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Preliminary Communication

Double hydrostannation of terminal alkynes in the presence of thiol

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Abstract

According to experimental conditions, arylthiol-promoted addition of tributyltin hydride to acetylenic bond leads either to double hydrostannation or stannylation.

Keywords: Double hydrostannation; Propargylic derivatives; Thiol; Alkyne

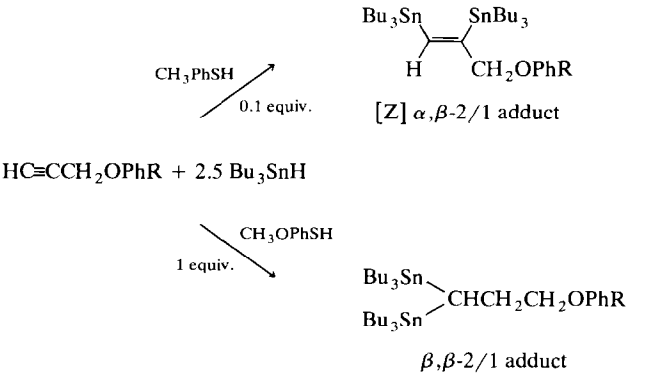
Recently, we disclosed new results on the arylthiol-catalyzed double stannylation of a propargyl sulfide [1]. Thus, in the presence of small amounts of p-thiocresol, hydrostannation of propargyl p-tolylsulfide promotes the unexpected formation of (Z)-1,2-bis(organostannyl)olefin, instead of yielding normal addition products. The best results were obtained in "a priori" non-radicalar experimental conditions, using 2.5 equivalents of tributyltin hydride at ambient temperature.

In order to assess the effect of the organosulfur moiety on the course of the reaction, we investigated the hydrostannation of related oxygenated propargylic compounds. Under the previously optimized experimental process, the double stannylation appears to be rather sluggish, giving the unsaturated α,β-2/1 adduct as expected, in ca. 30% yield.

Attempts to improve the yield by increasing the amount of catalyst have led to a drastic change in the course of the reaction: double hydrostannation takes place instead of double stannylation, leading to the formation of a saturated β,β-2/1 adduct in 65% yield, without the appearence of any trace of earlier unsaturated α,β-2/1 adduct. Nevertheless, the selectivity observed proved to be weak, due to the presence of a mixture of hexabutylditin, stannyl sulfide and α/β (Z/E) monostannylated 1:1 regioisomers.

Subsequent inspection of the effect of substituents in the aryl ring of the catalyst ($\Sigma_p = CH_3O$, F, NO_2 instead of CH_3, H) results in achieving a quasi-total selectivity towards the β, β-2/1 adduct with a 75% yield.

Thus, for the given substrate, the reaction could be directed to the double stannylation or to the double hydrostannation following the chosen experimental conditions [2]:



Selectivities reached with various catalysts are depicted in Table 1, together with some results obtained with model propargyl amine. It should be mentioned that, for unclear reasons, propargyl sulfides do not suffer the double hydrostannation process and lead to the double stannylation whatever the catalyst.

As appears from Table 1, the best results were obtained using 4-methoxybenzenethiol and oxygenated

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Table 1

$HC{\equiv}C(CRR^1)_nXR^2 \xrightarrow[1\ \text{equiv. } \Sigma_p\text{-ArSH}]{2.5\ \text{equiv. } Bu_3SnH} \begin{matrix} Bu_3Sn \\ Bu_3Sn \end{matrix}\!\!>\!CHCH_2(CRR^1)_nXR^2$

Σ_p-ArSH	X [a]	R^2	selectivity % [b]	yield % [c]
H	O	Ph	46/54	30
	NH	Ph	35/65	16
CH_3	O	Ph	60/40	35
	NH	Ph	51/49	19
CH_3O	O	Ph	98/2	73
		p-CH_3Ph	98/2	75
		H	85/15	80
		H [d]	73/27	35
		H [e]	94/6	75
		THP [f]	95/5	79
	NH	Ph	80/20	40
F	O	Ph	95/5	61
	NH	Ph	68/32	41
NO_2	O	Ph	14/86	traces
	NH	Ph	16/84	–

[a] $R = R^1 = H$ and $n = 1$ unless otherwise noted. [b] Selectivities: β,β-2/1 adduct/α and β(Z/E)-1/1 adduct %. [c] All yields refer to isolated purified products. [d] $R = CH_3$, $R^1 = H$. [e] $n = 2$. [f] THP: tetrahydropyran.

propargylic substrates. Herein, we successfully hydrostannate propargyl alcohol, homopropargyl alcohol and related derivatives.

Structural assignments of the tin hydride adducts were based mainly on the ^{119}Sn NMR spectra, which display the characteristic shape expected for two equivalents tins (only one signal). Obviously, the saturated α,β-2/1 adduct in which the second organotin group is bound to the less sterically hindered α-carbon atom is not formed.

The introduction of an asymmetric carbon atom in the molecule (see Table 1) resulted mainly in the formation of a characteristic two lines spectrum, indicating the presence of two magnetically non-equivalent tin atoms.

The use of radicalar initiators such as AIBN instead of 4-methoxybenzenethiol affords in our experimental conditions, only the classical monohydrostannylated α and β species. Moreover, Mitchell et al. [3] have not observed, on analogous acetylenic compounds, the hydrostannation of initial β-adduct, because of the reversibility of the radicalar addition leading to a low stabilized intermediate radical of the type Sn_2CHCH- [4]. Thus, in reactions leading to the formation of gem-2/1 adducts the thiol should probably play the role of radical inhibitor. This behaviour could be rationalized in terms of coordination between the electron-rich sulfur atom of the "catalyst" and the tin atom of the hydride. Hence, the polarisation of the tin–hydrogen bond should be increased, promoting ionic-like reactions.

The proposed new method appears to be a rapid and versatile route to gem-2/1 adducts, giving these compounds a new proficiency. We are currently investigating the scope and the mechanism of the present double hydrostannation and its applications to organic synthesis via transmetallation and γ elimination reactions.

Acknowledgements

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References and notes

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[2] The preparation of 3,3-bis(tributylstannyl)propanol represents a typical procedure for the synthesis of saturated $\beta\beta$-2/1 adducts: Tributyltin hydride [5] (13 g; 0.045 mol) was rapidly added in an inert atmosphere to a mixture of 4-methoxybenzenethiol (2.5 g; 0.018 mol) and propargyl alcohol (1 g; 0.018 mol) in anhydrous tetrahydrofuran (15 ml). The mixture was stirred at ambient temperature for 48 h and then purified at ca. 10^{-4} mmHg using a Kugelrohr apparatus. Rdt 80%. ^{119}Sn NMR (C_6D_6, 200 MHz) δ 10.3 [$^2J(^{119}Sn-^{117}Sn) = 159.8$ Hz)]; ^{13}C NMR ($CDCl_3$, 250 MHz) δ −0.7 [SnCHSn, $^1J(^{119}Sn-^{13}C) = 234.6$ Hz, $^1J(^{117}Sn-^{13}C) = 224$ Hz], 10.3 [$CH_2\alpha$, $^1J(^{119}Sn-^{13}C) = 308$ Hz, $^1J(^{117}Sn-^{13}C) = 293.7$ Hz]; 13.6 (CH_3); 27.6 [$CH_2\gamma$, $^3J(^{119/117}Sn-^{13}C) = 57.2$ Hz]; 29.4 [$CH_2\beta$, $[^2J(^{119/117}Sn-^{13}C) = 19.1$ Hz]; 34.7 [Sn_2CHCH_2, $^2J(^{119/117}Sn-^{13}C) = 21$ Hz]; 66.7 [CH_2OH, $^3J(^{119/117}Sn-^{13}C) = 43.9$ Hz]; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.65–1.8 (m, 55 H); 2.0 [q, 2H, $^3J(^1H-^1H) = 7.4$ Hz]; 3.5 [t, 2H, $^3J(^1H-^1H) = 7.1$ Hz]; MS: *m/z* 581/583/579 (100/82/94), 291/289/287 (68/53/31), 235/233/231 (29/23/14), 179/177/175/173 (71/23/26/9), 121/119/117 (27/21/10).

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