives[24] based on a convergent synthesis that involves a tin-cupration step of an enyne and two successive Stille reactions (Scheme 20).

Gambierol is a marine polycyclic ether that exhibits potent toxicity against mice. Recently it has been described the first total synthesis of gambierol.[25] The stereoselective construction of the highly sensitive triene side chain is again possible due to the strategic combination of the tin-cupration of acetylenes and the palladium mediated cross-coupling of vinylstannanes as outlined in Scheme 21.

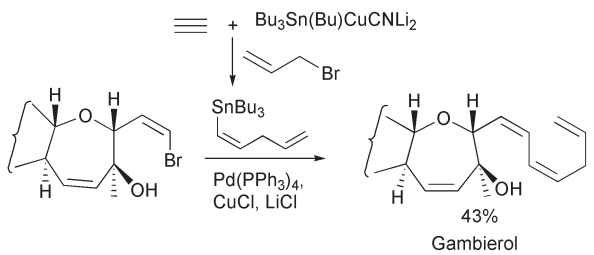
The total synthesis of furocaulerpin has been accomplished[26] in good yield with a total control of the *E* configuration of the central double bond by stannylcupration and iododestannylation reactions and subsequent construction of the dienyne moiety *via* cross-coupling with an alkynylstannane (Scheme 22).

The required building blocks for the total synthesis of Lankacidin C have been synthesized *via* stannylcupration of an internal alkyne, iododestannylation and Stille coupling of the so formed vinyl iodide with a vinylstannane obtained by stannylcupration of propargyl alcohol[27] (Scheme 23). It should be noted that lower order cuprates are used in this work.

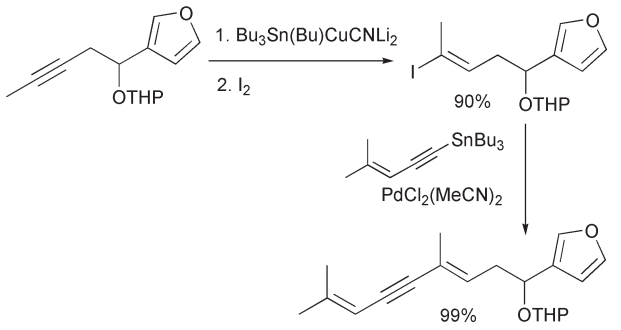
In another example, White uses the stannylcupration-methylation of a terminal alkyne as the stereoselective pathway to generate an (*E*)-iodoalkene which after coupling with a



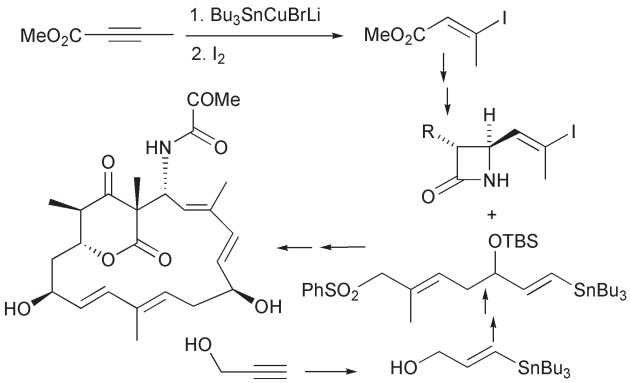
Scheme 20



Scheme 21



Scheme 22

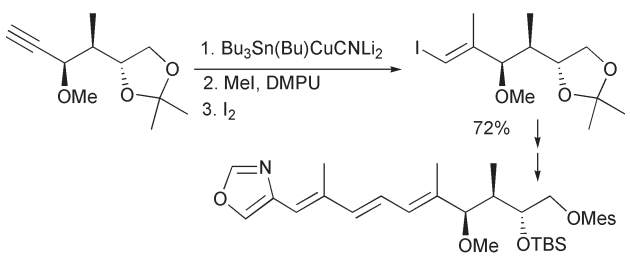


Scheme 23

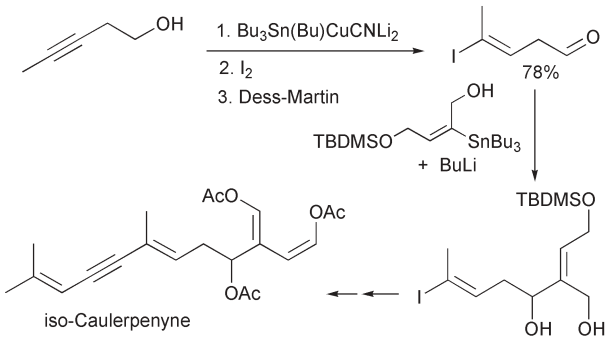
dienylstannane affords the conjugate (*E*,*E*,*E*)-triene unit of the antitumor agent rhizoxin[28] (Scheme 24).

As it has been shown, vinylstannanes are highly versatile synthetic tools in Organic Chemistry. For instance, the presence of a vinyltin moiety in a molecular structure allows further structural transformations which can be performed not only *via* a Stille cross-coupling, but also through an iododestannylation reaction or by transmetallation to a vinyllithium species and subsequent capture with electrophiles. Thus, total synthesis of Taxifolial A and iso-Caulerpenyne has been achieved[29] by addition of a vinyllithium intermediate (obtained from 2-butyn-1,4-diol by tin-cupration followed by tin–lithium exchange) to the oxovinyl iodide prepared by stannylcupration of 3-pentyn-1-ol and subsequent iododestannylation reaction (Scheme 25).

In the approach to the synthesis of many other natural products, the stannylcupration of alkynes followed by tin–metal exchange has been frequently used as the key step.[30,31] For instance, in the convergent synthesis designed for the



Scheme 24



Scheme 25

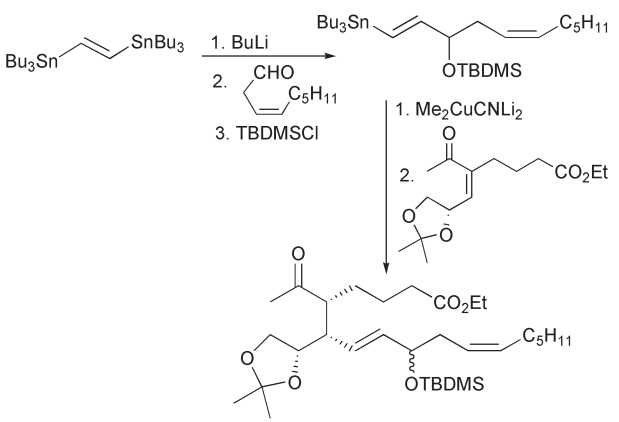
preparation of Iso(4)-levugladin E_2,[32] two sequential transmetallation-addition steps, starting from 1,2-bis(tributylstannyl)-ethene, are the key of the synthetic strategy (Scheme 26).

We have reported a new [2 + 2] annulation strategy for the synthesis of cyclobutenes[33] which involves stannylcupration of acetylenes or allenes, tin–lithium exchange and intramolecular nucleophilic displacement (Scheme 27). The method is useful for the synthesis of either 1- and 3-substituted cyclobutenes or methylenecyclobutanes.

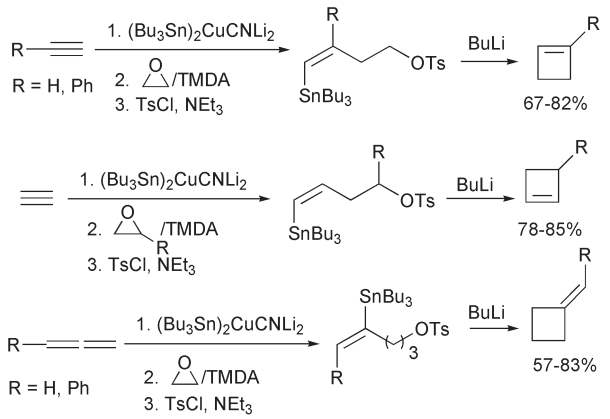
3.2 Remote stereocontrol promoted by the stannyl group

Over the past two decades one of the major efforts in the synthesis of natural products and related synthons has been the controlled construction of systems bearing multiple stereocenters. In this sense, organotin compounds have proven to be powerful intermediates in asymmetric synthesis.[34] We recently have reported that the addition of organometallic reagents to carbonyl groups can be sterically controlled with a high degree of efficiency, by the presence of a remote stannyl group.[35] The (*Z*)-β-stannylvinyl ketones used for this study have been obtained by stannylcupration of acetylene and capture of the intermediate cuprate with cyclic enones. The behavior of these cyclic substrates toward typical organolithium reagents shows that addition takes place diastereoselectively, *syn* to the vinyltin moiety (Scheme 28).

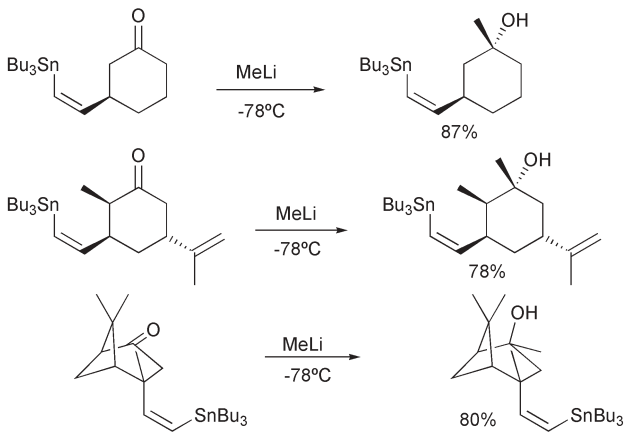
Chemical evidence for the participation of the tin group in the stereochemical course of the reaction can be obtained from the same reaction with a destannylated substrate which leads to an equimolar mixture of the two possible diastereoisomers.



Scheme 26



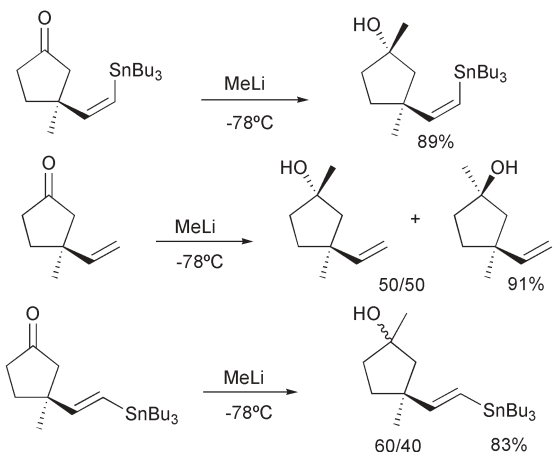
Scheme 27



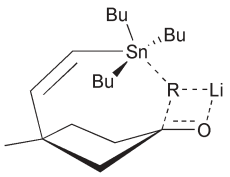
Scheme 28

Moreover the *cis* geometry of the alkene moiety plays a very important role in the final outcome: effectively the corresponding (*E*) isomer shows no diastereoselectivity in its reaction with organolithiums (Scheme 29).[35]

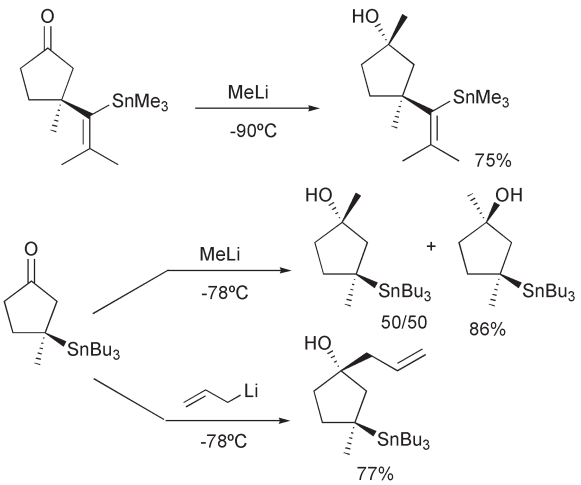
The mechanism proposed points to some kind of chelating effect with the tin and carbonyl groups anchoring the organolithium reagent between them (Scheme 30).[35] Theoretical data and deuterium labeling experiments support the hypothesis of an intramolecular delivery pathway.



Scheme 29



Scheme 30



Scheme 31

The influence of the distance between the tin and the carbonyl group on the stereocontrol of the process has also been studied. Thus, for a CO/Sn separation of 4 bonds, medium to high levels of diasteroselection are found in the addition process. However, if the CO/Sn distance is of 3 bonds the reaction leads to 1 : 1 mixtures of steroisomers. The total loss of selectivity found in this case can be associated with the long spatial distance between the tin center and the carbonyl group. It is noteworthy that allyllithiums compensate that distance leading to highly stereoselective reactions, which supports the anchoring effect proposed (Scheme 31).[35]

4 Conclusion

This report deals with the last advances in the synthesis of functionalized vinylstannanes and allylstannanes by way of stannylcupration of multiple bonds (alkenes and acetylenes) and capture of the intermediate cuprate with electrophiles. The organostannanes thus obtained have been used in multiple synthetic applications such as the stereospecific synthesis of conjugated dienes, enynes and polyenes, the synthesis of N- and O-heterocycles (pyrrolinones and furanones), the synthesis of several natural products (retinoids, Gambieral, Furocaulerpin, Lankacidin C, Taxifolial A, *etc.*) and the controlled introduction of new stereocenters through the presence of a remote tin group.

References

1 M. Pereyre, J. P. Quintard and A. Rahm, *Tin in Organic Synthesis*; Butterworth: London, 1987; A. G. Davies, *Organotin Chemistry*; VCH: Weinheim, 2004.
2 S. Casson and P. J. Kocienski, in *Organometallics Reagents in Organic Synthesis*; Academic Press: London, 1994; E. Negishi, in *Handbook of Organopalladium Chemistry for Organic Synthesis*; Wiley: Weinheim, 2004.
3 E. Piers and H. E. Morton, *J. Org. Chem.*, 1980, **45**, 4264.
4 E. Piers, J. M. Chong and H. E. Morton, *Tetrahedron*, 1989, **45**, 363; E. Piers, T. Wong and K. A. Ellis, *Can. J. Chem.*, 1992, **70**, 2058.
5 E. Piers and R. D. Tillyer, *J. Org. Chem.*, 1988, **53**, 5366.
6 E. Piers, J. M. Chong and B. A. Keay, *Tetrahedron Lett.*, 1985, **26**, 6265.
7 J. Thibonnet, V. Launay, M. Abarbri, A. Duchêne and J.-L. Parrain, *Tetrahedron Lett.*, 1998, **39**, 4277.
8 T. E. Nielsen, M. A. Cubillo de Dios and D. Tanner, *J. Org. Chem.*, 2002, **67**, 7309.
9 J. A. Cabezas and A. C. Oehlschlager, *Synthesis*, 1994, 432.
10 A. Barbero, P. Cuadrado, I. Fleming, A. M. González, F. J. Pulido and R. Rubio, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1657.
11 L. Capella, A. Degl'Innocenti, A. Mordini, G. Reginato, A. Ricci and G. Seconi, *Synthesis*, 1991, 1201; A. Casarini, B. Jousseaume, D. Lazzari, E. Porciatti, G. Reginato, A. Ricci and G. Seconi, *Synlett*, 1992, 981.
12 J.-F. Betzer and A. Pancrazi, *Synthesis*, 1999, 629 and references cited therein.
13 F. Suzenet, E. Blart and J.-P. Quintard, *Synlett*, 1998, 879.
14 H. Westmijze, K. Ruitenberg, J. Meijer and P. Vermeer, *Tetrahedron Lett.*, 1982, **23**, 2797.
15 I. Marek, A. Alexakis and J.-F. Normant, *Tetrahedron Lett.*, 1991, **32**, 6337; J. P. Marino, M. V. M. Emonds, P. J. Stengel, A. R. M. Oliveira, F. Simonelli and J. T. B. Ferreira, *Tetrahedron Lett.*, 1992, **33**, 49.
16 P. Cuadrado, A. M. González-Nogal and A. Sánchez, *J. Org. Chem.*, 2001, **66**, 1961.
17 A. Barbero, P. Cuadrado, I. Fleming, A. M. González and F. J. Pulido, *J. Chem. Soc., Perkin Trans. 1*, 1992, 327.
18 A. Barbero and F. J. Pulido, *Tetrahedron Lett.*, 2004, **45**, 3765.
19 J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 508.
20 J. Thibonnet, M. Abarbri, J.-L. Parrain and A. Duchêne, *Tetrahedron*, 2003, **59**, 4433.
21 G. Reginato, A. Mordini and M. Caracciolo, *J. Org. Chem.*, 1997, **62**, 6187.
22 G. Reginato, A. Mordini, M. Valacchi and R. Piccardi, *Tetrahedron: Asymmetry*, 2002, **13**, 595.
23 G. Reginato, A. Mordini, M. Verrucci, A. Degl'Innocenti and A. Capperucci, *Tetrahedron: Asymmetry*, 2000, **11**, 3759; G. Reginato, A. Mordini, A. Degl'Innocenti, S. Manganiello, A. Capperucci and G. Poli, *Tetrahedron*, 1998, **54**, 10227.
24 J. Thibonnet, M. Abarbri, A. Duchêne and J.-L. Parrain, *Synlett*, 1999, 141.
25 H. Fuwa, M. Sasaki, M. Satake and K. Tachibana, *Org. Lett.*, 2002, **4**, 2981.
26 L. Commeiras and J.-L. Parían, *Tetrahedron: Asymmetry*, 2004, **15**, 509.
27 C. T. Brain, A. Chen, A. Nelson, N. Tanikkul and E. J. Thomas, *Tetrahedron Lett.*, 2001, **42**, 1247.
28 J. D. White, M. A. Holoboski and N. J. Green, *Tetrahedron Lett.*, 1997, **38**, 7333.
29 L. Commeiras, M. Santelli and J.-L. Parrain, *Org. Lett.*, 2001, **3**, 1713.
30 J.-F. Betzer, J.-Y. Lallemand and A. Pancrazi, *Synthesis*, 1998, 522.
31 F. Delaloge, J. Prunet, A. Pancrazi and J.-Y. Lallemand, *Tetrahedron Lett.*, 1997, **38**, 273.
32 G. Subbanagounder, R. G. Salomon, K. K. Murthi, C. Brame and L. J. Roberts, *J. Org. Chem.*, 1997, **62**, 7658.
33 A. Barbero, P. Cuadrado, C. García, J. A. Rincón and F. J. Pulido, *J. Org. Chem.*, 1998, **63**, 7531.
34 J. A. Marshall, *Chem. Rev.*, 1996, **96**, 31.
35 A. Barbero, F. J. Pulido and J. A. Rincón, *J. Am. Chem. Soc.*, 2003, **125**, 12049; A. Barbero, F. J. Pulido, J. A. Rincón, P. Cuadrado, D. Galisteo and H. Martínez-García, *Angew. Chem. Int. Ed.*, 2001, **40**, 2101.