trans-Allylstannylation of certain acetylenes catalysed by $ZrCl_4$

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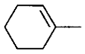
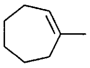
The *trans*-allylstannylation of simple acetylenes 1 is catalysed by $ZrCl_4$ to produce the corresponding alkenylstannanes 3 (or alkenes 4 upon protonolysis of the C–Sn bond) in a regio- and stereo-selective manner.

Allyl metallation of carbon–carbon triple bonds by allyl metals is a useful synthesis of 1,4-dienes. Several main group allyl metals, as well as allylic transition metals, have hitherto been utilized in such transformation.[1] The allyl metallation of activated alkynes, such as alkynyl ketones (Michael acceptor) and alkynols (functional group substituted alkynes), and/or the intramolecular allyl metallation proceed smoothly with various allyl metals.[1,2] However, the allyl metallation of simple unactivated alkynes **1** is not so easy and only a limited number of allyl metals are available for this purpose.[1,3] We report here that allylstannylation is catalysed by a Lewis acid such as $ZrCl_4$, and that the $ZrCl_4$ catalysed procedure yields the *trans*-allylstannation product **3** (or the corresponding destannation product **4** upon protonolysis) regio- and stereo-selectively [eqn. (1)]. The results are summarized in Table 1.

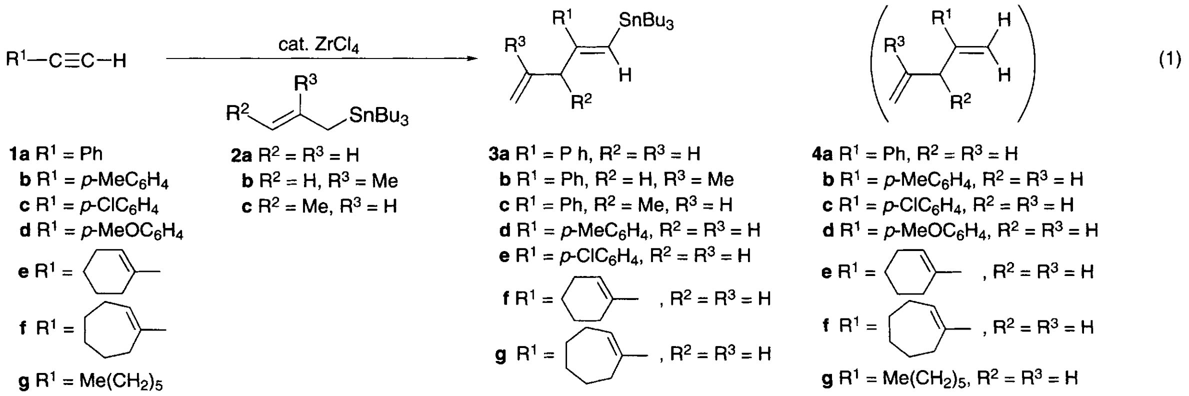
Allylstannylation of phenylacetylene in the presence of $ZrCl_4$ (0.5 equiv.) proceeded smoothly in toluene at −78 to 0 °C. The reaction was quenched with excess Et_3N at 0 °C and the product was purified by silica gel column chromatography (procedure A). The protonolysis product **4a** was obtained in 87% yield (entry 1). It was anticipated that protonolysis of the carbon–stannane bond would take place during work-up. Allylstannylation in the presence of $ZrCl_4$ (0.2 equiv.) followed by quenching the reaction mixture with saturated aq. $NaHCO_3$ at 0 °C, and subsequent purification by alumina column chromatography (procedure B) gave the alkenyltributylstannane **3a** in 83% yield (entry 2). The use of $ZrCl_4$ (1.0 equiv.) did not give a better yield than entry 1. When procedure A was used in the reaction using $ZrCl_4$ (0.2 equiv.), **4a** was obtained in 52% yield (entry 2). The use of $AlCl_3$ as a Lewis acid afforded the allylation product **4a** in very low yield (entry 3), perhaps owing to its higher Lewis acidity which may induce the transmetallation of allylstannane to the corresponding allyl aluminium derivative. Methallyl- (**2b**) and crotyl-stannane (**2c**) also underwent the addition to phenylacetylene to give the corresponding alkenylstannanes **3b** and **3c**, respectively, in allowable yields (entries 4 and 5). In the case of crotylstannane, only the γ-adduct **3c** was isolated. The allylation proceeded smoothly with other aryl substituted acetylenes **1b–d** (entries 6–8). The addition to a simple alkylacetylene such as octyne **1g** was sluggish and gave **4g** in only 25% yield (entry 11). However, the enynes **1e** and **1f** which are more reactive than a simple alkylacetylene afforded the desired adducts **3f** and **3g**, respectively, in very high yields (entries 9–10).

Synthesis of (*Z*)-1-tributylstannyl-2-phenylpenta-1,4-diene **3a** is representative. To a suspension of $ZrCl_4$ (47 mg, 0.2 equiv.) in toluene (1 ml) was added phenylacetylene **1a** (0.11 ml, 1 mmol) at −78 °C. The mixture was stirred for 30 min, and then allyltributylstannane **2a** (0.62 ml, 2 equiv.) was added at −78 °C. The mixture was stirred for 30 min at this temperature, and allowed to warm to 0 °C over 3–5 h. Excess amounts of saturated aq. $NaHCO_3$ were added at 0 °C (procedure A). Extraction with pentane, drying (Na_2SO_4), condensation under reduced pressure and purification by alumina column chromatography gave **3a** in 83% yield (360 mg). Work-up procedure B is as follows. Excess amounts of Et_3N was added at 0 °C.

Table 1 $ZrCl_4$ catalysed allylstannylation of alkynes

Entry	Lewis acid (equiv.)	**1** R^1	**2** R^2	R^3	Isolated yield[a] (%) **3**	**4**
1	$ZrCl_4$ (0.5)	Ph	H	H	—	87
2	$ZrCl_4$ (0.2)	Ph	H	H	83	52
3	$AlCl_3$ (0.5)	Ph	H	H	—	23
4	$ZrCl_4$ (0.2)	Ph	Me	H	56	—
5	$ZrCl_4$ (0.2)	Ph	H	Me	55	—
6	$ZrCl_4$ (0.2)	p-MeC_6H_4	H	H	84	78
7	$ZrCl_4$ (0.2)	p-ClC_6H_4	H	H	65	78
8	$ZrCl_4$ (0.2)	p-$MeOC_6H_4$	H	H	—	60
9	$ZrCl_4$ (0.2)		H	H	99[b]	82
10	$ZrCl_4$ (0.2)		H	H	82[b]	73
11	$ZrCl_4$ (0.2)	$Me(CH_2)_5$–	H	H	—	25

[a] Work-up procedures A and/or B were used, except where otherwise indicated. [b] Determined by ^1H NMR using *p*-xylene as an internal standard.



Hexane was added and the solid residue removed by filtration with celite. Condensation and purification by silica-gel column chromatography gave 2-phenylpenta-1,4-diene **4a** in 52% yield (74 mg).

The *trans*-addition of allylstannane was confirmed by NOE experiments using **3a**; treatment of **3a** with CF_3CO_2D gave the corresponding deuteriated product **5**, and NOE (14%) was observed between the alkenic hydrogen and the allylic hydrogens, Fig. 1. It is most probable that a complex between acetylenes and ZrL_n would be formed and the *trans*-addition of the tributylstannyl moiety to this complex would take place.

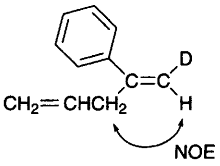


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Fig. 1

The present reaction pattern is similar to that of $ZrCl_4$ catalysed hydrostannylation of acetylenes, which was developed recently in our laboratory.[4]

References

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