Molybdenum-catalyzed hydrostannations of allenylcarbinols†

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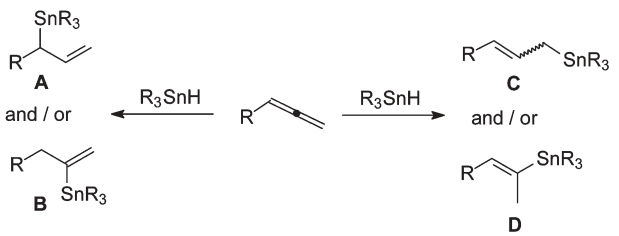
Allenylcarbinols undergo regioselective hydrostannation in the presence of $MoBl_3$, a catalyst which was developed for the hydrostannation of propargyl alcohols and derivatives; allylstannanes are formed preferentially, which can easily be converted into allyl iodides.

During the last few years functionalized allenes have become more and more interesting not only as targets in natural product synthesis, but also as valuable synthetic precursors for the synthesis of complex molecules.[1] In this context, carbon–carbon and carbon–heteroatom bond formations are of major interest, triggering the development of preparatively useful methods such as additions[2] or palladium-catalyzed transformations.[3] Besides cyclizations[4] especially transition metal-catalyzed hydrometallations such as hydroborations,[5] hydrozirconations[6] or hydrostannations[7] are synthetically useful transformations. Vinyl or allyl organometallics are obtained depending on the regioselectivity of the hydrometallation step. In principle (Scheme 1), four different products (**A–D**) are possible, and the product distribution depends on the reaction conditions used.

While in Lewis acid-catalyzed reactions of terminal allenes attack occurs at the internal double bond providing vinylstannanes **B**,[8] in the presence of most palladium complexes the terminal double bond reacts preferentially giving rise to allylstannanes **C** as an *E*/*Z* mixture.[9] Interestingly, the regioselectivity for the hydrostannation of the terminal double bond can be converted towards vinylstannanes **D** by switching from $Pd(PPh_3)_4$ to $Pd(OH)_2/C$.[10] Hydrostannations of allenes bearing suitable functional groups such as aryl halides[11] or further double bonds[12] allow subsequent cyclizations.

Recently, we developed a new molybdenum catalyst for hydrostannations of alkynes. $MoBl_3$ ($Mo(CO)_3(CN\mathit{t}Bu)_3$) was found to be an excellent catalyst for regioselective hydrostannations towards the internal vinylstannanes, being superior to the generally used palladium catalysts (Scheme 2).[13]



Scheme 1 Hydrostannation of allenes.

† Dedicated to Prof. Dr M. Veith on the occasion of his 60th birthday.

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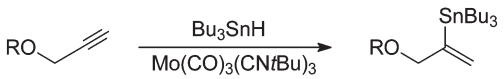
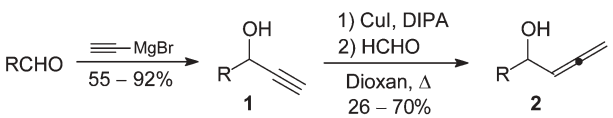


Scheme 2 Molybdenum-catalyzed hydrostannation of alkynes.

Herein, we now report on our investigations of $MoBl_3$-catalyzed hydrostannations of allenes. We chose allenylcarbinols **2** as substrates which could easily be obtained from the corresponding propargylic alcohols **1** according to Burgess and Jennings[14] (Scheme 3).

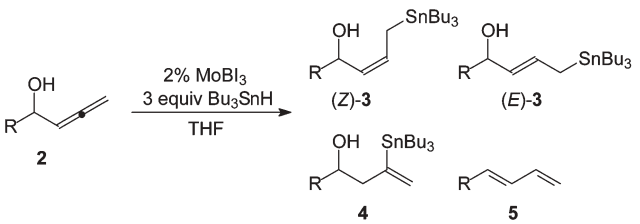
Those allenylcarbinols were subjected to the reaction conditions optimized for the hydrostannation of alkynes (THF, Δ) and the process was monitored by TLC. In general, the reactions were completed after 4 h, and therefore allenylcarbinols **2** are significantly more reactive than the corresponding propargyl derivatives **1**. The product ratio was determined by NMR. Overall, four different products were obtained, but products of type **B** and **D** were never observed. The results obtained are summarised in Table 1.

First we investigated the hydrostannation of the phenylethyl-substituted allenylcarbinol **2a**. Addition occurred exclusively at the terminal double bond and only to give the allylstannanes **3a**, which were obtained as an *E*/*Z* mixture in the ratio 1 : 2. To determine if



Scheme 3 Preparation of allenylcarbinols.

Table 1 Hydrostannation of allenylcarbinols **2**



Allene	R	Temp [°C]	Yield [%]	Ratio (*E*)-**3** : (*Z*)-**3** : **4** : **5**
2a	$PhCH_2CH_2$	55	68	1 : 2 : 0 : 0
2a	$PhCH_2CH_2$	rt	74	1 : 2 : 0 : 0
2b	2-NO_2Ph	55	76	12 : 12 : 1 : 0
2c	4-ClPh	55	68	1 : 1 : 0 : 0
2d	2,6-Cl_2Ph	55	74	1 : 2 : 0 : 0
2e	2,4,6-$(MeO)_3$Ph	55	86	1 : 0 : 1 : 2
2e	2,4,6-$(MeO)_3$Ph	rt	23[a]	10 : 0 : 6 : 1

[a] Only 1% $MoBl_3$, 2 equiv. Bu_3SnH used.

this ratio depends on the reaction conditions, *e.g.* on the temperature, we carried out the reaction also at room temperature. Under these milder conditions the yield was higher, but no influence on the product ratio was observed.

To figure out if electronic factors in the substituent R might have an influence on the product formation, we investigated several aromatic allenylcarbinols bearing electron-withdrawing and -donating groups. In the hydrostannation of *o*-nitrophenyl derivative **2b** the allylstannanes **3b** were by far the major products, the regioisomer **4b** was formed in trace amounts. Similar results were obtained in the reaction of *p*-chlorophenyl- and 2,6-dichlorophenyl-substituted substrates (**2c**, **2d**), but the situation changed dramatically with electron-rich aromatic systems such as the 2,4,6-trimethoxyphenyl derivative **2e**. In this case the elimination product **5e** was obtained preferentially, besides allylstannane (*E*)-**3e** and vinylstannane **4e**. Interestingly no (*Z*)-configured product was obtained in this case, and we assume that this isomer undergoes elimination according to Fig. 1.

Obviously the strong electron-donating groups facilitate the cleavage of the OH group, probably *via* stabilization of the carbenium ion intermediate. This would explain the high ratio of elimination product obtained under the standard conditions. To figure out if this proposal is reasonable, we investigated the reaction also under milder conditions. And indeed, the amount of elimination product could be reduced significantly.

The high selectivities towards the allyl and vinyl stannanes **3** and **4** can be explained by the following mechanistic rationale (Scheme 4). Probably in the first step some of the isonitrile ligands dissociate from the molybdenum opening free coordination sides for the oxidative addition of the tin hydride and coordination of the allene. Depending on the substrate used, only the terminal or both double bonds coordinate to the molybdenum giving rise to intermediates **A** and **B**. Subsequent hydrometallation should provide intermediates **A′** and **B′** with the metal fragment added to the sterically least hindered position. The products **3** and **4** were formed from these intermediates *via* reductive elimination. The *E*/*Z* isomers were formed by coordination to the two diastereotopic faces of the terminal double bond.

Probably this mechanism is slightly different from the one proposed for the hydrostannation of alkynes which seems to start with a transfer of the stannyl group and a subsequent hydrogen transfer in the reductive elimination step. But both possible mechanisms were also discussed for palladium-catalyzed hydrostannations. Therefore, it is reasonable that the situation with the molybdenum complexes is similar.

To improve the synthetic potential of this protocol we subjected the mixture of (*E*/*Z*)-**3b** to a metal–halogen exchange (Scheme 5). Although the isomeric mixture was used, the corresponding allyl iodide (*E*)-**6** was obtained as a single isomer in high yield. Obviously under these conditions only the thermodynamically most stable product is formed, which is an interesting substrate for further synthetic applications.

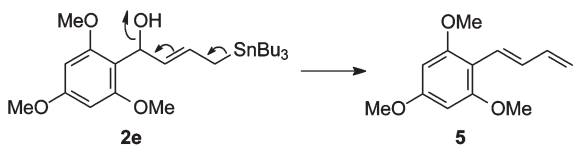
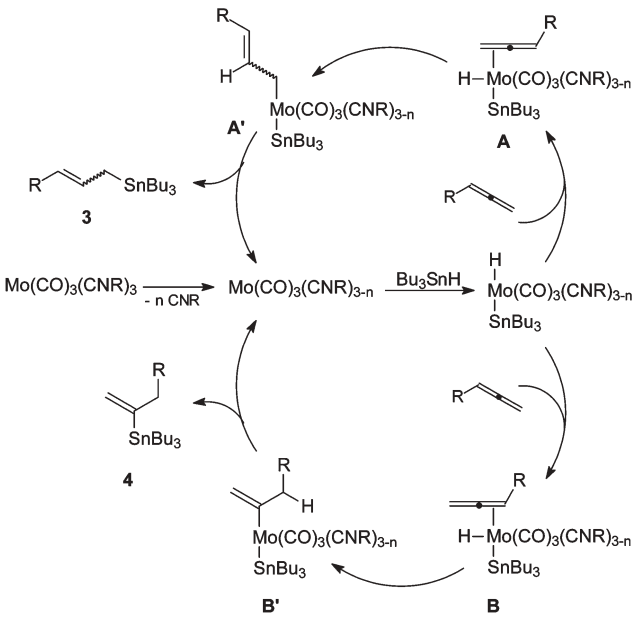
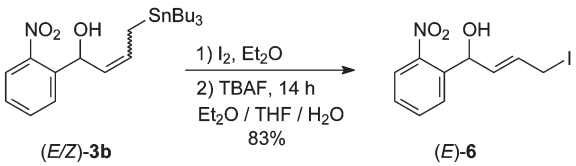


Fig. 1 Elimination of stannylated allyl alcohols.



Scheme 4 Proposed mechanism for the hydrostannation of allenes.



Scheme 5 Metal–halogen exchange of allylstannane **3**.

In conclusion we have shown that molybdenum-catalyzed hydrostannation of allenes proceeds regioselectively towards the sterically least hindered stannylated product. Further research concerning the selectivity and the reaction mechanism is currently in progress.

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