Rhodium-catalysed arylation of aldehydes with arylstannanes

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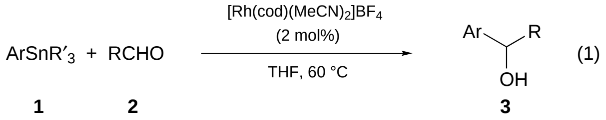
Aryltrimethylstannanes react with aldehydes in the presence of a catalytic amount of a cationic rhodium complex, $[Rh(cod)(MeCN)_2]BF_4$, affording the corresponding arylated secondary alcohols in good yields.

The addition of organometallic reagents to aldehydes has been the general method for the synthesis of secondary alcohols. Among these reagents, organolithium and organomagnesium (Grignard reagent) compounds are recognized to be the most versatile. However, limitations to their use arise from the very nature of the reagents, namely, their extraordinary reactivity as nucleophiles and bases. This feature often gives rise to undesired reactions in the synthesis of multifunctional compounds such as natural products. In order to realize chemoselective addition to aldehydes, various organometallic reagents have been investigated. Nozaki and Hiyama[1] and Kishi[2] reported the addition of organochromium compounds to aldehydes in the presence of a nickel catalyst. Although this reaction is highly chemoselective and displays wide compatibility with the functional groups in both reaction partners, a large excess (200–1600 mol%) of chromium salt is required. The allylation of aldehydes with allylstannanes promoted by a Lewis acid is one of the most promising reactions and has been applied successfully in organic systhesis.[3] Recently, this allylation was reported to be also catalysed by transition metal complexes such as those of rhodium,[4] palladium and platinum.[5] There is, however, no report on the addition of other organostannanes to aldehydes except 1-carboranylstannane,[6] a very special agent. We wish to report here a novel, highly chemoselective arylation reaction of aldehydes with arylstannanes catalysed by a cationic rhodium complex [eqn. (1)].



(1)

The general procedure is as follows. A mixture of 1.2 mmol of arylstannane **1**, 1.0 mmol of aldehyde **2** and 0.02 mmol of $[Rh(cod)(MeCN)_2]BF_4$ (cod = cycloocta-1,5-diene) in 1 ml of dried THF was stirred at 60 °C for an appropriate period of time under N_2 atmosphere in a sealed Schlenk tube. The reaction was monitored by TLC. The reaction was quenched by adding a small amount of water and then stirred for 1 h. After the solvent was removed *in vacuo*, the product was isolated by silica gel column chromatography.

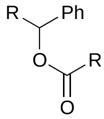
The results are summarized in Table 1. The arylation of benzaldehyde with trimethylphenylstannane proceeded smoothly in the presence of 2 mol% cationic rhodium complex $[Rh(cod)(MeCN)_2]BF_4$, affording diphenylmethanol in 85% isolated yield (entry 1). NMR examination of the reaction mixture prior to quenching the reaction by adding water indicated the formation of the corresponding stannyl ether. Therefore, the hydrolysis of the stannyl ether must take place during the work-up. Addition of phosphine ligands such as PPh_3 to $[Rh(cod)(MeCN)_2]BF_4$ inhibited the reaction. Neutral rhodium complexes such as $RhCl(PPh_3)_3$ and $[RhCl(cod)]_2$ did not promote the reaction, nor did the traditional Lewis acids like $TiCl_4$ and $BF_3 \cdot OEt_2$. The employment of tributylphenylstannane and tetraphenylstannane instead of trimethylphenylstannane gave diphenylmethanol in lower chemical yields of 65 and 17%, respectively (entries 2 and 3). The reaction of *p*-fluorophenyltrimethylstannane and *p*-methoxyphenyltrimethylstannane with benzaldehyde proceeded smoothly, affording the corresponding diarylmethanols in good

Table 1 Arylation reaction of aldehydes with arylstannanes catalysed by $[Rh(cod)(MeCN)_2]BF_4$[a]

			Reaction conditions		
Entry	Arylstannane **1**	Aldehyde **2**	*T*/°C	*t*/h	Yield (%)[b]
1	$PhSnMe_3$	PhCHO	60	5	85 (87)
2	$PhSnBu_3$	PhCHO	60	5	(65)
3	Ph_4Sn	PhCHO	60	20	(17)
4	*p*-$FC_6H_4SnMe_3$	PhCHO	60	2	88
5	*p*-$MeOC_6H_4SnMe_3$	PhCHO	60	2	91
6	$PhSnMe_3$	*p*-$MeOC_6H_4CHO$	60	24	85
7	$PhSnMe_3$	*p*-MeC_6H_4CHO	60	24	87
8	$PhSnMe_3$	*p*-ClC_6H_4CHO	60	5	91
9	$PhSnMe_3$	*p*-$MeC(O)C_6H_4CHO$	60	5	96
10	$PhSnMe_3$	*p*-$MeOC(O)C_6H_4CHO$	60	5	96
11	$PhSnMe_3$	*p*-$(NO_2)C_6H_4CHO$	60	5	94
12	$PhSnMe_3$	Furfural	60	5	91
13	$PhSnMe_3$	$C_5H_{11}CHO$	60	20	34 (40)[c]
14	$PhSnMe_3$	*c*-$C_6H_{11}CHO$	60	20	40[d]
15	$PhSnMe_3$	*tert*-C_4H_9CHO	60	20	54[e]
16	$PhSnMe_3$	Cyclohexanone	60	24	29

[a] A mixture of **1** (1.2 mmol), **2** (1.0 mmol) and $[Rh(cod)(MeCN)_2]BF_4$ (0.02 mmol) in THF (1 ml) was stirred under N_2 atmosphere. [b] Isolated yield based on **2**. Values in parentheses were determined by GC. [c] Ester **4a** (28%) was formed concomitantly. [d] Ester **4b** (36%) was formed concomitantly. [e] Ester **4c** (8%) was formed concomitantly.

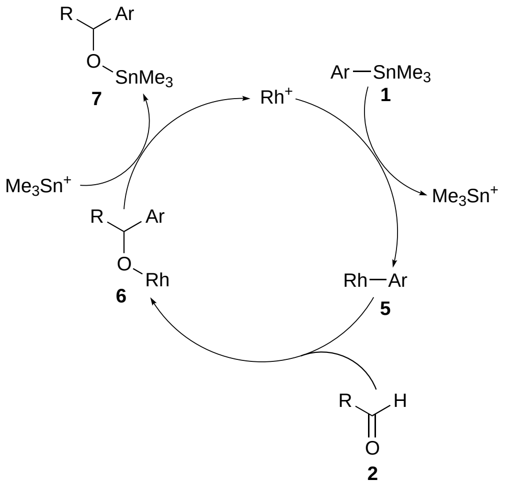
yields (entries 4 and 5). The reaction of trimethylphenylstannane with substituted benzaldehydes and furfural also proceeded smoothly, affording the corresponding diarylmethanol in good to excellent yields (entries 6 to 12). It is noted that the reaction was highly chemoselective, since other electrophilic functional groups in **2** such as the acetyl, methoxycarbonyl and nitro groups remained intact (entries 9, 10 and 11). The reactions of trimethylphenylstannane with aliphatic aldehydes, *i.e.* hexanal, cyclohexanecarboxaldehyde and trimethylacetaldehyde, afforded the corresponding alcohols in lower yields of 34, 40 and 54%, respectively (entries 13 to 15). In these cases, esters **4a**, **4b** and **4c** were formed as by-products in 28 (0.14 mmol), 36 (0.18 mmol) and 8% (0.04 mmol) yield, respectively. On the contrary, the reactions of trimethylphenylstannane with ketones, *i.e.* acetophenone and heptan-2-one, did not take place at all under similar conditions. The reaction with cyclohexanone proceeded sluggishly, affording the corresponding alcohol in 29% yield (entry 16). To ensure the chemoselectivity of the reaction toward aldehyde and ketone, a competitive reaction of benzaldehyde (1 mmol) and cyclohexanone (1 mmol) with trimethylphenylstannane (1 mmol) was carried out at 60 °C for 5 h. The yield of diphenylmethanol was 79% and that of 1-phenylcyclohexanol was only 4%, indicating that the addition of trimethylphenylstannane to benzaldehyde occurred preferentially.



4a R = C_5H_{11}
b R = c-C_6H_{11}
c R = Bu^t

To gain information on the reaction mechanism, the reactivity of $[Rh(cod)(MeCN)_2]BF_4$ toward benzaldehyde was studied. However, the cationic rhodium complex did not show any indication of a reaction with an equimolar amount of benzaldehyde in THF. The interaction of the rhodium complex with trimethylphenylstannane **1a** was then investigated. When 0.1 mmol of $[Rh(cod)(MeCN)_2]BF_4$ was treated with 1.0 equiv. of **1a** in 5.0 ml of THF at 25 °C for 20 h followed by quenching the reaction with water, the stannane **1a** was consumed completely, affording benzene (44% yield) and a trace amount of biphenyl. On quenching the reaction with D_2O instead of H_2O, the benzene formed was not deuteriated. On the other hand, 78% of the yielded benzene (62% yield) was deuteriated on carrying out the reaction in the presence of 1.0 mmol of D_2O. A control experiment confirmed that the stannane **1a** was inert to water. These results indicate the generation of a water-labile species from $[Rh(cod)(MeCN)_2]BF_4$ and the stannane **1a**, which we attribute to an unstable phenylrhodium species that should decompose rapidly to give benzene. Actually, the reaction of $[Rh(cod)(MeCN)_2]BF_4$ with 1.0 equiv. of **1a** in the presence of 2.0 equiv. of styrene gave *trans*-stilbene in 49% yield, which would be formed by a Heck-type reaction between the phenylrhodium species and the styrene.[7] We tried in vain to detect a peak corresponding to the species by ^1H and ^{13}C NMR measurement of the reaction performed in $[^2H_8]$THF. There are several reports on the transmetallation between transition metals and arylstannanes to give arylmetal species as are shown in the Stille coupling reaction.[8] It was also reported that a phenylrhodium complex, $RhPh(CO)(PPh_3)_2$, thermally decomposes into benzene,biphenyl and benzophenone.[9]

The presumed reaction pathway for the novel arylation reaction of aldehydes **2** with arylstannanes **1** is shown in Scheme 1. The transmetallation of the cationic rhodium complex with **1** would produce the arylrhodium intermediate **5**. Then, addition of **5** to an aldehyde would occur to afford a rhodium alkoxide complex **6**, which would afford the stannyl ether **7**. The presence of PPh_3 inhibited the reaction. This observation is in accord with that reported by Hegedus where alkyl- and aryl-rhodium(I) phosphine complexes prepared on the action of Grignard or organolithium reagents on the corresponding chlororhodium(I) complexes are unreactive to benzaldehyde.[10] Thus a phosphine-free phenylrhodium species is responsible for this reaction. The mechanism for the formation of the ester **4** would involve the insertion of another aldehyde **2** into the Rh–O bond of **6**. A similar mechanism was proposed by Slough in the Tishchenko-type disproportionation of aldehydes catalysed by rhodium complexes.[11]



Scheme 1

The reaction reported herein represents a new method for highly chemoselective arylation of aldehydes with aryltrimethylstannanes under neutral conditions using a catalytic amount of a cationic rhodium complex. Further work is now in progress to investigate the full scope of this reaction.

Footnote and References

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