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[A027]

Bulky Organotin Hydrides in Palladium Catalized Hydrostannation of Terminal Triple Bonds

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Introduction

Hydrostannation of alkynes is one of the most used routes for the synthesis of vinylstannanes, which are very useful in organic synthesis especially when they have a well-defined stereochemistry. [1]

Palladium catalyzed hydrostannation normally takes place with *syn* stereoselectivity as a result of their mechanism and also, in many cases, with good regioselectivities due to a combination of steric and electronic factors. [2]

It is considered that these reactions can take place through a catalytic cycle (Figure 1) that implies an oxidative addition followed by hydrometallation and reductive elimination. [3]

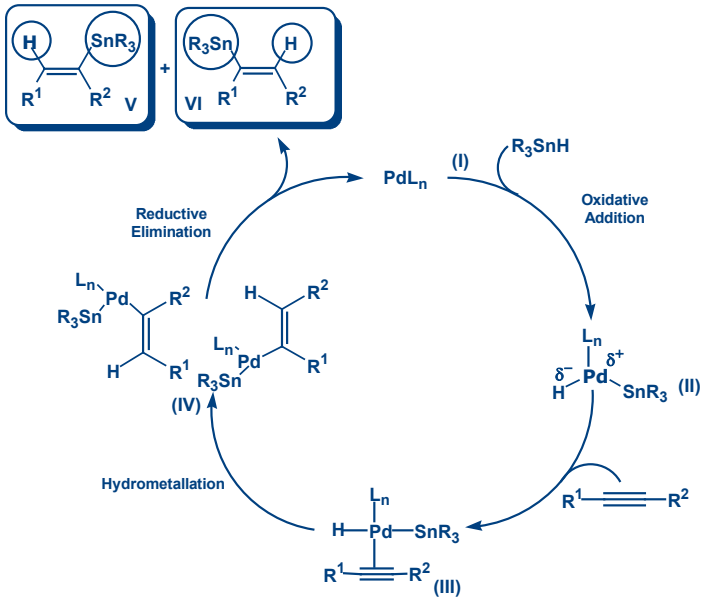

Figure 1

The oxidative addition of hydride to the metallic center (stage **I** → **II**) is followed by the coordination with the double bond (**II** → **III**). The resulting complex (**III**) is hydrometallated to give the vinyl-palladium (**IV**), which leads to the vinylstannane product by reductive elimination. It has been observed that the relative steric bulk of R^1 and R^2 determine the regiochemistry of the addition, that is, if the R_3Sn group is nearest (proximal) to R^1 or R^2. Thus, on the metal, the most bulky substituent R^1 will orient the substrate so that R^1 is located as remote as possible (distal) of the bulky R_3Sn group. By this way the formation of complex **III** is favoured, which leads to the preferential formation of regioisomer **V**.

In complex **II**, the electropositive palladium gives the hydride character of hydrogen atom. And besides if there is polarization of the π bond by effect of R^1 or R^2, the regioselectivity of the addition of **II** can also be affected, leading to regioisomer **VI**.

Also the relative importance of the steric *versus* electronic factors depends on the substrate and the catalyst employed.

Results and Discussion

On the basis of our experience with organotin compounds with bulky organic ligands and considering the synthetic importance of vinylstannanes with a specific geometry, we considered interesting to carry out palladium-catalyzed hydrostannation of monosubtituted alkynes with different bulky organotin hydrides.

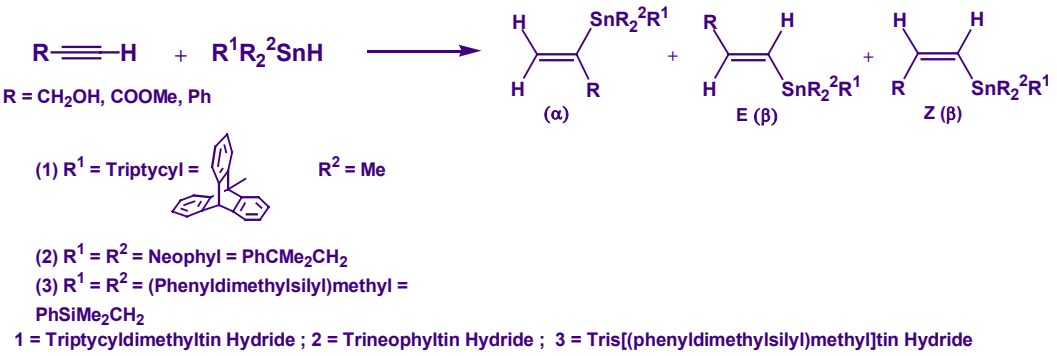

Figure 2

Taking into account our previous results with trineophyltin hydride [5] (**2**), we considered of interest to extend our studies to triptycyldimethyltin (**1**) and tris[(phenyldimethylsilyl)methyl]tin (**3**) hydrides [6]. The obtained results are summarized in the following Table:

Table 1. Palladium catalyzed addition of bulky triorganotin hydrides to monosubtituted alkynes.[a]

Compd. Nº	$R^1R_2^2SnH$	R	(α) (%)	E (β) (%)	Z (β) (%)	Yield[b] (%)	^{119}Sn (ppm)[c]
4 y **5**	$TripMe_2SnH$	CH_2OH	33 (**4**)	67 (**5**)		80%	**4**: -62,8 **5**: -60,3
6 y **7**	$TripMe_2SnH$	COOMe	89 (**6**)	---	11 (**7**)	87%	**6**: -58,0 **7**: -75,1
8 y **9**	$TripMe_2SnH$	Ph	54 (**8**)	46 (**9**)		85%	**8**: -57,4 **9**: -57,6
10 y **11**	$(PhSiMe_2CH_2)_3SnH$	CH_2OH	61 (**10**)	39 (**11**)		70%	**10**: -21,1 **11**: -19,0
12, 13 y **14**	$(PhSiMe_2CH_2)_3SnH$	COOMe	90 (**12**)	5 (**13**)	5 (**14**)	65%	**12**: -13,3 **13**: -16,9 **14**: -37,3
15, **16** y **17**	$(PhSiMe_2CH_2)_3SnH$	Ph	60 (**15**)	20 (**16**)	20 (**17**)	60%	**15**: -13,9 **16**: -15,6 **17**: -32,6
18 y **19**	$Neof_3SnH$	CH_2OH	70 (**18**)	30 (**19**)		67%	**18**: -85,6 **19**: -84,7
20 y **21**	$Neof_3SnH$	COOMe	69 (**20**)	31 (**21**)		82%	**20**: -76,8 **21**: -83,5
22	$Neof_3SnH$	Ph	100 (**22**)	---		99%	**22**: -79,8

[a] 2% $(PPh_3)_2PdCl_2$ in dry THF .
[b] Yields of isolated products.
[c] In $CDCl_3$; in ppm with respect to Me_4Sn.

It can be seen that only in the addition of trineophenyltin hydride (**2**) to phenylethyne one of the possible adducts (**22**) is obtained, and in most cases mixtures of both possible regioisomers adducts are obtained, corresponding to a *syn* attack, due

to perhaps of predominance of the electronic factors over the steric ones. However in only three cases (**7**, **14** and **17**) it was possible to observe small amounts of Z (β) adducts. Yields were between good to excellent (60-99%) and in all the cases the isomers could be satisfactorily separated.

To test the chemical reactivity of the new vinylstannanes, we perform Stille coupling between bromobenzene and vinylstannanes **6** and **17** (Figure 3).

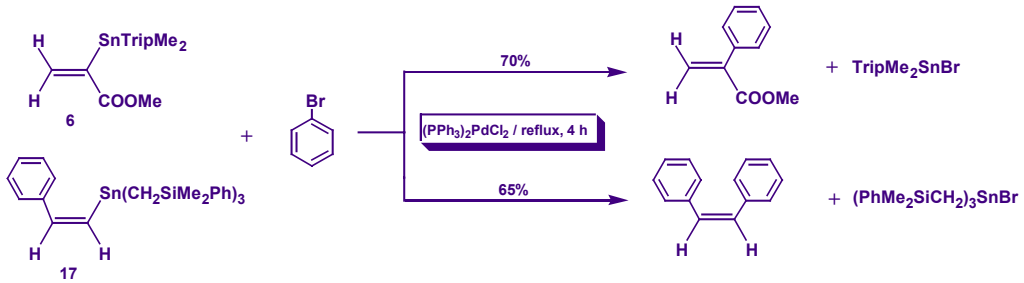

Figure 3

The obtained results indicate clearly that the chemical reactivity of the new vinylstannanes is similar to that of other vinyltriorganostannes.

Experimental Section

Hydrostannation:

General Procedure: To an alkyne solution (1equiv.) in dry THF, under inert atmosphere, was added $(PPh_3)_2PdCl_2$ (0.02 equiv.) followed by the corresponding hydride (1 equiv.). The mixture was shaken at room temperature until the initially yellow solution became dark brown (30-120 min). The reaction was monitored by IR spectroscopy, until disappearance of the Sn-H absorption band (approx. 1800 cm^{-1}). Solvent was removed at reduced pressure without heating. Purification of all organotin adducts was carried out by column chromatography, using silica gel 60.

Stille coupling [4]:

To a mixture of bromobenzene (1 equiv.), $(PPh_3)_2PdCl_2$ (0.02 equiv.) and a catalytic amount of 2,6-diterbuthyl-4-methyl-phenol under inert atmosphere was added a solution of vinylstannane (1 equiv.) in dry toluene at room temperature. The mixture was stirred under reflux and monitored by TLC. Column chromatography with silica gel 60 gave the desired coupling product.

All compounds were characterized by ^{1}H-, ^{13}C-y ^{119}Sn -NMR, IR spectroscopy and GLC-Mass.

Conclusions

These studies demonstrate that the palladium catalyzed additions of triptycyldimethyl- (**1**) and tris [(phenyldimethylsilyl)methyl] tin (**3**) hydrides to different terminal alkynes take place stereoselectivily, leading preferential to *syn* attack products.

All the stereoisomers can be isolated in good to excellent yields and their reactivity was tested.

It is remarkable that in the case of hydride **1** only one triptycyl group is enough to obtain the necessary steric constrain in order to control the stereochemistry.

Continuing efforts are directed toward the understanding of the stereo- and regiochemistry control of triple bond hydrostannation with bulky hydrides.

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References and notes

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