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The Stereoselective Functionalisation of 1,1-bis-(Tributylstannyl)ethenes

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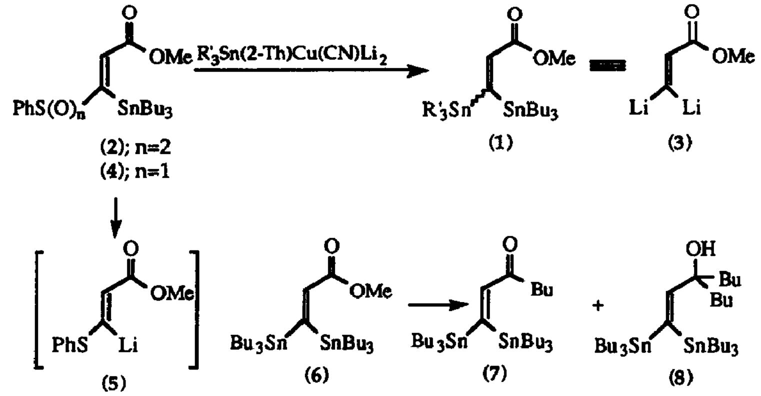
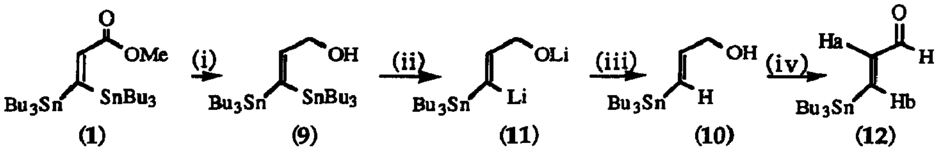
Abstract: *The stereoselective transmetallation and subsequent alkylation of functionalised 1,1-bis-(tributylstannyl)ethenes is reported.*

We recently reported[1] a general method for the preparation of the bis-stannylacrylates (1) from the corresponding vinyl stannanes (2), **Scheme 1**. Bi-metallic reagents such as (1) may be viewed as having the synthetic equivalence of the hypothetical di-anions (3), which are potentially of synthetic use for the synthesis of trisubstituted olefins.



Scheme 1

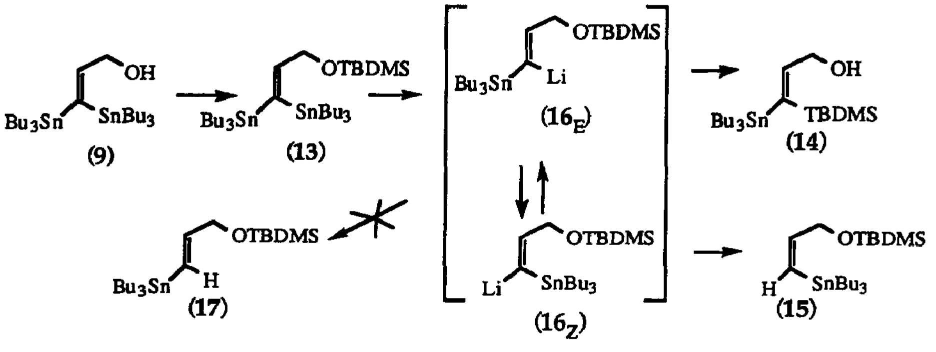
Surprisingly little is known in the literature[2] concerning the functionalisation of stannanes of the type (1); in this *Letter* we wish to communicate our initial observations in this area. Our initial experiments were concerned with determining the chemoselectivity, if any, associated with the transmetallation step. We[3] had already shown that the vinyl stannane (4) underwent clean transmetallation to a vinyl anion, depicted as (5), upon exposure to ^{n}BuLi (1.2 eq.; THF, -78°C), whereas a similar reaction[1] on the bis-stannane (6) resulted in the isolation of the ketone (7) and the alcohol (8) (36% and 42% respectively). Reduction of the ester (Dibal-H, 2.0 eq.; 0°C, 3 hrs.) afforded the alcohol (9) in excellent yield (94%), which upon reaction with ^{n}BuLi (4 eq.; -78°C; THF) underwent a relatively sluggish transmetallation reaction (8 hrs., -78°C.) generating the dianion (11), which upon protonation (NH4Cl; -78°C) afforded the known[4] *E*-olefin (10) in 54% isolated yield together with unreacted starting material (9) in 23% yield, **Scheme 2**. The transmetallation reaction proceeded at a much faster rate when conducted at higher temperatures, (2 eq. ^{n}BuLi; -20^{o}C; 1 hr.), again affording the *E*-olefin (**10**) as a single diastereoisomer, with a much increased overall yield (89%). Conversion of the acohol[4] (**10**) to the synthetically useful aldehyde (**12**) (PCC; CH_2Cl_2; rt) was readily accomplished in high yield (81%) which exhibited a well dispersed spin system for H_a and H_b (the ^3J coupling constants between H_a, H_b and $^{(117,119)}Sn$ being 19 and (52, 55) Hz respectively).



Reagents and conditions:- (i) DIBAL-H, 2 eq.; 0^{o}C; 94%; (ii) (a) ^{n}BuLi, 4 eq.; -78^{o}C; 8 hrs.; 54%; (b) ^{n}BuLi, 2 eq.; -20^{o}C, 1 hr.; 89%; (iii) NH_4Cl, -78^{o}C; (iv) PCC, CH_2Cl_2; 81%.

Scheme 2

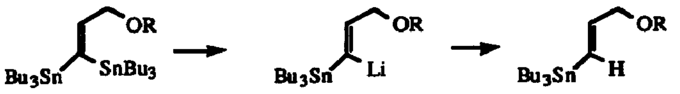
The effect of converting the free hydroxyl group of (**9**) into an ether moiety upon the stereoselectivity and rate of transmetallation was next examined. Reaction of the readily available TBDMS-ether (**13**) with ^{n}BuLi (1.5 eq.; -78^{o}C, 4 hrs.) resulted in the isolation of the alcohol (**14**) and the *Z*-vinyl stannane (**15**) as a separable 1:1 mixture in 75% isolated yield. A plausible explanation of these results invokes the formation of a configurationally unstable vinyl anion[5] (**16**$_{E,Z}$) which may be quenched either by a proton in an *intermolecular* sense generating the stannane (**15**) or by an *intramolecular* 1,4-silatropic shift generating the alcohol (**14**), **Scheme 3**.



Scheme 3

The fact that none of the stannane (**17**) was isolated would suggest that once formed (**16**$_E$) has a relatively short lifetime and undergoes a rapid internal quench[6] (to (**14**)) or isomerization to (**16**$_Z$).

The stereochemical course of the transmetallation/alkylation sequence was next investigated on the MOM- and MEM-ethers (**18**) and (**19**), which would be expected to effect greater stabilisation of the vinyl anions (**20**$_E$) and (**21**$_E$) due to their enhanced co-ordinating ability[7] relative to a silylether moiety as in (**13**). Substrates (**18**) and (**19**) were readily prepared from the corresponding alcohol (**9**) upon reaction with MOM-Cl or MEM-Cl in the pressence of Hunig's base in CH_2Cl_2 at ambient temperature (both in 91% yield). Transmetallation of the MOM-ether (**18**) proceeded rapidly (1.5 eq. nBuLi; THF; -78^{o}C; 1 hr.) to afford, after an ammonium chloride quench at -78^{o}C, the vinyl stannanes (**22**$_{E,Z}$) in 86% yield, with an *E*:*Z* ratio of 86:14. A similar reaction performed on the MEM-ether (**19**) afforded the corresponding vinyl stannanes (**23**$_{E,Z}$) in a marginally higher yield (88%), but with a similar *E*:*Z* ratio (85:15), **Scheme 4**.



(18), R=MOM
(19), R=MEM

(20_E), R=MOM
(21_E), R=MEM

(22), R=MOM
(23), R=MEM

Scheme 4

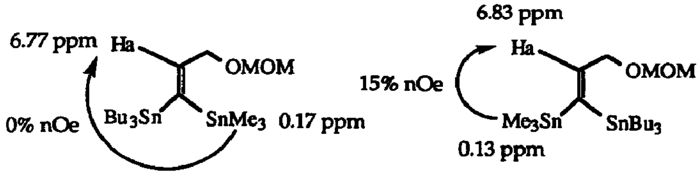
The vinyl anions (20) and (21) were found to undergo alkylation reactions with a variety of electrophiles (**Table**) in good overall yield with *E*:*Z* -ratios in excess of 7:3. Contrary to earlier reports[2], alkylation of vinyl anions such as (20) and (21) was observed to proceed cleanly with enolizable ketones, affording high yields of the corresponding carbinol (28). Stereochemical assignments were based upon the magnitude of the $^3J_{Sn\text{-}Ha}$ coupling constants[8] which are uniformly larger for the Z-isomer (*ca.* 115-160 Hz) when compared to the *E*-isomer (*ca.* 60-100 Hz) for each diastereoisomeric pair. Generally, each diasreoisomer could be separated either by "flash" chromatography or by medium pressure preparative HPLC. In the case of the bis-stannanes (26), the stereochemical assignments were based upon nOe difference studies on the separate diastereoisomers (**Figure**).

(18), R=MOM
(19), R=MEM

Starting Material$	Electrophile	Product$	Yield (%)	Isomer Ratio¶ (*E*:*Z*)
(18)	NH_4Cl	(22); E=H	86	86:14
(18)	PhCHO	(24); E=Ph(H)COH	89	81:19
(18)	TMS-Cl	(25); E=TMS	70	75:25
(18)	Me_3SnCl	(26); $E=SnMe_3$	46	77:23
(18)	PhSSPh	(27); E=SPh	72	73:27
(18)	CH_3COCH_3	(28); $(CH_3)_2COH$	95	70:30
(19)	NH_4Cl	(23); E=H	88	85:15
(19)	PhCHO	(29); Ph(H)COH	91	82:18

$ All new compounds were fully characterised by ^1H nmr, ^{13}C nmr, ir, high resoln. mass spectrometry.
¶Determined by ^1H nmr or HPLC.

Table



(26_E)

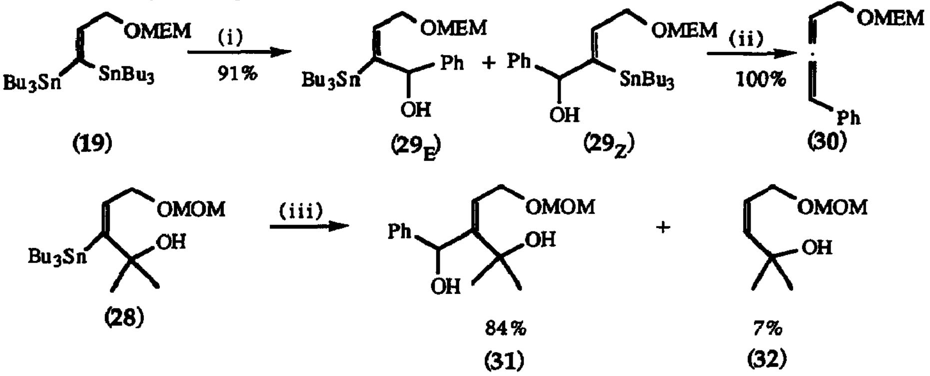
(26_Z)

Figure

It should be noted that vinyl stannanes such as (29) are relatively labile towards Lewis acids[9]. Attempted purification of (29) on commercial flash silica resulted in the isolation of the stannane (29) in diminished yield

(36%) together with appreciable quantities (26%) of the allene (**30**). Indeed, treatment of the purified stannane (**29**) with TFA in $CDCl_3$ resulted in a rapid and "quantitative" conversion to (**30**), **Scheme 5**.

The potential application of substrates such as (**28**) for the synthesis of trisubstituted olefins is briefly outlined in **Scheme 5**. Treatment of the diastereoisomerically pure stannane (**28**) with ^{n}BuLi (2.1 eq.; -78°C to -20°C; THF; 2 hrs.) followed by the addition of benzaldehyde (-78°C, 0.5 hrs.) afforded the isomerically pure diol (**31**) in 84% isolated yield, together with the olefin (**32**) in 7% yield.



Reagents and conditions:-(i) (a) ^{n}BuLi, 1.5 eq.; THF, -78°C; 1.5 hrs.; (b) PhCHO, -78°C 10 mins.; (ii) TFA; $CDCl_3$; 25°C; (iii) ^{n}BuLi, 2.1 eq., THF; -20°C; 2 hrs.; (b) PhCHO; -78°C.

Scheme 5

In conclusion, we have demonstrated that geminal bis-stannylethenes can undergo stereoselective, sequential transmetallation reactions providing access to a wide variety of functionalised olefins. Further studies in connection with the stereocontrolled syntheis synthesis of tri- and tetrasubstituted olefins and functionalised allenes are now under scrutiny.

Acknowledgements

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