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Regioselective Hydrostannation of Allenes Catalyzed by $Pd(OH)_2/C$

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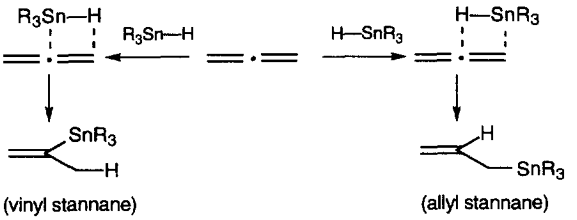
Abstract: A series of mono-substituted allenes **1–7** were shown to undergo regioselective hydrostannation when treated with Bu_3SnH in the presence of $Pd(OH)_2/C$ in THF to give the vinyl stannanes **11–17**. The use of $Pd(PPh_3)_4$, led to regioisomeric mixtures of allyl stannanes. © 1997 Elsevier Science Ltd.

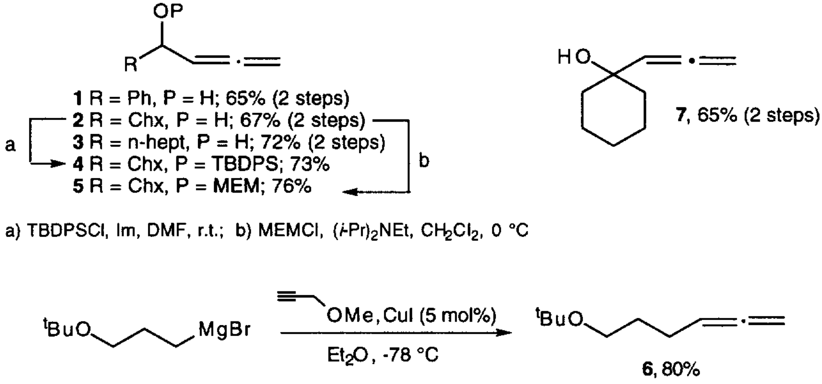
The use of organotin reagents has found widespread application in organic synthesis due to the wide variety of carbon-carbon bond forming reactions which they undergo.[1] In light of this versatility, the development of methods for the selective generation of this class of compounds is of great synthetic value. Previously, we have reported the palladium catalyzed hydrostannation of strained and unstrained alkenes and showed different catalysts were necessary for efficient hydrostannation.[2] In those studies it was discovered that the typical catalysts used for hydrostannation, such as $Pd(PPh_3)_4$, failed to hydrostannate unactivated alkenes. In particular, the use of $Pd(OH)_2/C$ was required in order for the hydrostannation of unstrained alkenes to proceed. Others have reported palladium catalyzed hydrostannation of a number of alkyl substituted allenes[3] and a single case of an oxy-allene, and in all cases allylstannanes were formed.[4]

There are two modes with which the H–Sn moiety can add across an allene (Scheme 1). Addition of the tin to the central carbon of the allene gives a vinyl stannane, while addition to the terminal carbon gives an allyl stannane. Thus it would be desirable to find appropriate conditions to efficiently form either of the possible products. We now report that using $Pd(OH)_2/C$ as the hydrostannation catalyst, regioselective hydrostannation occurs to form vinyl stannanes; complementary to results obtained using $Pd(PPh_3)_4$.



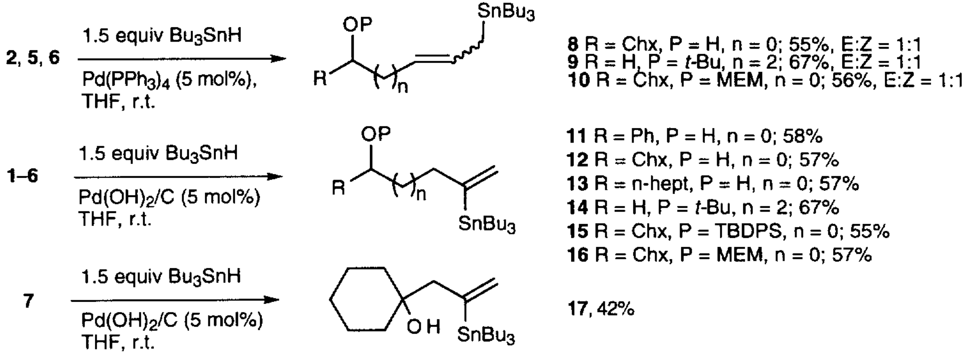
Scheme 1

The α-allenic alcohols **1**-**3**, **7** were prepared by a previously described procedure (Scheme 2).[5] Alcohol **2** was protected as the TBDPS ether with TBDPSCl and imidazole in DMF, to give the siloxy allenic ether **4**. Treating alcohol **2** with MEMCl and Hünig's base in dry CH_2Cl_2 afforded allenic ether **5**. Allene **6** was prepared by reacting the Grignard reagent prepared from 3-bromopropyl *t*-butyl ether with methyl propargyl ether under CuI catalysis at -78 °C in Et_2O (Scheme 2).[6]



Scheme 2

Initially we examined $Pd(PPh_3)_4$ as the catalyst for the hydrostannation of allenic alcohols. Slow addition of tributyltin hydride to allenes **2**, **5**, and **6** in the presence of 5 mol% $Pd(PPh_3)_4$ gave the allyl stannanes **8**, **9**, and **10** respectively in moderate yield but with no stereoselectivity (Scheme 3).[3,4a,7]

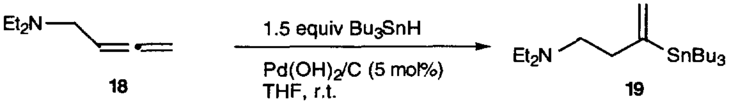


Scheme 3

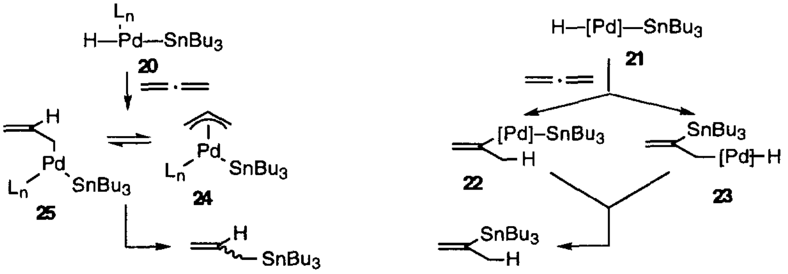
Concurrent with these studies was an examination of our recently reported conditions using a ligand-free heterogeneous catalyst, $Pd(OH)_2/C$. Thus treatment of a solution of allenes **1**-**7** in THF (0.1M) with tributyltin hydride (syringe pump addition over 1.5 hours), in the presence of 5 mol% $Pd(OH)_2/C$ gave the 2-tributylstannyl 1-alkenes **11**-**17** in 55-67% yield (Scheme 3). Examination of the crude ^1H NMR spectra revealed that the regioselectivity was at least 5:1 in favor of the vinyl stannane compared to all other products. Reaction with a soluble catalyst lacking phosphine ligands, Pd_2dba_3, gave a very complex mixture of products containing olefinic residues. Related vinylstannanes have previously been prepared by the addition of stannyl cuprates to alkynes,[8] from vinyl halides,[9] from stannylmetallation of alkynes[10] and from radical addition to alkynes and allenes.[4f, 11]

Allene **4** was synthesized to determine if a bulky group in the proximity of the reaction center would have any effect on the outcome of the reaction, and allene **5** was prepared to determine the effect of a chelating group which is potentially sensitive to reduction reactions. Both **4** and **5** reacted as well as the parent unprotected allenic alcohol **2**, indicating that the steric environment α to the allene does not affect the hydrostannation to any appreciable extent under these conditions. Similarly, the nature of the R group in allenic alcohols **1**, **2** and **3**, appears to play no significant role; all reacted in the same manner.

Allenyl amine **18** was also reacted with Bu_3SnH in the presence of $Pd(OH)_2/C$ and stannylamine **19** was isolated in a 41% yield (unoptimized).

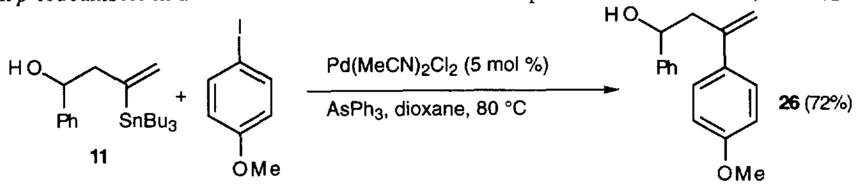


Although the mechanism of the hydrostannation is not known, we presume that the palladium(II) hydroxide is reduced by the tin hydride to a palladium(0) species which is the active catalyst. Subsequent oxidative insertion into the Sn-H bond would generate **21** (or **20** for the PdL_4 catalyst) which can hydropalladate or stannylpalladate the allene to give **22** or **23**. Reductive elimination would give the observed vinylstannane (Scheme 4). Our earlier studies with methylenecyclopropanes are most easily explained by invoking a hydropalladation reaction[2c] but we cannot rule out **23** (as the σ- or π-allyl species). The hydrostannation pathway using $Pd(PPh_3)_4$ is thought to proceed through the allyl palladium species **25**, which may be in equilibrium with the π-allyl complex **24**. Studies are ongoing to understand the changes in selectivity between the two catalyst systems.



Scheme 4

Finally, we have shown that the vinyl stannanes produced in the hydrostannation undergo facile coupling with aryl iodides to give the corresponding cross-coupled styrene derivatives. For example allenic alcohol **11** reacted with *p*-iodoanisole in dioxane at 80 °C for 1.5 hours in the presence of 5 mol% $Pd(MeCN)_2Cl_2/AsPh_3$ to



give the coupled product **26** in 72% isolated yield.[12]

In summary, we have demonstrated that mono-substituted allenes, with various functional groups, undergo regioselective hydrostannation with the nature of the resulting product governed by the catalyst used in the reaction. The use of $Pd(OH)_2/C$ gives the 2-tributylstannyl 1-alkenes, while $Pd(PPh_3)_4$ gives allyl stannanes, each of which offer synthetically useful possibilities in subsequent transformations.

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