

Preparation of 3,3-bis(Tributylstannyl)propenes, Potential New 1,3-Allyl Dianions

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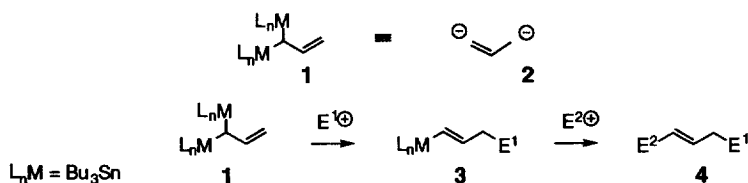
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Abstract : (*E*)-1-(*tert*-Butyldimethyl)silyloxy-3,3-bis(tributylstannyl)propene **11** as well as 1-*N,N*-diisopropylcarbamoyloxy-3,3-bis(tributylstannyl)propene **10** have been prepared upon addition of $\text{Bu}_3\text{Sn}(\text{Bu})\text{Cu}(\text{CN})\text{Li}_2$ **8** to diverse γ -heterosubstituted acrolein precursors, followed by addition of excess HMPA and of the required electrophile. A *E/Z* ratio of 95:5 was reached in the case of **11**. The reaction may occur through an addition-elimination-addition sequence where the stannylated acrolein **B** is thought to be a common intermediate. The best results were obtained upon single conjugate addition of **8** to (*E*)-3-(tributylstannyl)-2-propenal **12** (78%). A two-pot synthesis of the title compound was developed from the inexpensive malonaldehyde bis(dimethyl)acetal **14**. © 1997 Elsevier Science Ltd.

The use of geminal dimetallic species as versatile building blocks for the synthesis of complex molecules is becoming more and more popular, as illustrated by a recent review.¹ Strategies involving such species are particularly efficient since they allow several reactions in a single step as well as flexible multi-step sequences of great synthetic significance in terms of C-C bond formation with high chemo-, regio- and/or stereoselectivities.

Several 1,1-distannyl-1-alkenes (vinylic *gem*-distannanes) have been prepared and their chemistry has been explored.² On another hand, 1,1-hetero organometallic 1-alkenes or 2-alkenes where one tin atom is involved have also received some attention³ and Sn-Si hybrids were recently shown to be promising synthetic intermediates due to their high intrinsic chemo selectivity.⁴ C_3 alkyl units bearing 1,1-distannyl substituents are also known. Since the pioneering work of Leusink who first unambiguously identified such adducts,⁵ only few reports dealt with their preparation. Since 1992, different C_3 1,1-bis(tributylstannyl)alkyl derivatives have been described⁶ and some synthetic useful examples of the chemistry of these highly functionalised C_3 building blocks have just been reported.⁷ However, among the different bimetallic species investigated so far, the 1,1-distannyl-2-propenyl derivatives such as **1** (allyl *gem*-distannanes) have received little attention, perhaps due to their difficulty of preparation or their anticipated instability. To our knowledge, such 1,1-distannyl-2-alkenes have been prepared only recently by two different routes, *via* 1,3-bis(phenylseleno)propene intermediates⁸ or *via* Eschenmoser-Claisen rearrangement of a 1,1-distannyl-3-hydroxy-1-alkene.⁹

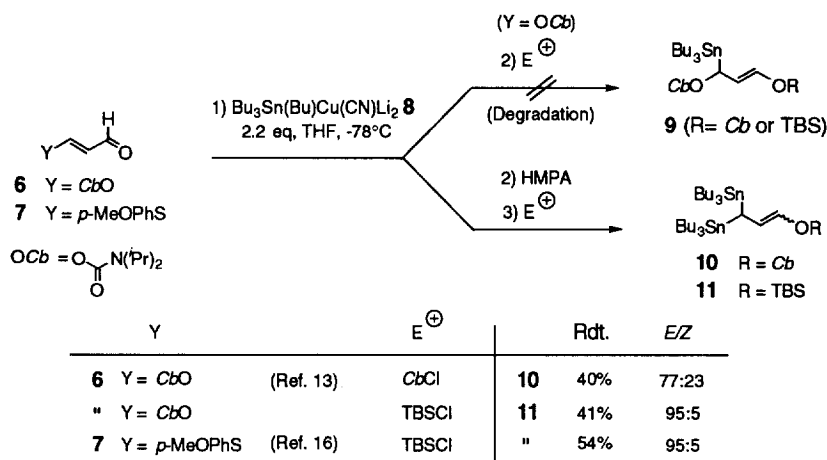
3,3-Bis(tributylstannyl)propenes such as **1** may be particularly interesting building blocks since they represent potential 1,3-allylic dianions of type **2** (Scheme 1).



Scheme 1

They may undergo, in a first set of reactions, homoaldol or allylation type reactions to give the corresponding vinylstannanes **3**.¹⁰ In a second set of reactions, these vinylstannanes could be suitable precursors of **4**, both through direct nucleophilic reactions after transmetalation¹¹ or *via* the widely used Pd(0)-catalysed Stille cross-coupling reactions.¹² We report here our recent results concerning the preparation of the title compounds which could also be seen as the enol ethers of 3,3-bis(tributylstannyl)propionaldehyde.

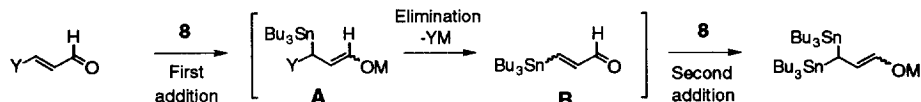
Along with our current search for new versatile allylic synthons which could be conveniently elongated at both ends, the conjugate addition of stannyl nucleophiles onto 3-(*N,N*-diisopropylcarbamoyloxy)acrolein **6** was studied.¹³ When aldehyde **6** was treated with the mixed higher order cuprate $\text{Bu}_3\text{Sn}(\text{Bu})\text{Cu}(\text{CN})\text{Li}_2$ **8**¹⁴ (2.2 eq), then quenched with either carbamoyl chloride (3 eq) or *tert*-butyldimethylsilyl chloride (3 eq), no trace of adducts **9** was detected and the starting material was totally degraded (Scheme 2). When an excess of HMPA (ca. 10 eq) was added before quenching the reaction mixture, a single new product was obtained in each case. After purification, the 3-*gem*-distannylated enol derivatives **10** (R = *Ocb*) and **11** (R = TBS) were isolated in 40% and 41% yield in a 77:23 and 95:5 *E/Z* isomers ratio respectively.¹⁵ No trace of the mono-addition products **9** was detected and the only other isolated compounds were stannyl by-products.



Scheme 2

To our knowledge no report deals with such type of double stannylation reaction. Interestingly, the distannanes **10** and particularly **11** are sufficiently stable to be purified by standard silica gel flash chromatography and can be stored for months in a freezer without particular care. In addition to the above assays, the sulfide derivative **7** was experimented as electrophile.¹⁶ Here again, no three-carbon adduct other than the expected *gem*-distannane **11** was isolated after quenching the reaction mixture with *tert*-butyldimethylsilyl chloride.

From a mechanistic point of view, it was reasonable to assume an initial conjugate addition-elimination sequence leading to the mono-stannylated vinylstannane **B** *via* the intermediate **A** (Scheme 3).

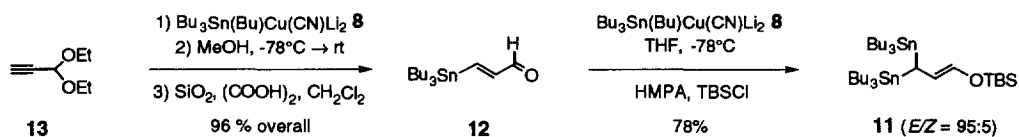


Scheme 3

The stannane **B** could be in turn subjected to a second conjugate addition of cuprate **8** to deliver, after quenching with the appropriate electrophile, the depicted *gem*-distannylated adducts. Although HMPA is known

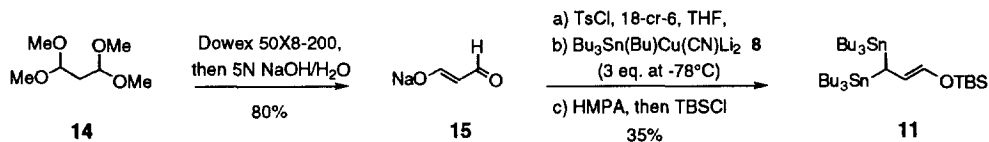
to accelerate *O*-silylation of enolates after conjugate addition of organocuprates to various α,β -unsaturated carbonyl electrophiles in presence of silylating agents,¹⁷ its exact role in the addition-elimination-addition sequence developed here deserves more studies. Recent findings from Oehlschlager *et al* on organocyanocuprate structure suggest a dissociation of initial mixed higher order heterocyanocuprates into Gilman type cuprates in presence of HMPA.¹⁸

In order to test the above postulated addition-elimination-addition sequence leading to **11**, it was decided to submit the known (*E*)-3-(tributylstannyl)-2-propenal **12** to the HMPA promoted cuprate reaction (Scheme 4). This aldehyde was efficiently prepared according to a known procedure starting from acetylenic acetal **13**¹⁹ and was subsequently subjected to the addition of $\text{Bu}_3\text{Sn}(\text{Bu})\text{Cu}(\text{CN})\text{Li}_2$ **8** in presence of HMPA. After quenching with TBSCl, the *gem*-distannane **11** was isolated by chromatography as a single product in 78% yield. This efficient synthetic sequence has been conducted on a 20g scale.



Scheme 4

The above route starting from aldehyde **12** offers a convenient access to the *gem*-distannane **11** although it required the rather expensive 3,3-diethoxypropyne **13** as starting material. Looking for an alternative route to **11** which could take advantage of the preceding addition-elimination sequence, we next turned to other easily available starting materials and commercial malonaldehyde bis(dimethyl)acetal **14** quickly emerged as a promising candidate (Scheme 5). Treatment of **14** with aqueous Dowex 50X8-200 followed, after filtration, by addition of a 5M NaOH aqueous solution up to pH 8 gave, after drying under vacuum and recrystallisation from H_2O /acetone, the expected sodium malonaldehyde **15** in 80% yield.²⁰ In a one-pot procedure, the latter sodium salt was transformed into the expected distannylated silyl enol ether **11**: *in-situ* conversion of **15** into the corresponding tosylate according to published procedure,²¹ followed, after cooling to -78°C , by sequential direct addition of the higher cuprate **8**, then HMPA and finally TBSCl, cleanly afforded a reaction mixture where the only detectable material was the expected *gem*-distannane **11**. This bi-metallic species was easily purified from other tin contaminants by two subsequent column-chromatography steps. Despite its modest 35% overall yield, this two-pot synthesis of **11** presents a practical alternative to the preceding route starting from **13**.



Scheme 5

In summary, in this paper is reported the first preparation of the *gem*-distannylated olefin derivatives **10** and **11**. Different synthetic routes were successfully tested according to an addition-elimination-addition sequence involving conjugate addition of $\text{Bu}_3\text{Sn}(\text{Bu})\text{Cu}(\text{CN})\text{Li}_2$ **8** to γ -heterosubstituted acrolein precursors in presence of HMPA. To date, single addition of cuprate **8** to the known mono-stannylated acrolein **12** appears the most efficient approach to the synthetically promising silyl enol ether **11**. Some preliminary results concerning the synthetic potentialities of this new bis-stannyl species are reported in the following paper.²²

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