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Rhodium-catalyzed arylation and alkenylation of imines with organostannanes

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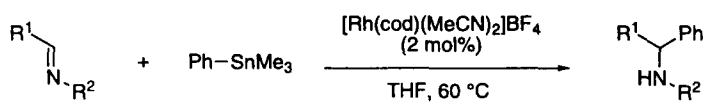
Abstract

A rhodium complex catalyzed the addition of aryl- and alkenyl-stannanes to activated aldimines under mild and neutral conditions, affording the corresponding amines in good yields. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: arylation; alkenylation; imine; organostannane; rhodium catalyst.

The addition of organometallic reagents to imines has been a useful method to synthesize amines. Organolithium and Grignard reagents are most generally used for this purpose.[1–3] However, limitations to their use sometimes arise from the very feature of these reagents, namely, their extraordinary reactivities as nucleophiles and bases. In order to avoid this problem, various organometallic reagents have been investigated. An organotin compound is a promising candidate for a chemoselective reagent, although it is generally necessary to use it with a catalyst. The allylation of imines with allylstannanes promoted by a Lewis acid[4] and a palladium or platinum complex[5] has been reported. Previously, we reported chemoselective addition of aryltrimethylstannanes **2** to aldehydes catalyzed by a cationic rhodium complex.[6,7] We have found that this arylation method is also applicable to activated aldimines **1** affording α-arylated amine derivatives **3** under mild and neutral conditions (Eq. 1).



1 **2a** **3** (1)

At first, we examined the arylation of *N*-benzylideneaniline with trimethylphenylstannane (**2a**), but no arylation occurred. This is probably due to the low electrophilicity of the imines. Then, *N*-sulfonylaldimines, which are activated by the electron-withdrawing sulfonyl group on the nitrogen atom, were employed as the substrates. The reaction of *N*-tosylbenzylideneimine (**1a**)[8] with **2a** proceeded

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Table 1
Arylation of aldimines **1** with trimethylphenylstannane (**2a**) catalyzed by a rhodium complex[a]

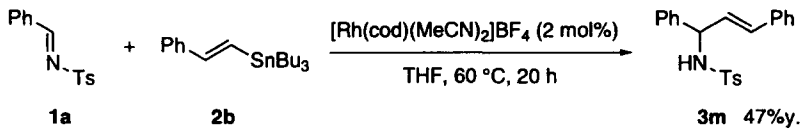
Entry	R^1	R^2	Aldimine	Reaction time / h	Product	Yield / %[b]
1	Ph	Ts	**1a**	19	**3a**	98
2[c]	Ph	Ts	**1a**	20	**3a**	81
3	*p*-MeO-C_6H_4	Ts	**1b**	5	**3b**	76
4	*o*-MeO-C_6H_4	Ts	**1c**	24	**3c**	75
5	*p*-Me_2N-C_6H_4	Ts	**1d**	20	**3d**	60
6	*o*-Cl-C_6H_4	Ts	**1e**	5	**3e**	79
7	*p*-Cl-C_6H_4	Ts	**1f**	20	**3f**	78
8	*p*-NO_2-C_6H_4	Ts	**1g**	20	**3g**	83
9	2-furyl	Ts	**1h**	20	**3h**	72
10	COOEt	Ts	**1i**	20	**3i**	65
11	Ph	$PO(OEt)_2$	**1j**	20	**3j**	84
12	Ph	COPh	**1k**	20	**3k**	48
13	Ph	$COOBu^t$	**1l**	20	**3l**	74

[a]Reaction conditions: **1** (1.0 mmol), **2a** (1.2 mmol), $[Rh(cod)(MeCN)_2]BF_4$ (0.02 mmol), 1 ml of THF, 60 °C, N_2 atmosphere. [b]Isolated yield. [c]$[RhCl(cod)]_2$ was used as the catalyst.

quantitatively in the presence of 2 mol% of the cationic rhodium complex, $[Rh(cod)(MeCN)_2]BF_4$, affording *N*-tosyldiphenylmethylamine (**3a**) in 98% isolated yield (Table 1, entry 1). The reaction of **1a** with **2a** using a neutral rhodium complex, $[RhCl(cod)]_2$, gave **3a** in lower yield of 81% (entry 2). *ortho*- And *para*-substituted *N*-tosylbenzylideneimines with both electron-withdrawing and -donating groups (**1b–1g**) also reacted with **2a**, affording the corresponding *N*-tosyldiarylmethylamines (**3b–3g**) in good isolated yields (entries 3–8). The reaction of *N*-tosylfurylideneimine (**1h**) with **2a** gave the product **3h** in 72% yield (entry 9). Ethyl tosyliminoacetate (**1i**),[9] having three electrophilic moieties, ester, imino, and sulfonyl groups, was phenylated selectively at the imino group with **2a**, affording *N*-tosylphenylglycine ethyl ester (**3i**) in 65% isolated yield (entry 10).

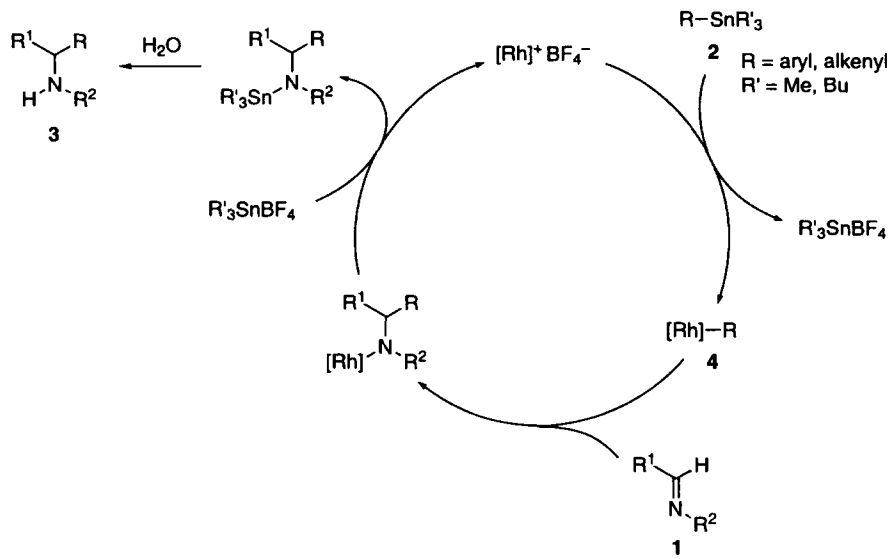
Other electron-withdrawing groups were examined as the activating group of the aldimines. The reaction of *N*-(diethoxyphosphoryl)benzylideneimine (**1j**)[10] with **2a** gave *N*-(diethoxyphosphoryl)-diphenylmethylamine (**3j**) in good yield of 84% (entry 11). Acyl and alkoxycarbonyl groups can also be employed as the activating group. Thus, *N*-benzoylbenzylideneimine (**1k**)[11] and *N*-(*tert*-butoxycarbonyl)benzylideneimine (**1l**)[12] reacted with **2a** under the same reaction conditions, affording *N*-benzoyl- and *N*-(*tert*-butoxycarbonyl)-diphenylmethylamine (**3k** and **3l**) in 48% and 74% yield, respectively (entries 12 and 13).

Then, we tried alkenylation of **1a** using tributyl-(*E*)-styrylstannane (**2b**). The reaction of **1a** with **2b** in the presence of 2 mol% of the cationic rhodium complex in THF at 60°C for 20 h gave *N*-tosyl-(*E*)-1,3-diphenyl-2-propenylamine (**3m**) in 47% isolated yield (Eq. 2). Although the yield was modest, this is the first example of addition of an alkenylstannane to a carbon-hetero atom double bond.



(2)

The reaction may involve the transmetallation between organostannanes **2** and Rh(I) complexes to give an organorhodium species **4** followed by insertion of the C=N double bond of the imine **1** into the resulting Rh–C bond (Scheme 1).[6,7]



Scheme 1. Proposed catalytic cycle. Ligands of rhodium complexes are omitted

The following is representative of the rhodium-catalyzed arylation and alkenylation of aldimines **1** with organostannanes **2**. A mixture of **1a** (259 mg, 1.0 mmol), **2a** (289 mg, 1.2 mmol), and $[Rh(cod)(MeCN)_2]BF_4$ (7.6 mg, 0.02 mmol) in 1 ml of dried THF was stirred at 60°C for 19 h 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 using $CHCl_3$:hexane:EtOAc (6:5:1) as an eluent. *N*-Tosyldiphenylmethylamine (**3a**) was obtained in 98% yield (331 mg) as a white solid. Mp 153.5–154.0°C.

In conclusion, the reaction reported represents a new method of highly chemoselective arylation and alkenylation of aldimines with organostannanes under mild and neutral conditions using a catalytic amount of a cationic rhodium complex. The organorhodium species generated via the transmetallation is assumed to be an active species of the present arylation and alkenylation of aldimines.

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