



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

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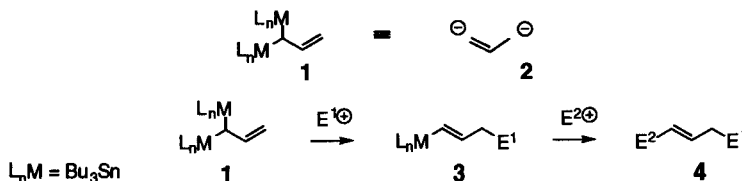
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Abstract : (*E*)-1-(*tert*-Butyldimethyl)silyloxy-3,3-bis(tributylstannyl)propene **11** as well as 1-*N,N*-diisopropylcarbamoyloxy-3,3-bis(tributylstannyl)propene **10** have been prepared upon addition of $\text{Bu}_3\text{Sn}(\text{Bu})\text{Cu}(\text{CN})\text{Li}_2$ **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.

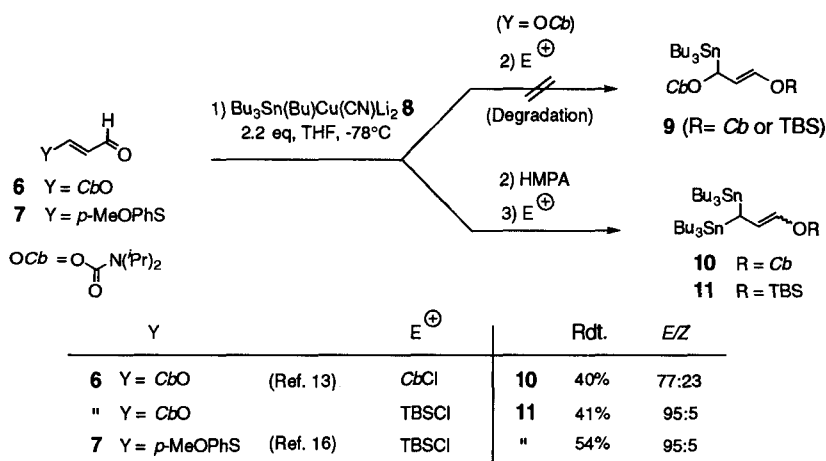
Several 1,1-distannyl-1-alkenes (vinylic *gem*-distannanes) have been prepared and their chemistry has been explored.² On another hand, 1,1-hetero organometallic 1-alkenes or 2-alkenes where one tin atom is involved have also received some attention³ and Sn-Si hybrids were recently shown to be promising 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 unstability. 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).



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 transmetallation¹¹ 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.

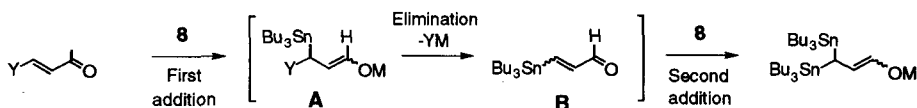
Along with our current search for new versatile allylic synthons which could be conveniently elongated at both ends, the conjugate addition of stannyl nucleophiles onto 3-(*N,N*-diisopropylcarbamoyloxy)acrolein **6** was studied.¹³ When aldehyde **6** was treated with the mixed higher order cuprate $\text{Bu}_3\text{Sn}(\text{Bu})\text{Cu}(\text{CN})\text{Li}_2$ **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** ($\text{R} = \text{OCb}$) and **11** ($\text{R} = \text{TBS}$) 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).

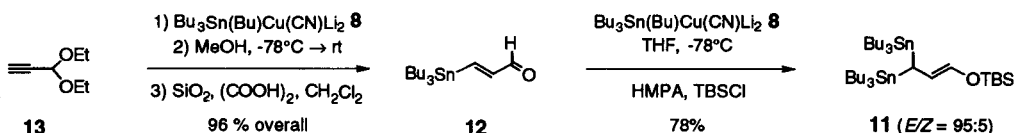


Scheme 3

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

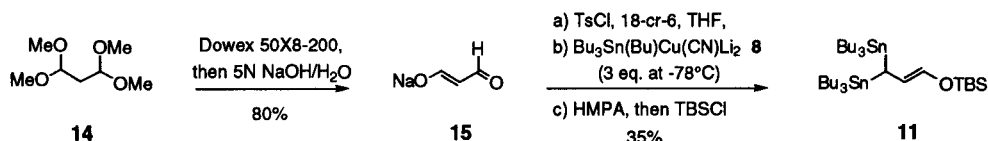
to accelerate *O*-silylation of enolates after conjugate addition of organocuprates to various α,β -unsaturated carbonyl electrophiles in presence of silylating agents,¹⁷ its exact role in the addition-elimination-addition sequence developed here deserves more studies. Recent findings from Oehlschlager *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 Bu₃Sn(Bu)Cu(CN)Li₂ **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 H₂O/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 Bu₃Sn(Bu)Cu(CN)Li₂ **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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- All new compounds have been fully characterized by ^1H NMR, ^{13}C NMR, IR, mass spectrometry and combustion analysis. Representative protocol : 1-(*tert*-Butyldimethyl)silyloxy-3,3-bis(tributylstannyl)propene **11** from **12**. To a suspension of CuCN (4.05 g, 45.3 mmol, 1.20 eq) in 270 mL of THF at -78°C was added dropwise a 1.55 M solution of butyllithium in hexanes (58.5 mL, 90.5 mmol, 2.40 eq). The mixture was stirred at -40°C for 30 min then cooled to -78°C . To the pale yellow solution was added dropwise tributyltin hydride (24.5 mL, 90.5 mmol, 2.40 eq). The dark yellow mixture was stirred at -40°C for 30 min then cooled to -78°C before dropwise addition of a solution of (*E*)-3-(tributylstannyl)-prop-2-enal **12** (13.0 g, 37.7 mmol) in 120 mL of THF. The resulting red solution was stirred at -78°C for 30 min and HMPA (66 mL, 0.38 mol, 10 eq) was added dropwise. After stirring at -78°C for a further 15 min, a solution of *tert*-butyldimethylsilyl chloride (17.0 g, 113 mmol, 3.00 eq) in 80 mL of THF was added dropwise. After 1 h at -78°C , 250 mL of saturated aqueous NaHCO_3 was added and the mixture was allowed to warm to room temperature. After decantation, the aqueous layer was extracted with 3x300 mL of diethyl ether and the combined organic layers were washed with brine, dried over MgSO_4 and concentrated. The crude product was purified by two successive silica gel flash chromatographies (100% petroleum ether) to give 20.35 g of **11** (72% yield, *E/Z* = 95:5). ^1H NMR (CDCl_3 , 400 MHz) δ 6.09 (d, 1H, *J* = 11.7 Hz, $J_{\text{Sn-H}}$ = 19.8 Hz), 5.24 (dd, 1H, *J* = 12.6, 11.7 Hz, $J_{\text{Sn-H}}$ = 29.2 Hz), 1.63 (d, 1H, *J* = 12.6, $J_{\text{Sn-H}}$ = 55.8 Hz), 1.46 (m, 12H), 1.34 (m, 12H), 0.90 (m, 39H), 0.12 (s, 6H). ^{13}C NMR (CDCl_3 , 50.3 MHz) δ 135.7 (CH, $J_{\text{Sn-C}}$ = 57 Hz), 114.9 (CH, $J_{\text{Sn-C}}$ = 42 Hz), 29.5 (CH_2 , $J_{\text{Sn-C}}$ = 19 Hz), 27.7 (CH_2 , $J_{\text{Sn-C}}$ = 56 Hz), 26.0 (CH_3), 18.5 (C), 13.8 (CH_3), 10.4 (CH_2 , $J_{117\text{Sn-C}}$ = 307 Hz, $J_{119\text{Sn-C}}$ = 293 Hz), 3.8 (CH, $J_{\text{Sn-C}}$ = 213 Hz), -4.9 (CH_3). Anal. Calcd. for $\text{C}_{33}\text{H}_{72}\text{OSiSn}_2$, 750.44, C : 52.82, H : 9.67. Found : C : 52.86, H : 9.66.
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