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New and simple one-step cobalt-catalyzed preparation of functionalized arylstannanes from the corresponding aryl bromides or iodides

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Received 22nd September 2004, Accepted 15th November 2004
First published as an Advance Article on the web 7th December 2004

A variety of functionalized arylstannanes are obtained in moderate to excellent yields by a one-step chemical procedure from corresponding halides and tributylstannyl chloride *via* cobalt catalysis.

The Stille coupling of aromatic rings requires the formation of arylstannanes.[1] This arises from the growing availability of organostannanes, their broad spectrum of tolerated functional groups and their stability towards moisture and air. The most common procedure is generally the transformation of an aryl halide to an organometallic reagent (Grignard,[2] lithium[3] or zinc[4]) and its reaction with trialkylstannyl chloride R_3SnCl (R = Me or Bu) which yields the corresponding arylstannane. However, the main difficulty with this method is the preliminary preparation of the organometallic reagent when the aromatic ring bears reactive functional substituents (COR, CN…). Alternatively, some functionalized arylstannanes can be directly prepared from aromatic halides by palladium catalyzed reaction of an excess of hexabutylditin with aryl halides ArX (X = Br, I).[5] Recently and given the growing interest of arylzinc species in chemical synthesis, a convenient method for the preparation of aromatic organozinc species has been discovered in our laboratory.[6] The versatility and simplicity of the original method are based on the direct activation of aryl bromides or iodides by low-valent cobalt(I) species arising from the reduction of cobalt(II) halide by zinc dust in acetonitrile.

In the course of our work on the cobalt-catalyzed preparation of organometallic compounds, the current paper deals with a method of preparation of functionalized arylstannanes from the corresponding arylzinc species. In fact, arylzinc species can neither be stored for a long time nor isolated. Furthermore, they have to be rapidly engaged in coupling reactions after their formation to avoid the formation of the symmetrical biaryl due to the presence of the cobalt in solution. We first verified that the two-step coupling reaction of aryl bromides and tributylstannyl chloride led to corresponding arylstannanes at room temperature without further addition of a catalyst (eq.1).

$$\underset{0.1\,\text{eq}}{CoBr_2} + \underset{1.5\text{eq}}{Zn} \xrightarrow[\text{2)ArBr 1 eq}]{\substack{\text{1)AllylCl 0.3 eq}\\ CH_3CN,\ CF_3CO_2H}} ArZnBr \xrightarrow{Bu_3SnCl\ \text{1 eq, r.t.}} ArSnBu_3 \qquad (1)$$

The behaviour of our arylzinc compounds, synthesized *via* cobalt catalysis in acetonitrile, towards Bu_3SnCl is similar to traditional behaviour. For example, p-$MeOC_6H_4SnBu_3$ and p-$EtOCOC_6H_4SnBu_3$ have been readily synthesized in two step sequences from the corresponding aryl bromides and Bu_3SnCl, using the reaction conditions detailed elsewhere for the preparation of ArZnBr: 0.1 equiv. of $CoBr_2$, 1.5 equiv. of zinc dust activated by 50 µl of trifluoroacetic acid and a 1.5 M aryl bromide concentration. Prior to the addition of aryl bromide in acetonitrile, a 5 min preliminary step was carried out using 0.3 equiv. of allyl chloride (3 equiv. *vs.* cobalt) in order to enhance the yield of the organozinc species and decrease the formation of the byproducts, especially ArH. After the formation of the organozinc compound, 1 equiv. of Bu_3SnCl was added to the solution at room temperature. The mixture was stirred for 30 min. Hydrolysis with NH_4Cl followed by diethyl ether extraction gives crude arylstannane in good yields. Purification by column chromatography (silica gel, pentane) gives the arylstannanes in 80% yield.

It seemed interesting to develop a convenient method for the one step synthesis of arylstannanes from aryl bromides or iodides. This procedure follows the protocol already described but after the usual preliminary step of 5 min of stirring with 0.3 equiv. of allyl chloride, the aryl halide (1 equiv.) and the tributylstannyl chloride are added simultaneously in acetonitrile at room temperature. The mixture is stirred until total consumption of the aryl bromide is achieved. The corresponding arylstannane is detected by GC using an internal standard (alkane). An inert atmosphere is not required. If the medium is heated at 50 °C after introduction of ArBr and Bu_3SnCl, the reaction proceeds faster and similar results are obtained (eq. 2).

$$\underset{0.1\text{eq}}{CoBr_2} + \underset{1.5\text{eq}}{Zn} \xrightarrow[\substack{\text{2)ArBr 1 eq}\\ Bu_3SnCl\ \text{1.1 eq}\\ 50\,^{\circ}C}]{\substack{\text{1)AllylCl 0.3 eq}\\ CH_3CN,\ CF_3CO_2H}} ArSnBu_3 \qquad (2)$$

We consequently applied this method to various aromatic bromides or iodides bearing electron-donating or electron-withdrawing groups in the *para*, *meta* and *ortho* series. The resulting products have been isolated and results are reported in Table 1.

Table 1 One-step synthesis of arylstannanes from ArX (X = Br, I) at 50 °C

Aryl bromide	Reaction time/h	Isolated yield (%)[a] of $ArSnBu_3$
4-MeOPhBr	0.5	96
4-MeOPhI	0.5	78 (Ar–Ar = 20%)
2-MeOPhBr	1	82
3-MeOPhBr	1.5	85
4-$(Me)_2$NPhBr	4	61
4-ClPhBr	1.5	63
2-EtOCOPhBr	1.5	88
4-EtOCOPhBr	1	90
4-MeCOPhBr	2	78
4-F_3CPhBr	24	56
4-HCOPhBr	1	66
2-NCPhBr	1	60
3-NCPhBr	1	75
4-NCPhBr	0.6	96

[a] Based on initial ArX. All products gave satisfactory ^1H, ^{13}C NMR and mass spectra.

DOI:10.1039/b417326k

These results show that this original method gives the expected arylstannane in good to excellent yields. The byproduct is only the reduction product in the case of aryl bromides, contrary to the two-step procedure where the homocoupling product is detected in small amounts. With more reactive compounds such as aromatic iodides, the homocoupling product is also formed in the one-step procedure. However, as already described in the formation of the arylzinc species formed by cobalt catalysis in acetonitrile, no organostannanes could be detected from the chlorobenzene which did not react. This confirms that Co(I) is not reactive towards aryl chloride. Then, bromochlorobenzene led to the mono arylstannane (4-$ClPhSnBu_3$). It can be pointed out that the position of the substituent has again a slight influence on the yields as revealed in the cases of bromoanisole or bromobenzoate (except in the case of bromobenzonitrile).

In the following series of experiments, we have tried to apply this method to heteroaromatic halides. Unfortunately, results were disappointing with bromopyridines and bromothiophenes at 50 °C. All the reactant was converted into the reduction compound with bromopyridine or 2-bromothiophene. In the case of 3-bromothiophene, poor yields were obtained under these conditions (28%). However, the thienylstannane can be generated from 2 and 3-bromothiophenes in good to excellent yield when the reaction is conducted at room temperature. The stannane species are obtained in 45 and 80% yield, respectively. 2-Thienyl bromide, which is more reactive, gives a large amount of the reduction product. However, bromopyridines always led to the reduction product even if the reaction was carried out at room temperature. This last behaviour was expected and is consistent with the fact that these products are not converted into the corresponding zinc species.

In summary, we have established that readily available cobalt halide, zinc dust and tributyl stannyl chloride are convenient for the facile preparation of arylstannanes from the corresponding aryl bromides (or iodides) in acetonitrile. The transmetalation between arylzinc species formed in the medium and tributyl stannyl chloride occurs in a single operation and makes this new chemical method an excellent alternative to classical routes.

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