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Regioselective hydrostannations catalyzed by molybdenum isonitrile complexes

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Abstract

Hydrostannations using $Mo(CO)_3(CN–{}^tBu)_3$ give rise to α-stannylated alcohols and ethers in a highly regioselective fashion. The yields and selectivities obtained with this catalyst are significantly higher in comparison to the results obtained with the commonly used palladium and rhodium catalysts. The influence of the isonitrile incorporated into the molybdenum complex is investigated. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Alkynes; Hydrostannation; Isonitriles; Molybdenum

1. Introduction

Metal catalyzed reactions are becoming more and more important for organic synthesis, especially because of the mild reaction conditions under which many of these reactions can be carried out [1]. Most of them also tolerate a wide range of functional groups and are, therefore, powerful tools for the synthesis of complex molecules. Palladium plays a dominant role under the metals used. Allylic alkylations, cyclizations and cross coupling reactions are working horses for the synthetic chemist [2]. During the last years, other metals such as tungsten [3] and molybdenum [4] gained an increased interest. For example, $Mo(CO_2)(CN–{}^tBu)_4$ was shown to be also a good catalyst for allylic alkylations [5]. Hydrometallation reactions, such as hydrostannations are versatile tools for the synthesis of interesting organometallic compounds. Vinylstannanes obtained by hydrostannations of alkynes [6] are important substrates for palladium-catalyzed cross coupling reactions (Stille coupling) [7].

Therefore, several approaches have been developed for the synthesis of these stannanes. The commonly used radical hydrostannation is only of limited value, because the radical pathway results in a mixture of regio- and stereoisomers [1], which are difficult to separate. Better results are obtained in transition metal catalyzed reactions. In palladium- [8] and rhodium-catalyzed [9] reactions the addition of the tin hydride occurs in a highly stereoselective fashion as a clean *syn* addition, as a result of the reaction mechanism [2].

Very recently, we reported a new hydrostannation catalyst based on molybdenum [10]. Herein we describe the influence of isonitrile ligands on the regioselectivity of the hydrostannation step.

2. Results and discussion

For our early investigations we chose $Mo(CO)_6$ and $Mo(CO)_3(CN–{}^tBu)_3$ ($MoBI_3$) as catalysts. We found that $Mo(CO)_6$ in principle can be used for hydrostannations, but the yields and selectivities obtained were moderate. Replacing three CO ligands by isoelectronic isonitrile ligands [11] resulted in a significant increase in the yield and the selectivity as well. ^{t}Butylisonitrile was chosen for steric reasons, with the expectation that the sterically demanding ^{t}butyl groups may have an influence on the regioselective outcome of the reaction. Isonitriles also have the advantage to stay in solution after dissociation from the metal, resulting in a pro-

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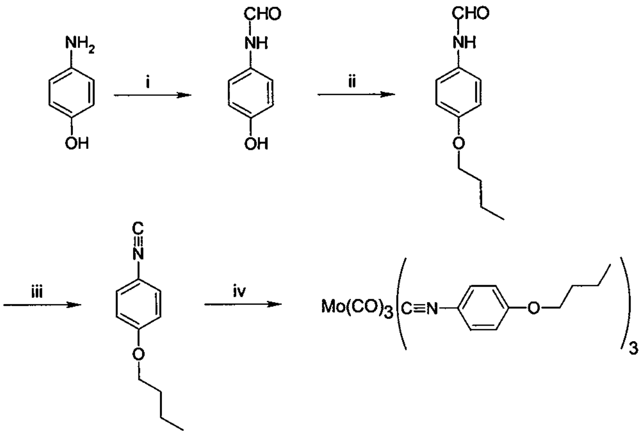
longed lifetime of the catalyst. Because of a weaker π-back donation from the metal to the isonitrile, in comparison to CO, the isonitriles are weaker bound in the complex. Therefore, they can dissociate easily, opening up free coordination sites on the catalytically active metal. Based on these reasons one might expect a strong influence of the number as well as of the nature of the isonitrile ligands. To investigate this influence, we chose THP-protected propargylic alcohol (Eq. (1)) as a substrate, because the vinylstannanes obtained are stable and can easily be purified without side reactions such as protodestannations [10].

Hydroquinone was added to the reaction mixture to suppress the radical pathway which can also occur at a raised temperature. The radical reaction should deteriorate the regioselectivity and should result in the additional formation of the (*Z*)-β-product. This (*Z*)-product was not found in any of our hydrostannation reactions. Therefore, we can be sure that the radical pathway is suppressed under our conditions, and the regioselectivities observed are caused from the catalyzed process.

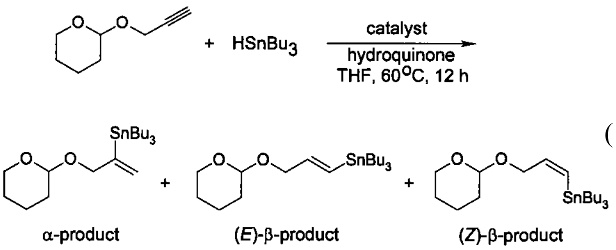
Table 1
Catalytic hydrostannations of the THP-propargylether

Entry	Catalyst	Yield (%)	Selectivity α:β
1	$Mo(CO)_6$	35	28:72
2	$Mo(CO)_5(CN–{}^tBu)$ ($MoBI_1$)	64	62:38
3	$Mo(CO)_4(CN–{}^tBu)_2$ ($MoBI_2$)	89	87:13
4	$Mo(CO)_3(CN–{}^tBu)_3$ ($MoBI_3$)	91	>95:<5
5	$Mo(CO)_2(CN–{}^tBu)_4$ ($MoBI_4$)	85	>95:<5



Scheme 1. Synthesis of the catalyst $Mo(CO)_3(CN–pPh–OBu)_3$ ($MoBPI_3$): (i) $HC(O)OC(O)CH_3$, CH_2Cl_2, 90%; (ii) KO^tBu, ^nBuBr, DMF, 65%; (iii) $POCl_3$, NEt_3, CH_2Cl_2, 98%; (iv) $Mo(CO)_6$, $CoCl_2 \cdot 2H_2O$, Toluol, 69%.

The results obtained with several isonitrile complexes are summarized in Table 1.



(1)

Subsequent substitution of CO ligands by the isonitrile (Table 1, entries 1–5) resulted in a dramatic increase in the yield and the selectivity as well. The best result was obtained with $Mo(CO)_3(CN–{}^tBu)_3$ ($MoBI_3$), an additional isonitrile ligand had no positive effect on the reaction. In contrast, the yield was somewhat lower, although this decrease is not significant. The lower yield might result from the lower stability of $Mo(CO)_2(CN–{}^tBu)_4$ ($MoBI_4$) in comparison to $MoBI_3$. In contrast to the latter complex, which is perfectly stable at room temperature even under air, $MoBI_4$ decomposes during storage even under argon at −18 °C. Obviously, three isonitrile ligands are the optimum, not only for the yield and selectivity but also for the stability of the catalyst.

To investigate the sterical and electronical influence of the isonitrile, we synthesized $Mo(CO_3)(CNPh)_3$ ($MoPI_3$) and the more electron rich $Mo(CO_3)(CN–pPh–OBu)_3$ ($MoBPI_3$) according to a procedure described by Albers et al. [11]. The isonitrile required for the latter complex was obtained in three steps starting from *p*-hydroxyaniline (Scheme 1).

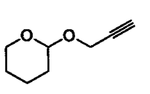
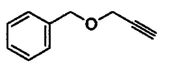
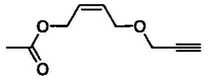
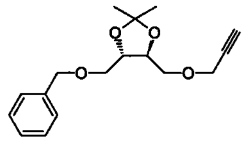
The influence of these three complexes on the hydrostannation of various propargylic ethers was investigated and the results are collected in Table 2. The sterical bulk of the ^{t}butyl groups in $MoBI_3$ obviously has a significant effect on the regioselectivity. The related phenyl derivative gave comparable yields, although the selectivities are lower in all cases. Introduction of the electron donating alkoxy groups on the aromatic ring system significantly increased the regioselectivity and one can assume, that not only steric reasons are responsible for the selectivities obtained, but also electronic factors. Further investigations are in progress.

3. Experimental

3.1. Synthesis of $Mo(CO_3)(CN–pPh–OBu)_3$ ($MoBPI_3$)

p-Butoxyphenylisonitrile (210 mg, 1.20 mmol) in toluene (1 ml) was added slowly to a suspension of $CoCl_2 \cdot 2H_2O$ (11 mg, 66 μmol) and $Mo(CO)_6$ (98 mg, 0.37 mmol) in toluene (2 ml) at 100 °C. The mixture

Table 2
Hydrostannations of substituted alkynes

No	Substrate	$MoBI_3$		$MoPI_3$		$MoBPI_3$	
		Yield (%)	Selectivity[a] α : β	Yield (%)	Selectivity[a] α : β	Yield (%)	Selectivity[a] α : β
1		91	>95 : <5	70	85 : 15	70	95 : 5
2		41	88 : 12	68	87 : 13	55	88 : 12
3		90	>95 : <5	62	81 : 19	72	85 : 15
4		70	92 : 8	88	88 : 12	88	90 : 10

[a] the isomeric ratio was determined by ^1H nmr

was refluxed for 1 h before the resulting black suspension was evaporated in vacuo. The residue obtained was purified by flash chromatography using CH_2Cl_2 as an eluent. Yield: 180 mg (0.255 mmol, 69%) of a green oil. ^1H-NMR (300 MHz, $CDCl_3$): $\delta = 0.96$ (t, $^3J = 7.4$ Hz, CH_3), 1.47 (sext, $^3J = 7.4$ Hz, CH_2–CH_3), 1.76 (q, $^3J = 6.6$ Hz, O–CH_2–CH_2), 3.95 (t, $^3J = 6.5$ Hz, O–CH_2), 6.85 (d, $^3J = 8.9$ Hz, CH–COBu), 7.27 (d, $^3J = 8.9$ Hz, CH–CNC). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 13.6$ (t, CH_3), 18.9 (t, CH_2–CH_3), 30.9 (t, O–CH_2–CH_2–), 67.9 (t, O–CH_2–), 114.8 (d, CH–COBu), 127.3 (d, CH–CNC), 158.9 (s, NC), quarternary C could not be determined. IR (KBr, cm^{-1}): 2140, 2095, 2014, 1923. FAB^+-HRMS; m/z (relative intensity, %): Calc. for $C_{36}H_{38}O_6N_3^{97}Mo$: 705.1796. Found: 705.1808 (46.5).

3.2. General procedure for hydrostannations

Alkyne (1 mmol) was dissolved in THF (2 ml). The catalyst (1 mol%) and hydroquinone (0.1 mol%) were added. The mixture was warmed to 60 °C before 3 mmol of Bu_3SnH was added. The solution was stirred at this temperature for further 12 h. After evaporation of the solvent in vacuo, the crude product was purified by flash chromatography (eluent: petrolether–EtOAc–1% NEt_3).

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